The impact of Sedimentary Coatings on the Diagenetic Nd Flux

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Abstract

Because ocean circulation impacts global heat transport, understanding the relationship between deep ocean circulation and climate is important for predicting the ocean's role in climate change. A common approach to reconstruct ocean circulation patterns employs the neodymium isotope compositions of authigenic phases recovered from marine sediments. In this approach, mild chemical extractions of these phases is thought to yield information regarding the ϵ_{Nd} of the bottom waters that are in contact with the underlying sediment package. However, recent pore fluid studies present evidence for neodymium cycling within the upper portions of the marine sediment package that drives a significant benthic flux of neodymium to the ocean. This internal sedimentary cycling has the potential to obfuscate any relationship between the neodymium signature recovered from the authigenic coating and the overlying neodymium signature of the seawater. For this manuscript, we present sedimentary leach results from three sites on the Oregon margin in the northeast Pacific Ocean. Our goal is to examine the potential

mechanisms controlling the exchange of Nd between the sedimentary package and the overlying water column, as well as the relationship between the ϵ_{Nd} composition of authigenic sedimentary coatings and that of the pore fluid. In our comparison of the neodymium concentrations and isotope compositions from the total sediment, sediment leachates, and pore fluid we find that the leachable components account for about half of the total solid-phase Nd, therefore representing a significant reservoir of reactive Nd within the sediment package. Based on these and other data, we propose that sediment diagenesis determines the ϵ_{Nd} of the pore fluid, which in turn controls the ϵ_{Nd} of the bottom water. Consistent with this notion, despite having 1 to 2 orders of magnitude greater Nd concentration than the bottom water, the pore fluid is still $<0.001\%$ of the total Nd reservoir in the upper sediment column. Therefore, the pore fluid reservoir is too small to maintain a unique signature, and instead must be controlled by the larger reservoir of Nd in the reactive coatings. In addition, to achieve mass balance, we find it necessary to invoke a cryptic radiogenic (ϵ_{Nd} of +10) trace mineral source of neodymium within the upper sediment column at our sites. When present, this cryptic trace metal results in more radiogenic pore fluid.

Keywords

Neodymium, diagenesis, benthic flux, ocean circulation

1.0 Introduction

The neodymium isotope composition (ϵ_{Nd}) of seawater is commonly used as a quasi-conservative tracer of ocean circulation (e.g. Frank 2002; Goldstein and

51 Hemming, 2003). The neodymium isotope value is reported as ϵ_{Nd} , defined as
 52 $[(^{143}Nd_{sample}/^{144}Nd_{sample})/(^{143}Nd_{CHUR}/^{144}Nd_{CHUR})-1] \times 10^4$ where CHUR is the
 53 Chondritic Uniform Reserve, used as an average earth value ($^{143}Nd/^{144}Nd$
 54 $=0.512638$; Jacobsen and Wasserburg, 1980). The ϵ_{Nd} of bottom water is thought to
 55 be recorded in marine sedimentary authigenic phases, including Fe or Mn
 56 (oxy)hydroxides that are directly precipitated from seawater (Frank, 2002). The
 57 changes in the ϵ_{Nd} of these authigenic phases over time are therefore interpreted as
 58 shifts in global ocean circulation (e.g. Haley et al., 2008; Piotrowski et al., 2005;
 59 Rutberg et al., 2000). However, authigenic ferromanganese ϵ_{Nd} is likely influenced
 60 by processes during early sediment diagenesis (e.g. Elderfield et al., 1981; Elderfield
 61 and Sholkovitz, 1987; Grousset et al., 1988) and may represent a mix of *in situ*
 62 authigenic and preformed Fe-Mn oxyhydroxides (Bayon et al., 2004). Furthermore,
 63 remobilization of these Fe-Mn oxyhydroxides during early diagenesis may also bias
 64 the ferromanganese ϵ_{Nd} signature (e.g. Elderfield et al., 1981; Elderfield and
 65 Sholkovitz, 1987; Palmer and Elderfield, 1986). In addition to these diagenetic
 66 caveats, the interpretation of ϵ_{Nd} as a paleoproxy for circulation is dependent on the
 67 quasi-conservative behavior of Nd throughout the global ocean (Tachikawa et al.,
 68 2003) and the ability to consistently recover a bottom water ϵ_{Nd} signature from the
 69 sediment record. However, Nd is not conservative in the global oceans and its
 70 behavior is not biogeochemically consistent with ϵ_{Nd} appearing to be conservative; a
 71 discrepancy coined the “Nd paradox” (Arsouze et al., 2009; Goldstein and Hemming,
 72 2003; Jones et al., 2008).

The main source of Nd to the ocean has conventionally been assumed to be the riverine dissolved load with a minor contribution from atmospheric deposition (e.g. Elderfield et al., 1990; Jones et al., 1994). In addition to concerns that result from the Nd paradox, observed changes to water mass ϵ_{Nd} along margins imply the presence of an additional Nd source (e.g. Jeandel et al., 1998; 2007). Furthermore, models indicate that the current budget of Nd does not account for 95% of the ocean's Nd and cannot reproduce modern ϵ_{Nd} distributions without additional Nd sources (Arsouze et al., 2009; Jones et al., 2008). If the dissolved river flux supplies only a fraction of the ocean's Nd, then other Nd sources must control the global distribution of ϵ_{Nd} . The particulate Nd flux to the ocean is nearly 100 times that of the dissolved riverine Nd flux (Oelkers et al., 2011). Jeandel et al. (2015) propose that dissolution in the water column of less than 3% of this particulate load can account for the “missing” Nd in the ocean. Alternatively, we have proposed that the role of the particles is most significant within the sediments, through post depositional Nd release driven by sediment diagenesis (Abbott et al., 2015 a, b). This idea builds upon studies that have highlighted the importance of sediments as a source of Nd to the ocean (e.g. Abbott et al., 2015a, b; Arsouze et al., 2009; Bayon et al., 2011; Carter et al., 2012; Elderfield and Sholkovitz, 1987; Freslon et al., 2014; Grousset et al., 1988; Haley and Klinkhammer, 2003; Jeandel et al., 2007; Lacan and Jeandel 2001, 2005; Sholkovitz and Elderfield, 1988; Sholkovitz et al., 1989; Tachikawa et al., 2003; Van de Flierdt et al., 2004; Wilson et al., 2013), and that this benthic source likely determines the ϵ_{Nd} distribution of the deep ocean (Abbott et al., 2015b).

The influence of the benthic flux on the bottom water ϵ_{Nd} will depend on both the magnitude and the ϵ_{Nd} value of the flux (Abbott et al., 2015b). An understanding of the mechanistic relationship among the sediment characteristics, the magnitude of the flux, and the ϵ_{Nd} of the pore fluid is required to estimate the influence of the benthic flux of Nd on bottom water ϵ_{Nd} along the ocean's flow path. Here, we attempt to constrain the factors and processes that control the magnitude and ϵ_{Nd} signature of the benthic flux.

2.0 Methods

Sediment cores were collected from three sites in the eastern North Pacific (**Figure 1**) in October 2012 (HH1200 and HH3000) and July 2013 (HH200).

Detailed sample collection and core collection techniques are published elsewhere (Abbott et al., 2015a; **Supplemental information**). These sites form an east-west transect near the mouth of the Umpqua River on the Oregon margin in a region influenced by seasonal upwelling. The sites are from water depths of 200 m (HH200), 1200 m (HH1200), and 3000 m (HH3000). The oxygen minimum zone in this region occurs between 500 and 1200 m water depth.

Sediment leaching procedures were used to collect an acid leachable fraction and reducible fraction. Subsamples of the freeze-dried sediment were weighed (2-3 g dry weight) and transferred to acid-rinsed Falcon ® Blue Max 50 mL polystyrene conical tubes. The leaching procedure began with three milli-Q water (MQ) rinses each time shaken by hand for one minute and centrifuged for 15 minutes, and then decanted to remove salts. Next, a 20 mL buffered acetic acid leach solution (0.5 M sodium acetate and 3.5 M glacial acetic acid in MQ; pH 3.5-4) was added and shaken

for 2 hours, centrifuged for 20 min, and 60% of the leachate was collected and stored in a clean Teflon vial (this solution will be referred to as the “acid leachable” fraction). The rationale for only collecting 60% of the leachate is that this approach reduces the risk of contamination from particles; the remaining 40% was discarded. Following the acetic acid and three more MQ rinses, a ~50 mM hydroxylamine leach solution (0.1M hydroxylamine hydrochloride, 5 M >99,9% pure glacial acetic acid and 0.7M sodium hydroxide in MQ; pH 3.5 - 4) was added and the solution was stirred for 2 hours, centrifuged for 20 min, and 60% of the leachate was collected and stored in clean Teflon (this solution will be referred to as the “reducible” fraction).

Leachate and total solid digest solutions were analyzed on the Thermo VG ExCell quadropole ICP-MS at the W.M. Keck Collaboratory for Plasma Mass Spectrometry at Oregon State University (ICP-MS specs in Abbott et al., 2015a) for rare earth element (REE) concentrations. REE concentrations for leachate and total solid are reported as ng REE per g dry sediment. Oxide formation on the ICP-MS was <3% based on monitoring of cerium oxide formation.

Total solid, leachate, and seawater samples were run through a series of columns to isolate the Sr and Nd fractions for isotope analyses. First, samples were eluted through columns consisting of 2 mL of AG-1x resin to remove Fe from the solution to increase the yield and efficiency of the remaining columns. The resin was cleaned with 6 mL of 6M HNO₃, 6 mL MQ, and then conditioned with 6 mL of 6M 1x distilled HCl. Samples were then re-dissolved in 1 mL of 6M distilled HCl, and centrifuged for 5 minutes at 13400 rpm before loading onto the column. Collection

of the sample began when the sample was loaded onto the column and completed with 5 mL of 6M distilled HCl. The eluate was dried completely, redissolved in 1M distilled HCl, and loaded onto cation exchange columns (1.8 mL AG50W-X8 HCl form resin). The AG50W-X8 resin was loaded with MQ, cleaned with 6 mL of 6M distilled HCl, and conditioned with 6 mL of 1M distilled HCl before the sample was loaded. Samples were eluted with 3 mL of 1M distilled HCl, 6 mL of MQ, and 4 mL of 2M distilled HNO₃ and then the Sr fraction was collected in 7 mL of 2M distilled HNO₃. After the collection of the Sr fraction, the REE fraction was collected in 10 mL of 6M distilled HNO₃.

The Sr fraction was further purified using 50 μ L Sr Spec Resin (Eichrom® part SR-B505, 50-100 μ m). Resin was cleaned with 300 μ L of H₂SO₄, MQ, and 3M HNO₃ before the 50 μ L sample was loaded in 3M HNO₃, and eluted with 600 μ L of 3M HNO₃. Sr was then collected in 500 μ L MQ. Immediately after collection, 3 mL of 3% HNO₃ was added to each sample. The samples were analyzed on the Nu Plasma ICP-MS multi collector in the Keck Laboratory at Oregon State University. Precision was determined by repeated analysis of an in-house standard, EMD, which yielded a mean $^{87}\text{Sr}/^{86}\text{Sr} = 0.708185$ with a 2σ standard deviation of ± 0.000051 (n=79). National Bureau of Standards reference material 987 (NBS-987) was measured for these analysis at $^{87}\text{Sr}/^{86}\text{Sr} = 0.710245$ with a 2σ standard deviation of ± 0.000052 (n = 91) normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. NBS-987 and EMD were analyzed, at a minimum, after every 6 samples and analyzed in replicate at the beginning and end of every sample group.

Neodymium was isolated from the REE fraction using 2 mL of 50-100 μm mesh Ln resin (Eichrom® part LN-B50-5). The column was cleaned with 4 mL of 6M HCl and 6 mL of MQ, and then conditioned in 4 mL of 0.1M HCl before the 0.5 mL sample was loaded in 0.1M HCl. The column was eluted with 15 mL of 0.1M HCl and 0.25M HCl before Nd was collected in 8 mL of 0.25M HCl. The samples were analyzed on the Nu Plasma multi-collector ICP-MS at Oregon State University for ^{144}Nd and ^{143}Nd . The SpecPure standard was used for in-house reproducibility, yielding a mean $^{144}\text{Nd}/^{143}\text{Nd} = 0.511205$ with a 2σ standard deviation of ± 0.000014 . The JNdi-1 standard was used for normalization to $^{144}\text{Nd}/^{143}\text{Nd} = 0.512115$ with a 2σ standard deviation of ± 0.000011 (reference value 0.512115 ± 0.000007 (Tanaka et al., 2000)). JNdi-1 and SpecPure were analyzed, at minimum, after every 6 samples and analyzed in replicate at the beginning and end of every batch run. The column chromatography procedural blank was ≤ 0.02 ppb Nd.

3.0 Results

3.1 Pore Fluid

Pore fluids are middle rare earth element (MREE) enriched relative to Post Archaen Australian Shale (PAAS) at all three sites (**Figure 2**, Abbott et al., 2015a). Pore fluids are heavy rare earth element (HREE) depleted relative to the total solid at HH200 and HH1200 (**Figure 2**). HH3000 pore fluids can be either depleted or enriched in HREE relative to the total solid depending on the interval, but they are generally HREE enriched compared to HH200 and HH1200 pore fluids (**Figure 2**).

The maximum concentration of Nd in the pore fluid increases and occurs deeper within the sediment column from HH200 to HH1200 to HH3000 (**Figure 3**,

Abbott et al 2015a, b). This trend does not correlate to any other measured variable in the pore fluids (**Figure 3; Supplemental Information Table 2**). Specifically, the maximum concentration of dissolved Fe in the pore fluid decreases in magnitude and occurs deeper within the sediment column from HH200 (~80 μM , 6 cm) to HH1200 (~35 μM , 9 cm) to HH3000 (~8 μM , 11 cm; **Figure 3**). Dissolved Mn is below detection at HH200 and HH1200, but reaches concentrations of 50 μM at HH3000. Additionally, the dissolved Li concentration profile at HH3000 has a steeper decrease with depth than observed in the pore fluid Li concentration profile at HH1200 (**Figure 3**). This decrease in dissolved Li is likely a result of Li incorporation during authigenic clay mineral formation (e.g. Stoffyn-Egli and Mackenzie, 1984). Li and P data are unavailable for pore fluids from HH200. At HH1200 dissolved P increases downcore from ~4 μM in near surface pore fluids to ~16 μM at 8 cm while dissolved P generally remains between 6 and 8 μM throughout the measured pore fluids at HH3000 with the lowest (~6 μM) occurring in the upper most pore fluids (**Figure 3**). As an aside, if phosphate precipitation or dissolution reactions were controlling REE concentrations (e.g. Schacht et al., 2010), we might expect the concentrations of P to covary with the Nd in the pore fluids, which is not the case. With the exception of the upper two data points from HH1200, the ϵ_{Nd} of the pore fluids is relatively constant at each site (**Figure 3**) and becomes less radiogenic from HH200 (average ϵ_{Nd} -0.2) to HH1200 (average ϵ_{Nd} -1.5) to HH3000 (average ϵ_{Nd} -1.8; **Figure 3; Abbott et al., 2015b**). Deviations from the site average pore fluid ϵ_{Nd} are largely restricted to the HH1200. We do not attempt to account for these minor deviations in our model (discussed below) and

instead focus on the average pore fluid ϵ_{Nd} at each site, which represents first order controls on the system. Pore fluid $^{87}\text{Sr}/^{86}\text{Sr}$ is indistinguishable from seawater at all sites (**Figure 4**).

3.2 Total Solid Phase

Total solid phase characteristics show little variation among sites. Total solid REE patterns are similar among all sites with both MREEs and HREEs enriched relative to PAAS (**Figure 2**, Abbott et al., 2015a). At all sites, total solid ϵ_{Nd} ranges between 0.0 and -2.5, but the average ϵ_{Nd} becomes less radiogenic from HH200 (-1.4) to HH1200 (-1.8) to HH3000 (-2.2, **Figure 5**). The concentration of Nd in the digests exhibits little variation within each core, but the concentration of Nd increases slightly with increasing water depth from HH200 (average $14 \mu\text{g g}^{-1}$) to HH1200 (average $16 \mu\text{g g}^{-1}$) to HH3000 (average $17 \mu\text{g g}^{-1}$). Bulk sediment organic carbon concentrations average between 1.7% and 2.0% at all sites, with a slight downcore decrease at HH1200 (**Figure 5**). Sedimentary Fe concentration is lowest at HH200 (<5%) and greatest at HH1200 (5 - 8%; **Supplemental Information Table 3**). Solid phase Mn concentrations are constant at ~450 ppm down-core at both HH200 and HH1200. However, Mn concentrations reach almost 3600 ppm in the surface sediments at HH3000 before decreasing to ~680 ppm at 7 cm (**Supplemental Information Table 3**). Solid-phase Ca concentrations decrease from HH200 ($1.6 \pm 0.03\%$) to HH1200 ($1.4 \pm 0.15\%$) to HH3000 ($1.0 \pm 0.08\%$, **Supplemental Information Table 3**). The $^{87}\text{Sr}/^{86}\text{Sr}$ of the sediment digests is constant with depth at each site and becomes increasingly more radiogenic with increasing water depth: the average $^{87}\text{Sr}/^{86}\text{Sr}$ at HH200 (0.70757) < HH1200

(0.70816) < HH3000 (0.70977) (**Figure 5**). This off-shore trend in sedimentary $^{87}\text{Sr}/^{86}\text{Sr}$ is consistent with published values for the Cascadia basin (Carpentier et al., 2014). Only the total solid at HH3000 has Sr isotopic values more radiogenic than seawater (**Figure 4, Figure 5**).

The mineralogy of the marine sediment was similar among all sites (**Supplemental Information Figure 1**). All samples consisted of quartz, albite, a white mica (illite or muscovite) and a chlorite mineral (clinochlore). The only difference between pre-leach and post-leach sediments that we could observe in the XRD analyses was the presence of crystalline halite in the pre-leach sediments, likely formed during sample freeze-drying.

Grain size distributions were consistent downcore at each site for both pre- and post-leach measurements (**Supplemental Information Table 1**). Pre-leach and post-leach distributions are largely bimodal. The primary peak is at $\sim 85\ \mu\text{m}$ at HH200 and $\sim 180\ \mu\text{m}$ in pre-leach samples at both HH1200 and HH3000. The secondary peak is between $450\ \mu\text{m}$ and $500\ \mu\text{m}$ in all pre-leached samples. The overall mean of the pre-leach distribution increases from HH3000 ($120\ \mu\text{m}$) to HH1200 ($185\ \mu\text{m}$) to HH200 ($205\ \mu\text{m}$; **Figure 6**). The post-leach distributions are bimodal, with the smallest overall mean at HH3000 ($\sim 20\ \mu\text{m}$) and larger means at both HH200 ($\sim 110\ \mu\text{m}$) and HH1200 ($\sim 140\ \mu\text{m}$; **Figure 6**). The most prevalent grain size is the smallest at HH3000 ($\sim 5\ \mu\text{m}$) and increases at HH1200 ($\sim 15\ \mu\text{m}$) and HH200 ($\sim 20\ \mu\text{m}$).

3.3 Leachates

The acid leachable solution becomes less radiogenic from HH200 (ϵ_{Nd} -1.1) and HH1200 (ϵ_{Nd} -1.2) to HH3000 (ϵ_{Nd} -1.9, **Figure 6**). The Fe in this leachate is on average higher at HH200 (87-141 $\mu\text{g mL}^{-1}$) than at HH1200 (66-135 $\mu\text{g mL}^{-1}$) and is lowest at HH3000 (53-66 $\mu\text{g mL}^{-1}$, **Supplemental Information Table 4; Figure 7**).

The reducible leachate has an average ϵ_{Nd} value between -0.6 and -0.9 at all sites with a maximum ϵ_{Nd} of 0.0 and a minimum ϵ_{Nd} of -1.7 (**Figure 6; Supplemental Information Table 5**). The ϵ_{Nd} of this leachate is relatively constant downcore at HH200 ($\epsilon_{\text{Nd}} \sim -0.6$) but changes downcore at 1200 m and 3000 m. Specifically, the reducible leachate at HH1200 m is more radiogenic with depth (ϵ_{Nd} -1.2 at 1.2 cm; ϵ_{Nd} -0.1 at 9.8 cm) and the reducible leachate at HH3000 m is less radiogenic with depth (ϵ_{Nd} -0.3 at 1.2 cm; -1.7 at 9.8 cm; **Figure 7**). Unlike in the acid leachable solution, the minimum (1300 $\mu\text{g g}^{-1}$) and maximum values (4300 $\mu\text{g g}^{-1}$) of Fe in the reducible leachate both occur at HH3000 (**Supplemental Information Table 4; Figure 7**).

At all locations, the ϵ_{Nd} of both leachates is more radiogenic than the total (pre-leach) solid (**Figure 7**). However, the acid leachable solution is most similar to the total solid at HH3000. The pore fluid is more radiogenic than both leachates at HH200, but only more radiogenic than the acid leachable solution at HH3000 (**Figure 7**). Reactive Nd (i.e., the sum of the two leachates) accounted for 55 to 70% of the Nd in the total solid with an average concentration per site between 5.4 and 8.2 $\mu\text{g Nd g}^{-1}$ sed (**Supplemental Information Table 6, Supplemental Information Figure 3**). Of the leachable Nd, 45% was acid leachable and 55% was reducible (**Supplemental Information Table 7**). The concentration of Nd in both

leachates increases with depth at all sites (**Supplemental Information Figure 2**). The leachate REE pattern is MREE enriched and HREE depleted (**Figure 2**), and the acid leachable solution is indistinguishable from the REE pattern of the reducible leachate. We should note here as a point of emphasis and clarification that although the acid leachable and reducible leachate distributions do vary from experiment to experiment, the ϵ_{Nd} of each leachate phase appears to be robust and consistent among experiments. This point suggests that the leaching procedure, although not necessarily quantitative, is targeting the same phase in each experiment.

4.0 Discussion

We have previously shown that there is a flux of Nd from sediment pore fluids into ocean bottom water and have suggested that this flux controls the bottom water ϵ_{Nd} value (Abbott et al., 2015 b). Here we present a diagenetic framework that outlines the important solid-phase processes that define the observed Nd behavior in marine pore fluids. This model separates the upper sediment column into two primary reservoirs, the pore fluid and the total solid (**Figure 8**). We consider there to be three main sub-components of the total solid that may interact with the pore fluids: particulate organic carbon (POC), lithogenic, and authigenic phases. POC does not appear to be an important reservoir because POC concentrations among all sites are similar and do not covary with any of the Nd pools (**Figure 5**). While the lithogenic component is often considered refractory, the surrounding fluid phase can be influenced by mineral dissolution and secondary precipitation processes (e.g. Jeandel and Oelkers, 2015; Rousseau et al., 2015; Tachikawa et al., 1999). Therefore, our model focuses on the lithogenic and authigenic components of the total solid

(**Figure 8**). It is important to emphasize that although we have various compositional information regarding the sedimentary solid phases, our authigenic component is operationally defined by our sediment leachate results.

4.1 Authigenic phases

The authigenic component is divided into acid leachable and reducible fractions that are defined by experimental leaching procedures. The idea that the different leaching reagents target different solid phases is supported by the Fe, Mn, and ϵ_{Nd} characteristics measured in the leachates (**Figure 7**). Specifically, compared to the acid leachable fraction, the Fe to Mn ratios are higher in the reducible fraction and the ϵ_{Nd} signatures are generally more radiogenic in the reducible fraction. The exception is at HH200 where the ϵ_{Nd} signatures of the acid leachable and reducible fractions are similar. The acid leachable ϵ_{Nd} more closely resembles the pore fluid at all sites than does the reducible fraction, suggesting that either the reducible phase contributes less Nd to the pore fluid or that the redox chemistry of the reducing leach effectively targets a specific phase. The net result is that the ϵ_{Nd} signature of the authigenic coatings does not resemble the overlying water column at any site. Since the Nd isotopic signature of Fe-Mn oxyhydroxides is considered a first indication of the source of the oxides (e.g. Bayon et al., 2011), we therefore suggest the REEs in the authigenic coatings are most likely acquired during early diagenesis, consistent with alteration of the authigenic phases during early diagenesis (Bayon et al., 2004; Elderfield et al., 1981; Elderfield and Sholkovitz 1987; Froelich et al., 1979; Grousset et al., 1988; Palmer and Elderfield, 1986).

The grain size distribution of the sediments can indicate the relative importance of authigenic phases in a given sample. For example, at HH3000 the pre-leach grain size distribution appears similar to the grain size distributions at HH1200 and HH200. Within this distribution, there is a wide size distribution and larger than expected grain size at our most distal site, HH3000 (**Figure 6**). However, the post-leach sediments show a narrower, well-defined distribution of smaller grain size. This shift from pre-leach to post-leach distribution is smaller at both HH1200 and HH200 (**Figure 6**). We consider the unexpectedly large grains in the pre-leach grain size distributions, especially seen at HH3000, to be an artifact of coagulation of grains due to surface coatings (**Figure 6**). We therefore suggest that the difference between pre- and post-leach grain size distributions indicates the presence of authigenic phases, which influence the measured “size” of the grains. Under this assumption, the greatest influence of the authigenic phase should be at HH3000 where the shift between the pre- and post-leach grain size distributions is the greatest (**Figure 6**). Indeed, the largest change in grain size distribution (HH3000) corresponds to the highest percent of leachable Nd at HH3000 (**Figure 6**). The greatest pore fluid concentrations of Nd at HH3000 are also concurrent with the largest fraction of REEs recovered in the combined leachate (i.e., authigenic) phases (**Figure 6**) indicating that the pore fluid Nd concentration is proportional to the amount of authigenic phases in the sediment. In other words, we suggest that diagenetic processes are controlling pore fluid Nd concentrations as well as pore fluid ϵ_{Nd} .

In our model, the lithogenic component is allowed to release Nd to the pore fluids but does not acquire Nd from the pore fluids, while the authigenic phases are not only formed from pore water, but are able to exchange with the surrounding pore fluid (**Figure 8**). Thus, we expect the authigenic phases to have the same ϵ_{Nd} as the pore fluid. However, the observed leachates do not resemble the ϵ_{Nd} of the pore fluid (**Figure 6**). We therefore propose that the ϵ_{Nd} and Nd concentration of the operationally defined authigenic phases (leachates) likely represents a combination of “true” authigenic phases and lithogenic contamination. Specifically, the leachates are recovering Nd from lithogenic phases in addition to the authigenic phases in the sediment samples. We suggest this additional lithogenic input is not readily contributing to the pore fluid based on the difference in ϵ_{Nd} between the pore fluid and the leachates. We suggest that the pore fluid is a robust indicator of the ‘true’ authigenic phase ϵ_{Nd} because of the exchange between pore fluid and the authigenic phases, and we further suggest that any difference between the pore fluid and the leachate is an artifact of the leaching procedure targeting additional phases.

4.2 Constraints on pore fluid ϵ_{Nd}

Compared to the total solid phase, the Nd in the pore fluid accounts for less than 0.001% of the total Nd concentration per unit volume (**Figure 6; Supplemental Information Table 7**). Calculations of a sediment-pore fluid distribution coefficient (K_d) using background pore fluid Nd concentrations of 250 pmol L⁻¹ measured at HH200 and total solid Nd concentrations of 13.8 $\mu\text{g g}^{-1}$ result in a K_d of 1.8×10^5 , similar to the minimum sediment-seawater K_d of 1.5×10^5 reported by Takata et al. (2016). Using seawater values from sites HH200 (12 pmol

L⁻¹) and HH3000 (36 pmol L⁻¹) our calculated sediment-seawater K_d ranges from 1.2 × 10⁶ and 3.7 × 10⁶, similar to the maximum sediment-seawater K_d of 1.8 × 10⁶ reported by Takata et al. (2016). The small Nd concentration in the pore fluid reservoir relative to the Nd concentration in the total solid phases means that pore fluids cannot maintain a unique ϵ_{Nd} signature: even a small exchange between the pore fluids and the authigenic or lithogenic reservoirs will dominate the pore fluid signal. Being a surface exchange process, the exchange between pore fluid and the authigenic phases is likely dependent upon the exposed surface area of the authigenic phases, as has been observed with other surface processes (e.g. dissolution, Schott et al., 2009, Schott et al., 2012). In this way, the greater the size of the authigenic reservoir (i.e., the more authigenic coating is present), the greater the capacity of the upper sediment column to sustain a benthic flux. Assuming exchange between the authigenic phases and the pore fluid, the Nd release from the authigenic phase must be greater than any Nd precipitation within an authigenic phase for Nd to accumulate in the pore fluid. If this difference between release and precipitation is a constant fraction of the authigenic reservoir, then the resulting buildup of Nd in the pore fluids will be greater in sediments with more authigenic phases, as observed here.

As described above, we expect the pore fluid ϵ_{Nd} to resemble the ϵ_{Nd} of the source of Nd to the fluids; however, the measured pore fluid ϵ_{Nd} is more radiogenic than the total solid ϵ_{Nd} , the reducible ϵ_{Nd} , and the acid leachable ϵ_{Nd} at HH200 (**Figure 6**). Therefore, to be consistent, our model requires a more radiogenic source of ϵ_{Nd} to be able to explain the pore fluid ϵ_{Nd} at HH200. The initial bottom

water chemistry of pore fluids cannot provide this radiogenic source because the mass of Nd derived from bottom water is quantitatively insignificant and because the bottom water is less radiogenic than the pore fluids. Of the acid leachable, the reducible, and the lithogenic components, the lithogenic component is the only ϵ_{Nd} not directly measured (**Table 1**). However, we can calculate the ϵ_{Nd} and Nd concentration for the lithogenic component, to determine whether the lithogenic component is a radiogenic Nd source. We calculate the lithogenic component as

$$\epsilon_{Nd_{Lith}} = \frac{((\epsilon_{Nd_{Total}} \times [Nd]_{Total}) - (\epsilon_{Nd_{Auth}} \times [Nd]_{Auth}))}{[Nd]_{Lith}} \quad (1)$$

where the *Total* is the measured total solid phase, *Auth* is a weighted sum of the acid leachable and reducible leachates, and *Lith* is the remaining lithogenic component. The result of this calculation is an $\epsilon_{Nd_{Lith}}$ of -2 at HH200, -2.5 at HH1200, and -3.1 at HH3000 (**Table 1**), meaning that as a whole, the lithogenic component cannot provide a source of radiogenic Nd. However, we know that the lithogenic component consists of multiple major mineral phases (e.g., quartz, albite, a white mica, and clinocllore; **Supplemental Information Figure 1**). Therefore, preferential contribution from a single mineral phase within the lithogenic component is possible. Preferential contribution is consistent with laboratory leaching experiments in which the ϵ_{Nd} obtained was dependent on the fraction of the particles reacting with the leach solution (Wilson et al., 2012; Wilson et al., 2013).

4.3 Cryptic trace mineral

A radiogenic trace mineral may provide the “unmeasured” radiogenic source required to explain the pore fluid ϵ_{Nd} signature in the absence of any measurable highly radiogenic source. This trace mineral adds complexity, but serves as an example as increasing pore fluid data sets become available for a more comprehensive model. Currently, the proposal of a trace mineral preferentially dominating the particulate-fluid interaction is consistent with observations in the modern ocean and in the laboratory (e.g. Jeandel et al., 2015; Pearce et al., 2013; Rousseau et al., 2015; Wilson et al., 2012; Wilson et al., 2013). Evidence for this radiogenic trace mineral exists in bottom water from HH200. At HH200, we were able to measure the ϵ_{Nd} signatures of a filtered bottom water sample and an unfiltered bottom water sample. Being closest to the shore, HH200 is likely to be most influenced by a reactive trace mineral, considering the release of Nd from suspended particulate matter is rapid (3 ± 1 weeks, Rousseau et al., 2015) and the more distal, deeper sediments have more developed and recycled authigenic phases. The unfiltered bottom water sample represents a combination of the filtered bottom water and what is essentially an acid leach of the particles in the water due to sample acidification. We observe that the ϵ_{Nd} of the unfiltered bottom water ($\epsilon_{NdUBW} = +0.7$) is more radiogenic than the ϵ_{Nd} of the filtered bottom water ($\epsilon_{NdBW} = -1.8$; **Table 1**). Assuming that the acidification of the unfiltered bottom water only adds Nd from the reactive trace mineral, and limiting the contribution of Nd to 20% of the concentration of Nd in the filtered bottom water, we can calculate the ϵ_{Nd} of the trace mineral needed to produce the change in ϵ_{Nd} between the unfiltered and filtered bottom water as:

$$\epsilon_{Nd_{UBW}} \times [Nd]_{UBW} = \epsilon_{Nd_{Trace}} \times [Nd]_{Trace} + \epsilon_{Nd_{BW}} \times [Nd]_{BW}$$

(2)

The result is a trace mineral with $\epsilon_{Nd_{Trace}} = +10$ to produce the observed shift in bottom water ϵ_{Nd} (equation 2). An ϵ_{Nd} of +10 is within the range of minerals coming from the Depleted Western Terranes in the region, including the Intermontane Belt, Coast Mountain Belt, Cascade Arc, and Vancouver Island (ϵ_{Nd} 0 to +11; Carpentier et al., 2014). More specifically, the Paleozoic mid-oceanic ridge basalts that comprise the Cache Creek terrane included in the Depleted Western Terranes, have ϵ_{Nd} between +7.7 and 10.2 (Smith and Lambert, 1995). The possibility of basaltic particles that could alter fluid ϵ_{Nd} and contribute REES to the solution has previously been experimentally investigated (Pearce et al., 2013). Therefore, inferring that a trace amount of this locally sourced reactive mineral with $\epsilon_{Nd_{Trace}} = +10$ is present in the sediments along the Oregon margin is at least possible.

In our model the trace mineral reacts readily, resulting in a significant contribution of radiogenic Nd to the pore fluid in less mature shallow sediments (i.e. HH200) where this trace mineral is extant. At HH200, we can estimate the percent Nd in the pore fluid coming from the trace mineral as:

$$\epsilon_{Nd_{PW}} \times [Nd]_{PW} = (\epsilon_{Nd_{AL}} \times [Nd]_{AL}) + (\epsilon_{Nd_{Trace}} \times [Nd]_{Trace})$$

(3)

wherein we assume the difference between the measured pore fluid ϵ_{Nd} ($\epsilon_{Nd_{PW}}$) and the acid leachable ϵ_{Nd} ($\epsilon_{Nd_{AL}}$) is completely due to the contribution of Nd

to the pore fluid from a trace mineral with $\epsilon_{NdTrace}$ of +10. The result is that only 3% of the Nd in the pore fluid at HH200 needs to come from the trace mineral to explain the observed ϵ_{NdPW} (-0.2; equation 3, **Figure 6**). Following the logic that the trace mineral is more prevalent in the shallow sediments closer to a terrestrial source, it follows that the trace mineral should be detectable in one or more local rivers. However, many rivers with differing ϵ_{Nd} signatures (e.g. VanLaningham et al., 2008) contribute to the Oregon margin. Additionally, seasonal variability in the ϵ_{Nd} signature of rivers could make detection of the cryptic phase time dependent (e.g. Viers et al., 2008). Combined, these complexities mean that extensive spatial and temporal sampling in each river would be necessary to discern the trace mineral in the riverine system.

We speculate that the contribution of radiogenic Nd from this trace mineral becomes less significant as the amount of the trace mineral remaining in the total solid decreases with sediment maturity (**Figure 8**). REE patterns support a greater contribution from such a reactive trace mineral in the less mature (shallower) sediments at HH200. That is, the REE pattern of the pore fluid is most different from the REE pattern of the total solid at HH200 and most similar at HH3000 (**Figure 2**). The similarity of the REE patterns of pore fluids and total solid at HH3000 is consistent with the absence of a reactive trace mineral in these more mature sediments. In addition to REE patterns, a decrease in the reactive trace mineral is supported by more radiogenic total solid at HH200 compared to HH3000 (**Figure 5, Table 1**). Specifically, the average total solid ϵ_{Nd} (ϵ_{NdTS}) changes from -1.4 at HH200 to -1.8 at HH1200 to -2.2 at HH3000. Using the $\epsilon_{NdTrace} = +10$ calculated above, we

can determine the percent of Nd in the trace mineral component of the total solid (TS) at HH200 that is not present at HH3000 if the only factor changing the total solid ϵ_{Nd} is the loss of the trace mineral offshore. We determine $[Nd]_{Trace}$ as

$$\epsilon_{Nd_{TS3000}} \times [Nd]_{TS3000} = (\epsilon_{Nd_{TS200}} \times [Nd]_{TS200}) - (\epsilon_{Nd_{Trace}} \times [Nd]_{trace}) \quad (4)$$

where $[Nd]_{trace}$ and $[Nd]_{TS3000}$ are fractions between 0 and 1 and must sum to $[Nd]_{TS200}$ ($[Nd]_{TS200} = 1$). The result is that $[Nd]_{trace}$ is 0.09; in other words 9% of the Nd in the total solid at HH200 is coming from the reactive trace mineral ($\epsilon_{Nd_{Trace}} = +10$). This calculation demonstrates that the difference in the total solid ϵ_{Nd} between HH200 and HH3000 can be explained by the decreasing presence of the trace mineral, consistent with our model for explaining observed pore fluid ϵ_{Nd} (equation 4, **Figure 8**).

Acknowledging that Sr has different geochemistry than Nd, the $^{87}Sr/^{86}Sr$ measured in the pore fluid, leachates, and total solid phase are consistent with our diagenetic model for Nd. The pore fluid Sr reservoir is small compared to the solid phases, accounting for ~1% of the concentration of Sr in the upper sediment column per unit volume. The pore fluid $^{87}Sr/^{86}Sr$ is within error of seawater (**Figure 4**). The $^{87}Sr/^{86}Sr$ of both leachates is between the $^{87}Sr/^{86}Sr$ of the pore fluid and the $^{87}Sr/^{86}Sr$ of the total solid at all sites. As with leachate ϵ_{Nd} , the greatest deviation in leachate $^{87}Sr/^{86}Sr$ from pore fluid $^{87}Sr/^{86}Sr$ occurs at HH200 supporting our assertion that the leachates are contaminated with the lithogenic phase (**Figure 4**).

On average, the Sr in the acid leachable solution is 45% of the Sr in the upper sediment column by volume. The remaining 55% of Sr is split evenly between the reducible leachate and the refractory phase with a molar Sr/Ca of between 0.003 and 0.008 in all leachates (**Supplemental Information Table 4**). For the total solid, the increase in $^{87}\text{Sr}/^{86}\text{Sr}$ from HH200 (0.707565) to HH3000 (0.709773) is consistent with the corresponding decrease in ϵ_{Nd} (**Figure 5**). Both the lower $^{87}\text{Sr}/^{86}\text{Sr}$ and higher ϵ_{Nd} at HH200 support a greater contribution from the depleted western terranes than at HH1200 or HH3000 (depleted western terranes 0.702000-0.706000; e.g. DePaolo and Wasserbug, 1976; Carpentier et al., 2014).

4.4 Applicability to ϵ_{Nd} distribution of the global ocean

In the modern ocean, a first order relationship has been observed between salinity and ϵ_{Nd} (VonBlanckenburg, 1999). The core of North Atlantic Deep Water maintains an ϵ_{Nd} of -13.5 along its flow path, becoming more radiogenic towards the south with the input of more radiogenic bottom water from Southern Ocean deep water formation. However, in the North Pacific, there is a change in the deep-water ϵ_{Nd} signal that occurs despite the absence of deep-water formation. Isotopic models have been unable to explain this alteration when ϵ_{Nd} is treated as a conservative tracer with riverine point sources (Arsouze et al., 2009; Jones et al., 2008). We suggest that the ϵ_{Nd} of the deep Pacific is instead determined by the ϵ_{Nd} of the benthic flux. As seen at all of our sites, the ϵ_{Nd} of the flux provides a source that is more radiogenic than the bottom water. Therefore, as the bottom water continues to be exposed to the flux along its flow path, the ϵ_{Nd} of the bottom water becomes more radiogenic. Models confirm that the addition of a deep Pacific source of

radiogenic Nd can bring model outputs from the interior ocean to within one ϵ unit of modern observations (Jones et al., 2008). In this way the benthic flux of Nd to the ocean can explain the observed ϵ_{Nd} gradient in the North Pacific, as well as the non-conservative behavior of Nd in the water column. This “benthic flux” hypothesis has the potential to fundamentally change our understanding of REE cycling and the biogeochemical cycle of ϵ_{Nd} in the ocean. This hypothesis needs to be further evaluated in other ocean basins and in a variety of sediment compositions. Furthermore, this model implies that the use of authigenic coatings as a proxy for bottom water ϵ_{Nd} in the past, may not, strictly speaking, be viable.

5.0 Conclusions

Pore fluid and sediment samples from three sites along the Oregon margin were collected and analyzed to evaluate the role of sediment diagenesis on pore fluid Nd composition. At these sites, sediment diagenesis dictates the Nd concentrations and ϵ_{Nd} in pore fluids. Because the flux of pore fluid Nd is a major source of Nd to the oceans, these diagenetic processes also can control the ϵ_{Nd} distribution of bottom water in regions with a large benthic flux. We find no simple relationship between diagenetic Nd enrichment and bulk mineralogy or organic carbon degradation. The Nd in the pore fluid is <0.001% of the total Nd reservoir in the sediment column, and because of the small size of this reservoir, it is sensitive to small imbalances in exchanges with the total solid phase. Within the total solid, the authigenic phases are a large and reactive reservoir of Nd, constituting ~50% of the Nd in the total solid. We propose that the magnitude of the benthic flux at each site is a result of the development of reactive authigenic phases during sediment

diagenesis. The more mature sediments at HH3000 support the greatest pore fluid Nd concentrations and benthic flux. The less mature sediments at HH200 support lower pore fluid Nd concentrations and have pore fluid ϵ_{Nd} influenced by the presence of trace minerals that are more radiogenic in their composition. This model provides a foundation for identifying sediment characteristics that are likely to result in a large benthic flux or result in a benthic flux with an ϵ_{Nd} influenced by exchange with a variety of lithogenic phases.

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Main Text Figure and Table Captions

Figure 1 Study Sites. Map shows the location of study sites at water depths of 200 m, 500 m, 1200 m, and 3000 m on the Oregon Margin in the northeast Pacific Ocean. The benthic flux of Nd to the ocean was calculated at 200 m, 1200 m, and 3000 m (Abbott et al., 2015a,b). Water column profiles show dissolved oxygen (left) and ϵ_{Nd} (right). The dissolved oxygen profile is only shown at 3000 m, as the profiles were indistinguishable among sites at this scale. ϵ_{Nd} is shown for HH200 (squares), HH1200 (diamonds), and HH3000 (circles).

Figure 2 Rare Earth Element Patterns. REEs are normalized to PAAS and Pr. Pr normalization is based on published pore fluid Pr values from these sites (Abbott et al., 2015a). The Pr normalization allows direct comparison of the pattern variability in the lower absolute concentration samples to the patterns in the higher concentration samples. Total solid (black) and total leachate (striped) represents the range in pattern from all sites. Pore fluid patterns are shown individually for HH200 (pink), HH1200 (blue), and HH3000 (green). The reader is referred to the web version of this article for interpretation of the color version of this figure.

Figure 3 Fluid Phase Characteristics. Pore fluid profiles from **A)** HH200, **B)** HH1200, and **C)** HH3000 for dissolved iron, manganese, lithium, phosphorous, neodymium and ϵ_{Nd} . Mn was below the detection limit at HH200 and HH1200 for all sampled intervals. Li and P data are not available from HH200. Error bars for Fe, Mn, P, and Nd are smaller than symbol size. Black arrows on ϵ_{Nd} profiles indicate bottom water ϵ_{Nd} signatures.

Figure 4 $^{87}Sr/^{86}Sr$. $^{87}Sr/^{86}Sr$ for acid leachable (triangle) and reducible leachates (diamonds), total solid (solid squares), and pore fluids (striped squares). Pore fluid $^{87}Sr/^{86}Sr$ is indistinguishable from seawater (grey shading, 0.70918, Henderson et al., 2004) at all sites. Error bars represent 2σ . a) Expanded y scale to display acid leachable variations and b) full y scale to display variations in all phases.

Figure 5 Solid Phase Characteristics. Total solid profiles from **A)** HH200, **B)** HH1200, and **C)** HH3000 for ϵ_{Nd} , Nd concentration, percent organic carbon (%OC), Fe/Al, Mn/Al, and $^{87}Sr/^{86}Sr$. The shaded bar for $^{87}Sr/^{86}Sr$ indicates the global seawater value. Parentheses indicate values not included in interpretations.

Figure 6 Mechanism Indicators. **A)** ϵ_{Nd} profiles for the acid leachable (light grey), the reducible (dark grey) fractions, the total solid (black), and the pore fluid (striped) for HH200, HH1200, and HH3000. **B)** Relative distribution of Nd among acid leachable (light grey), reducible (dark grey), refractory phase (black), and pore fluid (values) per cubic centimeter for HH200, HH1200, and HH3000. **C)** Average grain size distributions for pre-leach (black outline) and post-leach (grey shading) samples from HH200, HH1200, and HH3000.

Figure 7 *Leachate Characteristics*. Fe, Mn, Fe/Mn, Fe/Al, Mn/Al and ϵ_{Nd} for **A)** acid leachable and **B)** reducible fractions from HH200 (squares), HH1200 (triangles), and HH3000 (circles).

Figure 8 *Diagenetic Model*. Schematic representation of the sources and sinks of Nd to the pore fluids at a shallow, less evolved site such as HH200 (**A**) and a deeper, more diagenetically evolved site such as HH3000 (**B**). Total solid phase includes a trace mineral phase (black dots), an authigenic labile coating, authigenic oxides and a lithogenic (refractory) component. The particle is drawn approximately to scale. Calculated ϵ_{Nd} values are in *italics*, measured ϵ_{Nd} values are in **bold**. All concentrations are in ng cm⁻³.

Table 1 *Reservoir ϵ_{Nd}* . Site average ϵ_{Nd} and Nd concentrations for bottom water, pore fluid, total leachate, acid leachable fraction, reducible leachate, total solid, and lithogenic reservoirs for HH200, HH1200, and HH3000. Concentrations are in ng cm⁻³. The total leachate is a weighted average of the acid leachable and reducible leachates. The total solid includes the lithogenic and total leachate reservoirs. * indicates unfiltered bottom water. Reservoirs for which ϵ_{Nd} was calculated instead of measured directly are indicated by **. ^a the average pore fluid ϵ_{Nd} for HH1200 excludes the upper two intervals. Including the intervals the average pore fluid ϵ_{Nd} for HH1200 would be -1.9.

	HH200		HH1200		HH3000	
	ϵNd	[Nd]	ϵNd	[Nd]	ϵNd	[Nd]
Bottom Water	-1.8; 0.7*	0.003; 0.004*	-2.5	0.004	-2.3	0.004
Pore Fluid	-0.2	0.025	-1.5 ^a	0.035	-1.8	0.049
Total Leachate**	-0.8	4700	-1.0	5700	-1.3	6500
Acid Leachable	-1.1	1600	-1.2	2200	-1.9	1200
Reducable	-0.6	3100	-0.8	3500	-0.9	5300
Total Solid	-1.4	16000	-1.5	18000	-2.2	20000
Lithogenic**	-2.0	6200	-2.5	6500	-3.2	7000

Table 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

a) HH200

b) HH1200

c) HH3000

Figure 6

A) Weak Leachate

B) Strong Leachate

Figure 7

Figure 8