

AN ABSTRACT OF THE DISSERTATION OF

April N. Abbott for the degree of Doctor of Philosophy in Ocean, Earth, and Atmospheric Sciences presented on December 11, 2015.

Title: Influence of a Sedimentary Source of Nd on Deep Ocean ϵ Nd Distributions

Abstract approved: _____

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Ocean circulation is an important component in Earth's climate system. Predicting future climate and circulation changes requires an improved understanding of the past relationship between climate and ocean currents. The neodymium isotope composition (ϵ Nd) of water masses is frequently used as a quasi-conservative tracer to reconstruct ocean circulation. The current budget of Nd in the ocean cannot account for upwards of 95% of the Nd entering the ocean, hindering interpretations of the ϵ Nd tracer. This study aims to determine the magnitude of the sedimentary source of Nd to the global ocean, characterize the influence of the flux of Nd on the ϵ Nd distribution in the global ocean, and identify the diagenetic factors that control the magnitude of the flux. To address these goals, I compare pore fluids, overlying water column, and sediments from eight sites on the continental margin off Oregon and California (USA). These sites lie above, within, and below the Northeast Pacific's oxygen minimum zone and represent shelf-to slope settings at water depths between 80 and 3000 m.

Concentrations of the rare earth elements (REEs), including Nd, in the pore fluids are up to two orders of magnitude higher than the REE concentrations in seawater. All pore fluid REE profiles exhibit shallow subsurface (2-10 cm) concentration maxima. Fractionation of the REEs occurs during mobilization and transport through the sediment

column, indicated by changes in the rare earth patterns above and below the pore fluid REE concentration maximum. Based on the pore fluid concentration gradient, I calculate the benthic flux from the pore fluids to the ocean. These calculations show a flux of Nd to the ocean increasing from $3 \text{ pmol cm}^{-2} \text{ yr}^{-1}$ at our 200 m site to $32 \text{ pmol cm}^{-2} \text{ yr}^{-1}$ at our 3000 m site. No corresponding change in pore fluid phosphorous, iron, organic carbon, or silica among sites is observed. Additionally, the major mineralogy remains constant among sites.

Extrapolating our flux estimates over the global ocean, I estimate a global benthic Nd flux between 18×10^6 and 110×10^6 mol annually. I conclude that the benthic flux of Nd to the ocean is the dominant source of Nd to the global ocean. The ϵNd of this flux ranges from -0.2 at our 200 m site, to -1.5 at our 1200 m site and, -1.8 at our 3000 m site. At our deepest (3000 m) site, the bottom water ϵNd (-2.3) is between the value expected for the water mass (-3.3) and the ϵNd of the flux (-1.8). The magnitude of this flux and the time a water mass is exposed to this flux determines the distribution of ϵNd . The degree of change in bottom water ϵNd depends on the difference between the initial ϵNd of the bottom water and the ϵNd of the flux. The benthic flux can determine the ϵNd of bottom water in a short enough time to create the heterogeneous ϵNd observed in the modern ocean. Additionally, the benthic flux provides a mechanism for the observed alterations in ϵNd in the deep North Pacific in the absence of Pacific deep-water formation.

Based on ϵNd of the pore fluids, total sediment, and sediment leachates, I propose that the magnitude of the flux is a function of the authigenic coatings formed during sediment diagenesis. Because the pore fluid Nd represents less than 0.001% of the Nd in any given volume of the upper sediment column, changes in Nd must be driven by larger Nd reservoirs in the solid phases. The leachable Nd (acid leachable: $1 - 7 \text{ } \mu\text{g Nd g}^{-1}$ sediment; reducible $2 - 8 \text{ } \mu\text{g Nd g}^{-1}$ sediment) represents a large reactive Nd reservoir, accounting for ~50% of the Nd in any given volume. Because the total sediment digest and leachates are less radiogenic than pore water at our 200 m site, I infer that there are radiogenic trace mineral phases undergoing active exchange with the pore fluid reservoir. When present, this trace mineral disproportionally influences the ϵNd of the flux.

The exchange of Nd between the authigenic coatings and the pore fluid in the upper sediment column means that the ϵ_{Nd} of the true coatings will be the same as the pore fluids. However, leaching procedures result in a contaminated authigenic coating ϵ_{Nd} signature, especially in the presence of reactive trace minerals. In regions with a large benthic flux, the authigenic coatings determine the ϵ_{Nd} of the bottom water. Therefore, in these regions the coatings will resemble ϵ_{Nd} of the bottom water. The ϵ_{Nd} of the bottom water cannot drive the ϵ_{Nd} of the coatings because the amount of Nd in the bottom water is quantitatively insignificant.

Based on the findings that the benthic source is the dominant source of Nd to the ocean, the ϵ_{Nd} of this flux can determine the ϵ_{Nd} of the bottom water, and the ϵ_{Nd} of the authigenic coating is not determined by the ϵ_{Nd} of the bottom water, a reinterpretation of the ϵ_{Nd} records is necessary. Because the ϵ_{Nd} of bottom water is not conservative, the ϵ_{Nd} record cannot be strictly interpreted as water mass mixing. The inverse relationship between ocean circulation speed and exposure time can result in differing ϵ_{Nd} values with no change in circulation path. Additionally, the end member water mass ϵ_{Nd} values are likely to have changed through time. Specifically, any shift in deep-water formation would result in the bottom water being exposed to a different ϵ_{Nd} from the benthic flux. With reinterpretation that recognizes these influences, the ϵ_{Nd} tracer may remain a useful proxy of past ocean circulation.

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Influence of a Sedimentary Source of Nd on Deep Ocean ϵ Nd Distributions

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

April N. Abbott, Author

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Chapter 1: Introduction

Throughout geologic time, Earth's orbit has controlled the global climate with the interaction of regular, predictable changes in Earth's tilt, eccentricity, and precession (e.g. Emiliani, 1955). However, humans are altering these predictable cycles by altering Earth's carbon cycle and increasing the amount of green house gases, such as CO₂, in Earth's atmosphere. The changes imparted by humans are drastic enough to have resulted in new geological epoch, the anthropocene. With this modern climate change, atmospheric CO₂ levels are now higher than at any time in the last 800,000 years resulting in decreased dissolved oxygen and more acidic waters (Kump et al., 2009). Climate change influences the temperature on land and in the sea, as well as the oxygenation and pH of the ocean (Gruber, 2011). As Earth continues into the anthropocene, society's ability to successfully prepare and adapt to a changing global environment will be partly dependent upon our ability to forecast both the magnitude and direction of climate change. The consequences of future climate change depend on feedbacks between the land, the ocean, and the atmosphere. For instance, the warming of Earth's atmosphere can slow the Atlantic Meridional Overturning Circulation (AMOC) via an increased input of fresh water in the North Atlantic (as recently observed e.g. Rahmstorf et al., 2015). The increased freshwater from ice melt creates a cold fresh lens of water that acts as a barrier to deep-water formation, thus inhibiting AMOC. Another example of these feedbacks is that the warming of deep water can destabilize methane hydrates, resulting in a release of methane to the atmosphere. Since methane is a potent green house gas, its release then drives additional atmospheric warming (e.g. Lunt et al. 2011). The ability to reconstruct these interactions between ocean, land, and atmosphere in the various climates of Earth's past will help constrain the potential response of the

global ocean to higher CO₂ and warmer mean global temperatures that will result from modern climate change.

Thermohaline circulation in the ocean is most simply described as a conveyor, with the progression of deep water from the Atlantic into the Indian and Pacific basins (Broecker, 1991; Figure 1.1). The result of this circulation pattern is the oldest waters are found in the deep Pacific, at the end of the deep circulation path and before upwelling back to the surface (Broecker, 1991; Figure 1.1). Modern thermohaline circulation is driven by the formation of cold, saline, high-density water masses at high latitudes (e.g. Broecker, 1991). Specifically, deep-water formation occurs in the North Atlantic (North Atlantic Deep Water, NADW) and the Southern Ocean (Antarctic Bottom Water, AABW). While direct observation of modern ocean circulation is possible, circulation changes in the past cannot be directly measured.

Multiple tracers are used in paleoceanographic studies to reconstruct ocean circulation. For instance, Cd/Ca, Zn/Ca, and $\delta^{13}\text{C}$ records from foraminifera testes are used to distinguish between nutrient rich and nutrient poor water masses at a location through time (e.g. Frank, 2002; Bryan and Marchitto, 2010; Table 1.1). However, the species of foraminifera can introduce vital effects to these records (Bryan and Marchitto, 2010). Additionally, these tracers are prone to thermodynamic effects (Table 1.1; e.g. Frank, 2002). While both of these tracers can qualitatively characterize the overlying water mass, they are ineffective at quantifying the relative contribution of various water masses. Furthermore, as nutrient concentration tracers the Cd/Ca, Zn/Ca, and $\delta^{13}\text{C}$ records are largely dominated by processes in the surface ocean preventing inference of the origin of deep-water masses (Frank, 2002).

Isotopic tracers can provide a more quantitative approach to reconstructing ocean circulation. Effective isotopic tracers of water mass circulation must have a long enough residence time to allow for a definitive water mass signature but not such a long residence time that the ocean is homogeneous. For instance, the residence time of Th is too short (Th) and the residence times of Sr, Hf, and Os are too long (Sr) to distinguish water masses (Frank, 2002; Goldstein and Hemming, 2003; Table 1.1). The spatial extent of isotopic records may also be limited, for example the Pb isotope record is only available from regions of the ocean with Fe-Mn nodules (Goldstein and Hemming, 2003). Nd is important to paleoceanographic reconstructions because the neodymium isotope composition (ϵNd) can be used to quantify water mass mixing, ϵNd records can be recovered ubiquitously throughout the ocean, and because the residence time of Nd in the ocean allows water mass ϵNd to be differentiated (e.g. Frank, 2002; Goldstein and Hemming 2003; Table 1.1). The locations of deep-water formation form the foundation from which the neodymium isotope composition of seawater (ϵNd) can be used as a paleocirculation tracer because ϵNd appears to reflect water mass provenance (Goldstein and Hemming, 2003). Because the residence time of Nd in the ocean (between 300 and 600 years; Piepgras and Wasserburg, 1983; Goldstein et al., 1984; Jeandel et al., 1995; Tachikawa et al., 1999, 2003; Siddall et al., 2008; Arsouze et al., 2009) is shorter than the average mixing time of the deep ocean (1500 years; Broecker and Peng, 1982) the heterogeneity in ϵNd among water masses is maintained. End member ϵNd values are assumed constant through time based on modern water mass characteristics; specifically $\epsilon\text{Nd} -13.5$ for North Atlantic Deep Water (NADW; Piepgras and Wasserburg, 1980; Von Blanckenburg, 1999), between -9 and -10 in the Southern Ocean deep water masses

(Stichel et al., 2012), and more radiogenic values for Pacific Ocean deep water masses (ϵNd between -3 and -5; Piepgras and Jacobsen, 1988; Amakawa et al., 2004). Other water masses can therefore be interpreted as a mix of these end members. The interpretation of ϵNd as a reflection of the location of water mass origin is largely based on riverine dissolved load being the dominant source for the dissolved Nd budget of water masses (e.g. Goldstein and Jacobsen, 1988; Elderfield et al., 1990; Ingri et al., 2000). That is, current interpretations assume the only change to water mass ϵNd is through mixing the contribution of two known sources (i.e. NADW, PDW). If ϵNd is conservative and only changed through mixing, then the contribution of each source can be calculated. For instance, the mixing of the Atlantic and Pacific Ocean end members through global ocean circulation results in intermediate values (e.g. Antarctic Circumpolar Current $\epsilon\text{Nd} = -8.7$, Carter et al., 2012; Indian Ocean $\epsilon\text{Nd} = -3.5$ surface, -7 deep, Goldstein and Hemming, 2003). To change the ϵNd value at a given location a change in the proportion of the end member water masses is required. Therefore, changes in ϵNd over time are considered a reflection of shifts in global ocean circulation (e.g. Rutberg et al., 2000; Piotrowski et al., 2004, 2005; Haley et al., 2008; Colin et al., 2010; Murphy and Thomas, 2010). Indeed seawater, ferromanganese crusts, and nodules show a distinct provinciality between the ocean basins (Piepgras et al., 1979; Jacobsen and Wasserburg, 1980; Piepgras and Wasserburg, 1982; Albarède et al., 1997) and ϵNd displays a strong first order relationship with salinity (Von Blanckenburg, 1999) supporting the use of ϵNd as a water mass tracer (Figure 1.2).

ϵNd is defined as $[(^{143}\text{Nd}_{\text{sample}}/^{144}\text{Nd}_{\text{sample}})/(^{143}\text{Nd}_{\text{CHUR}}/^{144}\text{Nd}_{\text{CHUR}})-1] \times 10^4$ where CHUR is the Chondritic Uniform Reserve, used as an average earth value ($^{143}\text{Nd}/^{144}\text{Nd}$

=0.512638; Jacobsen and Wasserburg, 1980; Wasserburg et al., 1981). Because ^{143}Nd is produced as an alpha decay product of samarium (^{147}Sm) whereas ^{144}Nd is stable, $^{143}\text{Nd}/^{144}\text{Nd}$ can change through time with the ingrowth of ^{147}Sm to ^{143}Nd with a half life of 1.06×10^{11} years (Piepgras and Jacobsen, 1988). Earth's land masses have heterogeneous ϵNd signatures. This heterogeneity is driven by the partial melting of Earth's mantle. A partial melt is when only a portion of the mantle liquefies, while the rest remains in a solid state. During a partial melt, the composition of the melt may be different than the composition of the original bulk (for Nd on Earth, the original bulk is considered to be CHUR). Specifically, Nd is preferentially lost to the melt phase relative to Sm; Sm is preferentially retained in the remaining solid (e.g. DePaolo and Wasserburg, 1976). This separation between the solid and liquid phases during a partial melt occurs because ^{143}Nd is less compatible than Sm. That is, as an element Nd has a stronger preference than Sm for the liquid phase, as opposed to the solid phase (e.g. Frank, 2002). The preferential retention of Sm in the solid phase results in a Sm enriched mantle over time (Frank, 2002). In other words, the partial melting of Earth's mantle results in igneous rocks with lower $^{143}\text{Nd}/^{144}\text{Nd}$ relative to the bulk mantle (more negative ϵNd) and residual mantle with higher $^{143}\text{Nd}/^{144}\text{Nd}$ relative to the starting bulk mantle (more positive ϵNd ; Figure 1.3; DePaolo and Wasserburg, 1976). Therefore, ϵNd varies as a function of age (decay of ^{147}Sm to ^{143}Nd) as well as the initial Sm/Nd ratio, resulting in a generally low $^{143}\text{Nd}/^{144}\text{Nd}$ (negative ϵNd) for continents relative to the mantle and bulk earth (Goldstein and Hemming, 2003).

Current interpretations of ϵNd as a quasi-conservative tracer of water-mass circulation assume that the ϵNd of a water mass after subduction is only altered through

water mass mixing. Interpretations of ϵNd rely on the riverine dissolved load being the dominant source of Nd to the ocean and do not allow for any additional sources of Nd to the deep ocean that could alter the ϵNd of a water mass after it has left the surface. However, numerous attempts to balance the modern Nd budget in the ocean have been unsuccessful (e.g. Keasler and Loveland 1982; Bertram and Elderfield, 1993; van de Flierdt et al., 2004; Singh et al., 2012) and there is a disparity between non-conservative Nd concentrations and conservative Nd isotopes, coined the “neodymium paradox” (e.g. Tachikawa et al., 1999). Modeling of ϵNd distributions using global ocean circulation models suggest that a source “missing” from the current budget may account for upwards of 95% of the Nd in the ocean (Arsouze et al., 2009). The ambiguities in the modern budget of Nd in the ocean complicate the use of ϵNd as a circulation tracer because if the sources required to balance the oceanic Nd budget add Nd to a water mass after subduction (i.e. along the flow path), then the ϵNd of that water mass may be altered. The possibility of a source of Nd to the bottom water is supported by typical oceanic Nd profiles that are depleted in Nd near the surface and enriched at depth, with a greater gradient in the Pacific Ocean than in the Atlantic Ocean (Lacan et al., 2012). Many possible sources have been invoked to explain the missing source in the modern budget including water column processes (e.g. Rasmussen et al., 1998; Oka et al., 2009; Stichel et al., 2012), aerosols (Grousset et al. 1988; Bayon et al., 2004), submarine groundwater discharge (Johannesson and Burdige, 2007; Johannesson et al., 2011; Kim and Kim, 2014), and the sediments (e.g. Arsouze et al., 2007; Haley and Klinkhammer, 2003; Jeandel et al., 2007; Lacan and Jeandel 2001, 2004a, b, c, 2005a, b; Wilson et al., 2013).

The reconciliation of water column processes with observed ϵNd distributions has been challenging. Water column processes alone cannot account for the observed ϵNd alteration in the deep Pacific. For instance, water column processes including scavenging and remobilization have been proposed to explain the vertical concentration profile of Nd in the ocean in which Nd concentrations are lowest at the surface and increase with depth in water (e.g. Rasmussen et al., 1998; Oka et al., 2009; Stichel et al., 2012). Additionally, observed surface Nd concentrations are too low to result from conservative mixing of water masses (e.g. Oka et al., 2009). One proposed mechanism is that living diatoms will scavenge the Nd in surface waters. Then, as these relatively large phytoplankton die and sink through the water column, the scavenged Nd will be remobilized (e.g. Akagi et al., 2013). Smaller phytoplankton can temporarily decrease the dissolved Nd in the surface ocean during a bloom, however the concentrations of dissolved rare earth elements (including Nd) return to pre-bloom levels suggesting no significant vertical transport (Hara et al., 2009). Additionally, the change in ϵNd that accompanies the Nd concentration change makes reconciliation with water column processes unfeasible. Producing the observed bottom water Nd concentrations with only these vertical water column processes is implausible because of the high mass transfer that would be required to create the upwards of one unit shift in ϵNd in the bottom water associated with the increased Nd concentration (Lacan and Jeandel, 2005; Arsouze et al., 2009; Carter et al., 2012; Grasse et al., 2012; Grenier et al., 2013).

Neodymium is a lanthanide element. The lanthanides, or rare earth elements (REEs), behave as a coherent group of elements that exhibit limited mobility or fractionation during most geological processes (McLennan 1991). The chemical

behavior of REEs varies predictably with increasing atomic number because of the decrease in ionic radius as the inner 4f-electron shell fills (e.g. Goldstein and Hemming, 2003). This predictable behavior makes the REEs an important geochemical tool for better understanding the processes that impact the Nd budget of the ocean. The REEs dominantly exist in the trivalent state in the environment under a wide range of conditions (Byrne and Kim, 1993; Byrne et al., 1996). Eu and Ce are exceptions due to their redox sensitivity; specifically Ce^{3+} can be oxidized to Ce^{4+} (abiotically or biologically mediated) and Eu^{3+} can be reduced to Eu^{2+} (Byrne and Kim, 1993; Byrne et al., 1996; Leybourne and Johannesson, 2008). The similarity in chemical behavior combined with predictable fractionation have made the REEs widely used geochemical tracers with applications including igneous petrology, cosmo-chemistry, sedimentology, tectonics, and water-rock interactions (Hanson, 1980; Henderson, 1984; Taylor and McLennan, 1985; Nesbitt, 1979; Sholkovitz, 1995; Di Leonardo et al., 2009). Fractionation among the REEs is observed by examining the REE “patterns”, which are the REE concentrations normalized to shale values. REE patterns are tools for mechanistic diagnosis of depositional and diagenetic processes (e.g., Cullers et al., 1987; Byrne and Kim, 1990; McLennan, 1991; Bellanca et al., 1997; Sholkovitz et al., 1999; Haley et al., 2004; Piper et al., 2007; Bau et al., 2013). The normalization of REE patterns allows comparison of REEs among samples with different absolute concentration and accounts for the higher natural abundance of light REEs relative to heavy REEs to facilitate inter-REE comparison (Byrne and Sholkovitz, 1996). REEs are often grouped into light rare earths (LREEs), middle rare earths (MREEs), and heavy REEs (HREEs).

Throughout this dissertation, I refer to LREEs consisting of La, Ce, Pr, and Nd; MREEs consisting of Eu, Gd, Tb, and Dy; and the HREEs consisting of Er, Tm, Yb, and Lu.

In seawater, HREEs are enriched relative to “bulk earth” (represented by Post Archaen Australian Shale (PAAS, values after Nance and Taylor 1976) or Oregon Bulk Sediment (ORBS, Figure 1.4, Abbott et al., 2015a)) with deep-water samples having more enrichment than shallow water (Figure 1.5). The REE pattern of rivers (Sholkovitz, 1996; Sholkovitz et al., 1999) and estuaries (Figure 1.6; Sholkovitz, 1996; Sholkovitz and Szymczak, 2000) does not resemble that of seawater (Figure 1.5; Elderfield and Greaves, 1982; Klinkhammer et al., 1983; Alibo and Nozaki, 1999). This difference in pattern is expected with fractionation occurring between rivers and the ocean. Fractionation in estuaries has been suggested to increase the relative HREE enrichment of the dissolved REEs bringing the river pattern closer to seawater as it approaches the ocean (Sholkovitz and Szymczak, 2000). In seawater, HREEs preferentially complex with carbonates, which stabilize the dissolved HREE resulting in a HREE enriched pattern (Cantrell and Byrne, 1987; Lee and Byrne, 1993; Lou and Byrne, 2004; Kim et al., 2012; Figure 1.5). In the ocean, REEs are affected by particle dissolution, dissimilar source and sink terms, complexation, oxide scavenging, and REE incorporation into solid phases (Elderfield and Greaves, 1982; Cantrell and Byrne, 1987; Elderfield, 1988; Byrne and Kim, 1990; Elderfield, 1993; Lee and Byrne, 1993; Schijf and Byrne, 2004; Leybourne and Johannesson, 2008; Akagi, 2013). The apparent redox sensitivity of the REEs is due to the incorporation of REEs during Fe oxide precipitation (Gutjahr et al., 2007). REE fractionation varies as a result of, among other factors, REE speciation, the nature of the complexing agent, ionic strength, pH, and the presence of sulfates, phosphates, or

siderophores (e.g. Wood 1990; Byrne and Li 1995; Viers et al., 1997; Dia et al., 2000, Tang and Johannesson 2003; Schijf and Byrne, 2004; Tang and Johannesson, 2010; Akagi, 2013; Bau et al., 2013). For instance, changing physico-chemical conditions such as carbonate alkalinity in pore water can shift the preferential complexation of the REEs between organic and carbonate ligands (Pourret et al., 2008; Rongemaille et al., 2011).

Abiotic and biotic depositional and diagenetic processes can have unique fractionation patterns (e.g. Sholkovitz et al., 1994; Akagi, 2013; Bau et al., 2013). For instance, reducing sediments with suboxic pore fluids the HREE enrichment pattern characteristic of seawater is flattened resulting in a linear pattern (Haley et al., 2004; Kim et al., 2012). Additionally, complexation with siderophores increases the overall concentration of dissolved REEs and produces a positive Ce anomaly and MREE enrichment in the dissolved REEs relative to the source (Bau et al., 2013). Microbial activity can be an important biotic control on REE patterns as well (e.g. Moffet, 1990; Pol et al., 2014). For example, methanotrophic activity may result in a LREE depleted pattern in dissolved REEs because the LREEs are effectively utilized for growth by methanotrophs (Pol et al., 2014). REEs with a higher atomic number than Nd appear unable to be accommodated into the methanotrophs' amino acid structure (Pol et al. 2014). Furthermore, the negative Ce anomaly in seawater is a result of microbially mediated oxidation (Figure 1.5; Moffet, 1990).

However, the interpretation of REE patterns is rarely straightforward. Any given environment is influenced by multiple factors, and observations that hold true in one location may not hold true elsewhere. For instance, the three primary patterns of REEs observed in marine pore fluids have been associated with the source of the REEs to these

fluids (Haley et al., 2004). A particulate organic carbon source results in a REE pattern with a constant but moderate increase from light to heavy (“linear” Figure 1.7), a Ce oxide source results in an HREE enriched pattern, and an Fe oxide source results in a MREE enriched pattern (Figure 1.7; Haley et al., 2004). However, in other cases particulate organic carbon was associated with a preferential release of LREEs (Kim et al., 2012). In the second chapter of this dissertation I demonstrate that MREE enriched REE patterns in pore fluids show no simple relationship with Fe at our sites (Abbott et al., 2015a). I conclude from the data presented in the second chapter that at our sites, the changes in REE pattern from one pore fluid interval to another demonstrate fractionation during mobilization and transport within the upper sedimentary column.

More broadly, the second chapter of this dissertation addresses the modern budget of Nd in the ocean focusing on a potential source of Nd from the sediments. The sediments have been suggested as a source of Nd to the ocean by many studies (e.g. Arsouze et al., 2007; Haley and Klinkhammer, 2003; Jeandel et al., 2007; Lacan and Jeandel 2001, 2004a, b, c, 2005a, b; Wilson et al., 2013). To evaluate the magnitude of a benthic Nd flux to the ocean, sediment cores and water column samples were collected from eight sites along the Oregon-California margin. These sites have water depths between 80 and 3000 m and transect the oxygen minimum zone (500 to 1200 m). The neodymium concentration in pore fluid samples provides the data to calculate the diffusive flux of Nd from the sediments to the ocean. Extrapolated globally, this flux could account for as much as 95% of Nd missing from the modern budget. Additionally, the resulting REE pattern of the flux is different among sites with the most seawater-like HREE enrichment co-occurring with the largest calculated diffusive flux. This HREE

enriched pattern at HH3000 further supports the suggestion that the benthic source is the dominant source of Nd to the ocean.

The third chapter of this dissertation examines the ramifications of a benthic flux of Nd to the ϵNd distribution in the global ocean. Specifically, this chapter focuses on three of the eight sites to examine the ϵNd of the flux (HH200, HH1200, and HH3000). This study aims to quantify the influence of a benthic source of Nd on bottom water ϵNd and mechanistically explain the poorly understood processes coined “boundary exchange” (Lacan and Jeandel 2001, 2004a, b, c, 2005a, b; Arsouze et al., 2007; Jeandel et al., 2007; Rickli et al., 2014). The observed ϵNd of the flux from all three sites is more radiogenic than the local bottom water (Abbott et al., 2015b); consistent with the deep radiogenic source needed for general ocean circulation models to be able to predict the observed ϵNd of the Pacific Ocean (Jones et al., 2008). At any given location the expected ϵNd of bottom water due to the mixing of Atlantic and Pacific end members through modern ocean circulation is generally similar to the ϵNd of the detrital particles in the same location, thus complicating efforts to distinguish the influence of the particles relative to the influence of water mass mixing on the observed bottom water ϵNd (Jeandel et al., 2007; Wilson et al., 2013). However, in chapter 3 I use a model to demonstrate that a benthic source of Nd to the ocean can exert control over the Pacific Ocean’s deep-water ϵNd distribution. Additionally, I use the measured bottom water ϵNd and the bottom water ϵNd predicted for the water mass to demonstrate that bottom water ϵNd is between the expected water mass ϵNd and the measured pore fluid ϵNd . I suggest that the difference between the expected water mass ϵNd and the measured bottom water ϵNd is a

function of the amount of time a water mass is in contact with the sediments, the magnitude of the benthic flux, and the ϵNd of the benthic flux.

The fourth chapter examines the factors that determine the magnitude and ϵNd signature of the benthic flux. Chapters 2 and 3 of this dissertation add to multiple studies supporting the sediments as a significant influence on the Nd budget of the ocean (Elderfield and Sholkovitz, 1987; Sholkovitz et al., 1989; Sholkovitz, 1992; Haley et al., 2004; Arsouze et al., 2009; Abbott et al., 2015a). The influence of the sediments has been proposed to be via lithogenic inputs (Henry et al., 1994; Tachikawa et al. 1999; Jeandel et al., 2007, Jeandel et al., 2015), detrital release in the nephroid layer (Stichel et al., 2015), and sediment dissolution (Sholkovitz, 1992; Arsouze et al., 2009; Rousseau et al., 2015). Less than 3% dissolution of the sediments deposited by the annual load of global rivers is required to supply over 90% of Nd to the global ocean (Jeandel et al., 2015 and *sources therein*). Despite the underscored importance of the sedimentary influence on the oceanic Nd budget, the factors and mechanisms dominating this sedimentary source have remained poorly constrained. In chapter 4, I argue that the diagenesis of sediments is responsible for determining the benthic flux of Nd. This idea is leveraged off the observations from the two previous chapters, but here I specifically suggest that authigenic coatings formed during diagenesis result in a pore fluid Nd concentration proportional to the amount of coating.

For current interpretations of the sedimentary record of ϵNd to be correct, the ϵNd of the water mass must be consistently and accurately preserved in the sediment record and this signal must be able to be faithfully recovered. Chapter 3 illustrated that pore fluid ϵNd does not have the same value as bottom water, but the possibility remains that a

record of pore fluid signatures could still be useful in ocean circulation studies. While the unique pore fluid ϵNd signature potentially has implications for other sources of ϵNd records, including foraminiferal tests, fish teeth, and authigenic sediment coatings (ex. Thomas et al., 2003; Haley et al., 2008; Gourlan et al., 2008; Le Houedec et al., 2012; Thomas et al., 2014) in the fourth chapter, I focus on the ϵNd recorded in authigenic sediment coatings and the relationship between the ϵNd of the leachate and the ϵNd of the pore fluid. Many complications arise in interpreting ϵNd records from sedimentary coatings. For instance, the ϵNd of the authigenic coatings recovered in the leachates do not consistently reproduce pore fluid ϵNd . Because the authigenic sediment coatings recovered by leaching procedures are operationally defined, this raises the question what signal is being recovered by the leach? Leaching methods are inconsistent among studies and often adjusted to the nature of the sediments at a specific site (for instance, eliminating a step in the absence of carbonate; Sholkovitz, 1989; Piotrowski et al., 2005; Gutjahr et al., 2007; Haley et al., 2008). Many leaching procedures are designed to target the Fe-Mn oxyhydroxide coatings of sediments (ex. Bayon et al., 2004; Gutjahr et al., 2007) and others are more vaguely focused on an operationally defined labile coating. Various artifacts have been observed as a result of leaching procedures (e.g. Sholkovitz, 1989; Wilson et al., 2013). Factors including the duration of the leaching procedure, molarity and pH of the leaching solution, and choice of the leaching reagent have all been shown to impact the ϵNd of the leachate (Wilson et al., 2013). In the fourth chapter, I suggest the presence of a cryptic radiogenic reactive trace mineral that preferentially influences the leachates. This trace mineral is more abundant at HH200, and thus results in greater leachate contamination. The presence of a trace mineral phase may change

through time with changes in weathering, bioturbation, and chemical dissolution. For instance, increased sedimentation rate and increased bioturbation have been observed to limit the impacts of chemical dissolution (Bralower et al., 2015). If bioturbation limits dissolution, then the decreasing bioturbation with expanding oxygen minimum zones (e.g. Gruber, 2011) may promote increased dissolution resulting in a quicker disappearance of the trace mineral.

In summary, first order observations suggest that ϵNd can serve as a quasi-conservative water mass tracer through time with changes being recorded in authigenic sediment coatings, foraminifera, corals, and Fe-Mn nodules. However, ambiguities in the modern budget and disparities between the behavior of Nd concentrations and Nd in the isotopes in the ocean challenge the interpretation of these ϵNd records. Specifically, the suggestion that most of the Nd in the ocean comes from a benthic source fundamentally challenges using ϵNd as a conservative tracer of ocean circulation that reflects deep-water ϵNd values through time.

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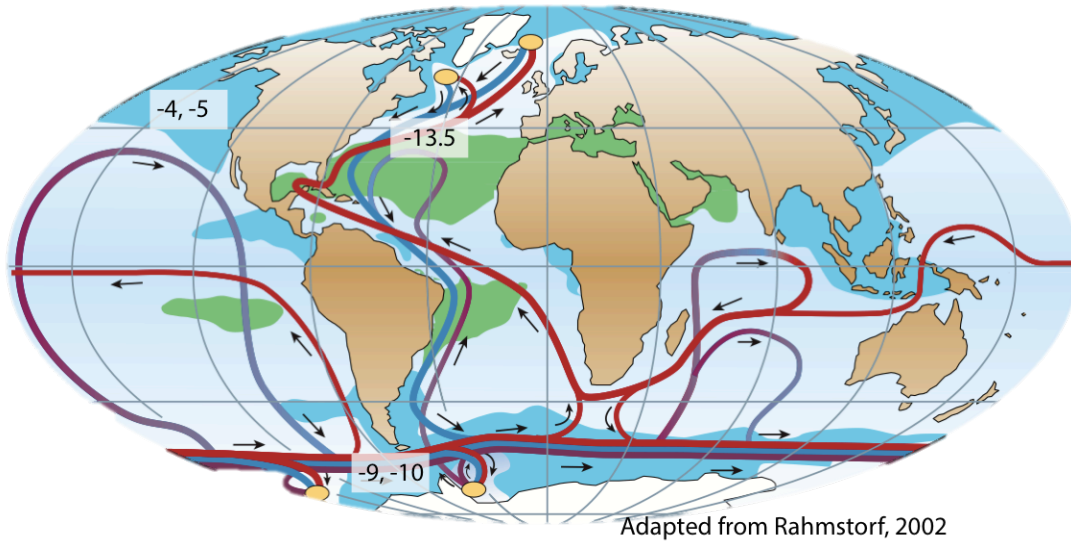
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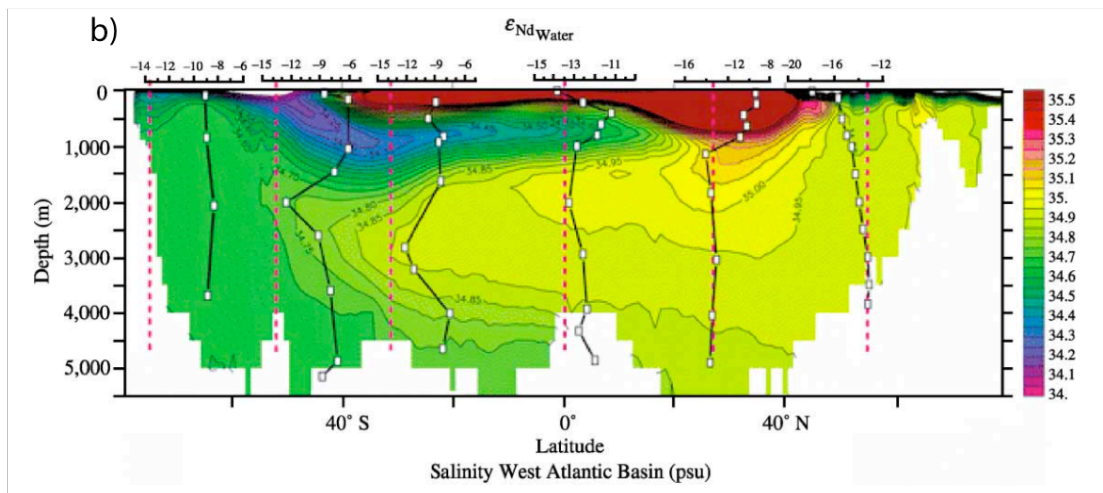
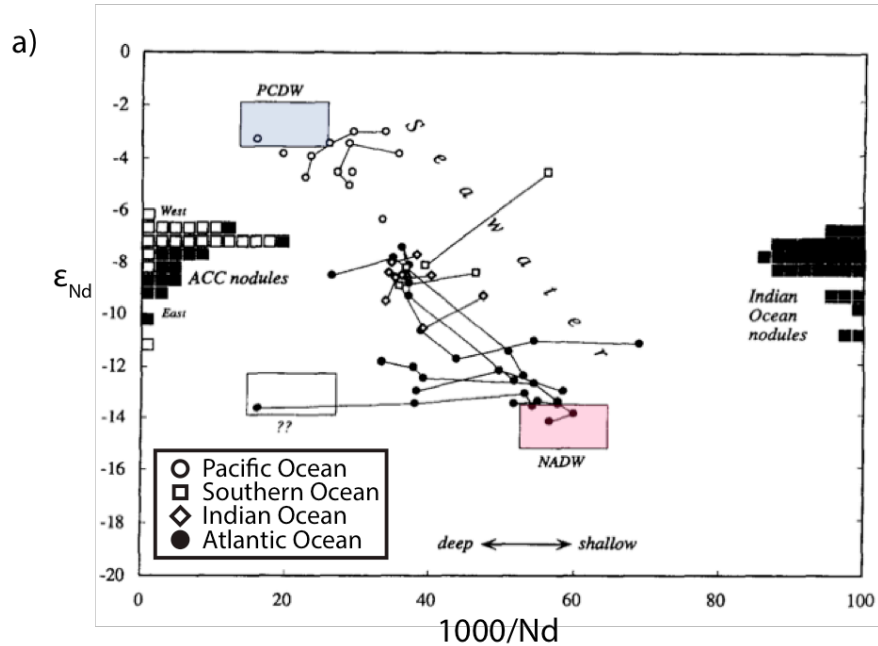
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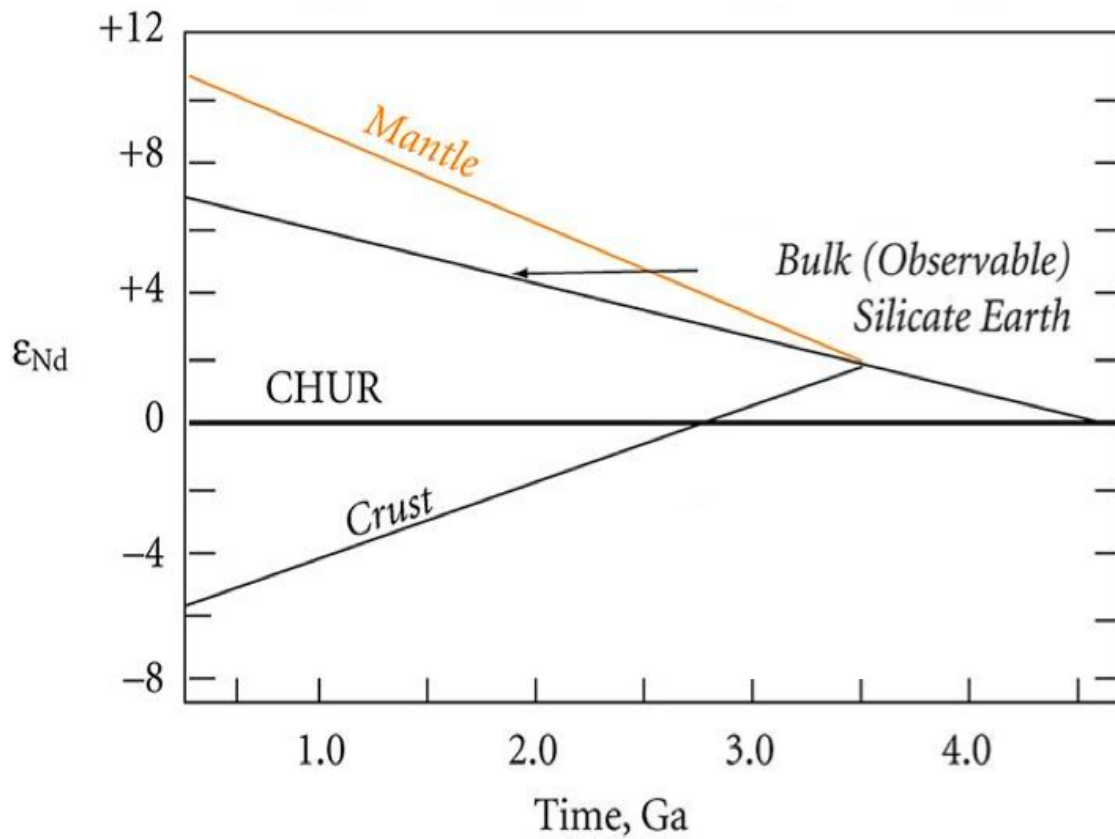
1.1 Modern thermohaline circulation.

Simplified schematic depicting major warm (red) and cool (blue) currents in the global ocean. Deep water ϵNd values for North Atlantic Deep Water (-13.5; Von Blanckenburg 1999), Antarctic Bottom Water (-9 to -10, Stichel et al., 2012), and North Pacific Deep Water (-4 to -5, Amakawa et al., 2004) are labeled in white boxes. Ocean regions shaded in green have salinity in excess of 36 ppm and regions in dark blue have salinities less than 34 ppm (Rahmstorf, 2002).



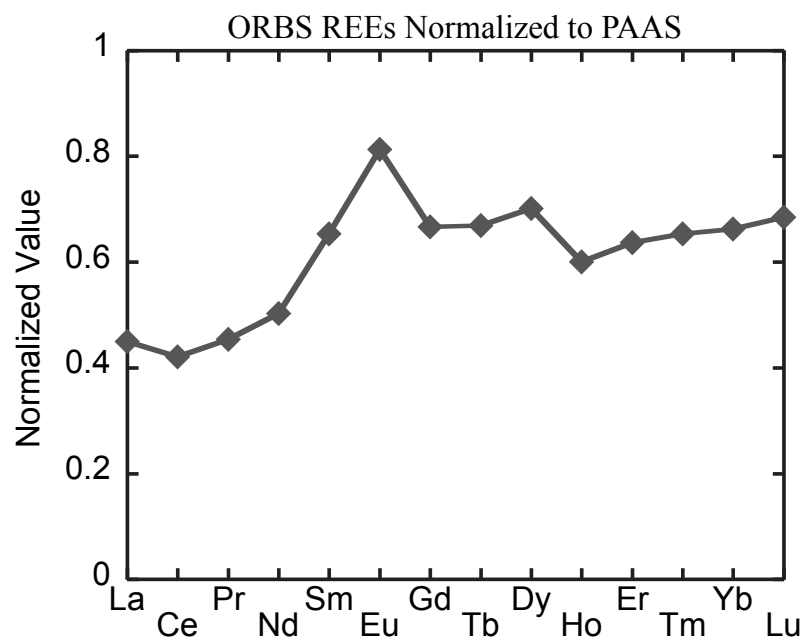
1.2 ϵ_{Nd} as a tracer of water mass circulation.

a) Figure from Albarède et al. 1997 plotting deep-sea water and Mn nodule ϵ_{Nd} from the Atlantic (solid circles), Pacific (open circles), Southern (open squares), and Indian Ocean (open diamond) basins against the concentration of Nd to depict the provinciality between the ocean basins. By basin, nodule ϵ_{Nd} is consistent with ambient ocean water ϵ_{Nd} . b) Figure from Von Blanckenburg 1999 depicting the first order relationship between salinity (color scale) and ϵ_{Nd} (open squares) in the Atlantic Ocean. North Atlantic Deep Water (NADW) is indicated by yellow on the salinity scale and has a consistent ϵ_{Nd} of -13.5.



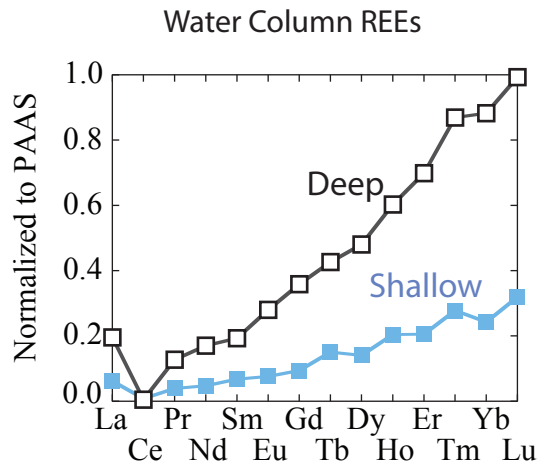
1.3 ϵ_{Nd} evolution

Evolution of crust, mantle, observable bulk earth, and CHUR $^{143}\text{Nd}/^{144}\text{Nd}$ presented as ϵ_{Nd} through time (Figure from White, 2013). The crustal evolution (crust) depicted is for crust created at 3.5 Ga and the corresponding residual mantle (mantle). The evolution of a continuously depleted mantle is also shown (Bulk).



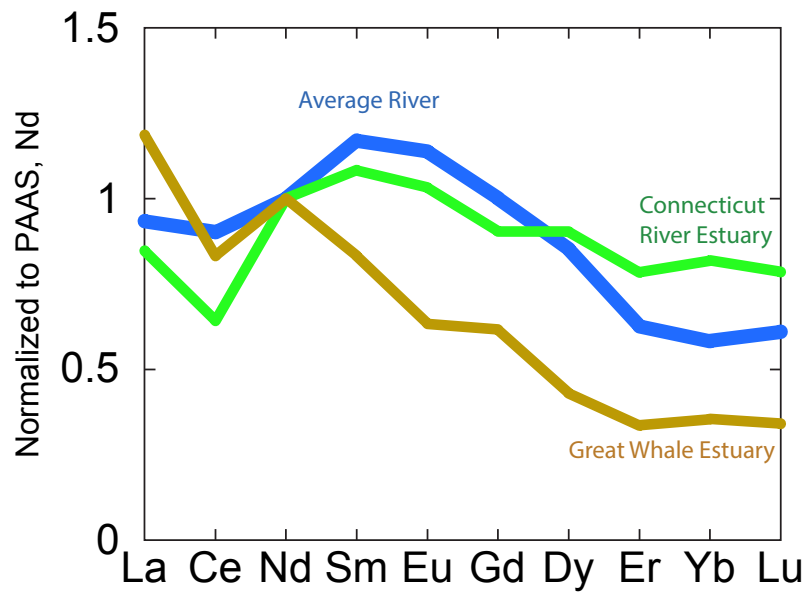
1.4 ORBS normalized to PAAS.

REE pattern of Oregon Bulk Sediment (ORBS) normalized to PAAS (Post Archean Australian Shale).



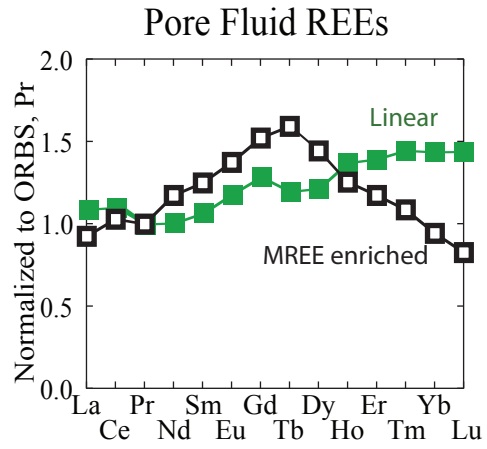
1.5 Seawater REE patterns

REE patterns in seawater for a deep (>3000 m) and shallow (<300 m) water sample. Seawater becomes more HREE enriched with depth in water column. A negative Ce anomaly is apparent in the deep-water sample. The Ce anomaly is defined as the difference between the predicted Ce value based on concentrations of neighboring La and Pr compared to the observed Ce value.



1.6 Dissolved REE patterns

Dissolved REE patterns in river and estuaries as reported in Sholkovitz, 1996. Average river water (blue) from major river samples and two estuary patterns (Connecticut River Estuary in green and Great Whale Estuary in brown).



1.7 Pore fluid REE patterns

Typical MREE-enriched and linear pore fluid REE patterns. HREE enriched pattern not shown.

Tracer	Key Features
Nd	+Quantitatively describe water mass mixing +Not influenced by hydrothermal input +Not fractionated during weathering +residence time between 200 and 1000 years +single source (continental weathering) +multiple recording phases (forams, sediment coatings, fish teeth) -modern budget incomplete -potential of diagenetic mobility -very low abundance in seawater
$\delta^{13}\text{C}$	+anticorrelated with nutrient concentration due to incorporation into organic matter -not quantitative -non conservative effects from temperature, nutrients, and amount of carbonate ion concentrations
Pb	+efficiently transferred to sediments via nonreversible scavenging +residence time between 50 and 400 years -substantial overlap between oceanic basalts and continental rocks -records only preserved in Fe-Mn crusts and nodules -anthropogenic overprint on modern signature -fractionation during weathering -mantle signature recorded near mid ocean ridges; continental signature in distal nodules
Cd/Ca	+can distinguish low and high nutrient water masses -not quantitative -influenced by thermodynamic effects
Zn/Ca	+can distinguish low and high nutrient water masses -not quantitative -influenced by foraminifera vital effects
Th	+ubiquitous record in sediment coatings -short residence time (5-20 yrs)
Be	+variability in ratio in ocean mainly caused by oceanic processes +^{10}Be correlates with age of water mass due to remineralization -continental erosion and atmospheric fallout sources +residence time between 200 and 1000 years
Hf	+residence time of ~2000 years -continental erosion and hydrothermal sources -records only preserved in Fe-Mn crusts and nodules -ratio unique for zircons which are concentrated in sand fraction
Os	- residence time of 10,000 to 20,000 years -many sources (peridotite leaching, cosmic particles, continental erosion)
Sr	- well mixed in the ocean - continental erosion, hydrothermal, and carbonate dissolution sources -can be influenced by weathering and metamorphism -high natural abundance in the ocean

**key features from references contained in Frank 2002, Goldstein and Hemming 2003, Byran and Marchitto 2010*

1.1 Commonly used oceanographic tracers and key features.

Features indicated by ‘+’ are helpful in reconstructions of ocean circulation.

Chapter 2: The sedimentary flux of dissolved rare earth elements to the ocean

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Abstract

We determined pore fluid rare earth element (REE) concentrations in near-surface sediments retrieved from the continental margin off Oregon and California (USA). These sites represent shelf-to-slope settings, which lie above, within, and below the oxygen minimum zone of the Northeast Pacific. The sediments are characterized by varying degrees of net iron reduction, with pore waters from the shelf sites being generally ferruginous, and the slope sediments having less-pronounced iron reduction zones that originate deeper in the sediment package. REE concentrations show maxima in shallow (upper 2-10 cm) subsurface pore fluids across all sites with concentrations that rise more than two orders of magnitude higher than seawater. These pore fluid enrichments highlight the importance of a sedimentary source of REEs to the ocean's water column. Here we use our measurements to estimate the diffusive flux of Nd out of ocean sediments resulting in a global flux between 18 and $110 \times 10^6 \text{ mol Nd yr}^{-1}$. While we do assume that our pore fluid profiles as well as the very limited data previously published are representation of a wide array of ocean environments, this calculated flux can account for the modeled missing Nd source flux ($76 \times 10^6 \text{ mol Nd yr}^{-1}$) in global budgets (Arsouze et al., 2009). Pore fluid normalized REE patterns show distinct variation in the middle REE and heavy REE enrichments with sediment depth and amongst sites. These patterns show that the heavy REE enrichment of pore fluids at our deep slope site (3000 m water depth) is closest to the heavy REE enrichment of seawater. This observation supports the view that REE cycling within the upper ten centimeters of deep-sea marine sediments, as opposed to shallower continental shelf and slope sediments, plays a significant role in controlling the integrated global REE flux from the pore fluids and

consequently the broad-scale REE pattern in seawater.

2.1 Introduction

The lanthanides, also referred to as the rare earth elements (REEs), are a series of elements that exist dominantly in a trivalent state in the environment, with the exceptions of Eu and Ce, which can exist as Eu (II) and Ce (IV) (Elderfield and Greaves, 1982). In the ocean, the REEs are generally depleted in surface waters and show increasing enrichment with depth (Elderfield, 1988; Bertram and Elderfield, 1993; Goldstein and Hemming, 2003; Lacan et al., 2012). Additionally, the REEs are typically found in higher concentrations in the deep Pacific relative to the deep Atlantic Ocean (e.g., Goldstein and Hemming, 2003). These observations suggest that particle scavenging within the upper water column and particle dissolution and exchange at depth control the oceanic distribution of the REEs (Elderfield, 1988; Bertram and Elderfield, 1993; Sholkovitz et al., 1994). In addition to these general trends for the REEs, specific trends for Ce are observed because of the anomalous behavior of Ce (IV) (e.g. Moffet, 1990). A Ce anomaly reflects microbially mediated oxidation followed by preferential scavenging of Ce (IV) in seawater (Moffet, 1990). The Ce anomaly is defined as the difference ratio of the predicted Ce based on neighboring REEs to the measured Ce (e.g. Elderfield 1988; Byrne and Sholkovitz, 1996; Grenier et al., 2013; Pearce et al., 2013). As such, the Ce anomaly is dependent on the behavior and concentrations of neighboring trivalent REEs and must be interpreted with caution (Elderfield and Pagett, 1986; De Baar et al., 1988; Sholkovitz et al., 1989; Bau and Dulski, 1996; Alibo and Nozaki, 1999; Tachikawa et al., 1999; Haley et al., 2004; Kim et al., 2012).

Individual REEs and the REEs as a series are powerful geochemical tracers because of their predictable behavior and they have been used in oceanographic studies

highlighting redox conditions (e.g., Liu et al., 1988; Sholkovitz and Schneider, 1991), particulate exchange and scavenging processes (e.g. Andersson et al., 2008; Oka et al., 2009), and water mass transport (e.g. Scher and Martin, 2004; Andersson et al., 2008; Haley et al., 2008). While these and many other efforts (e.g. Goldberg et al., 1963; Palmer and Elderfield, 1986; Sholkovitz, 1990, 1992; German et al., 1995; Sherrell et al., 1999; Schijf and Byrne, 2004; Schacht et al., 2010; Johannesson et al., 2011; Haley et al., 2013) have greatly expanded our knowledge of marine REEs, our understanding of the sources of REEs to seawater as well as the processes that define the seawater REE signature is incomplete. Although the riverine flux is, at present, thought to be the primary input of REEs to the oceans (e.g. Martin et al., 1976; Greaves et al., 1994; Sholkovitz et al., 1999) attempts to balance the budget of the REEs have not been entirely successful (e.g. Keasler and Loveland 1982; Bertram and Elderfield, 1993; van de Flierdt et al., 2004). Recent work has proposed submarine groundwater discharge as a potentially significant source for Nd in the accounting of REE fluxes to the oceans (Johannesson and Burdige, 2007; Johannesson et al., 2011). Similarly, the flux of REEs from marine pore fluids has been suggested to be a significant source of marine REEs, with calculated pore fluid exchange rates being higher than the combined total of all other marine source fluxes (Elderfield and Sholkovitz, 1987; Sholkovitz et al., 1989; Sholkovitz, 1992; Haley et al., 2003; Arsouze et al., 2009). Because of these and other outstanding questions regarding the marine REE cycle, there are significant limitations with respect to the utility of REEs in oceanographic studies.

Understanding how the REEs fractionate from one another under various natural conditions can supply additional information that will allow us to address a number of

these outstanding questions regarding global REE cycles. Fractionation among the REEs is observed by examining the REE “patterns”, which are the REE concentrations normalized to shale values. This normalization facilitates inter-REE comparisons despite large variations in natural abundances. These REE patterns are tools for diagnosing the potential processes that control the distribution and fractionation of REEs (e.g. Sholkovitz et al., 1999; Haley et al., 2004). Fractionation across the series of REEs occurs because of the systematic decrease in ionic radius with increasing atomic number due to the progressive filling of inner f-shell electrons. This fractionation suggests that the budget for each REE may be somewhat different. Particulate-water interactions, dissimilar source and sink terms, complexation, oxide scavenging, and REE incorporation into solid phases can each contribute to changes in the ocean’s REE pattern (Cantrell and Byrne, 1987; Lee and Byrne, 1993; Schijf and Byrne, 2004; Leybourne and Johannesson, 2008; Akagi, 2013). The resulting fractionation varies as a result of, among other factors, the nature of the complexing agent (e.g. inorganic and organic ligands, carbonate, oxalate, silicic acid), the presence of sulfates or phosphates, pH, and ionic strength (e.g. Cantrell and Byrne, 1987; Schijf and Byrne, 2004; Tang and Johannesson, 2010; Akagi, 2013). Each of the above processes, including complexation and oxide scavenging, may have a unique characteristic fractionation. The ability to associate a specific pattern with a factor (e.g. pH, complexation agent) or a process (e.g. complexation, oxide scavenging) facilitates interpretations of pattern changes and controls on the REE budget (e.g. Sholkovitz et al., 1994; Akagi, 2013).

Processes causing REE fractionation determine the oceanic REE pattern, which is clearly altered from the pattern of various potential sources of REE including the riverine

source (e.g. Elderfield et al., 1990; Sholkovitz et al., 1999; Leybourne and Johannesson, 2008, Stolpe et al., 2013) and the pattern of riverine suspended particles (Sholkovitz et al., 1999, Censi et al., 2007, Stolpe et al., 2013). When normalized to shale, seawater is characterized by a heavy REE (HREE, including Er, Tm, Yb, and Lu) enriched pattern with a pronounced negative Ce anomaly (Goldberg et al., 1963; Högdahl et al., 1968; Elderfield and Greaves, 1982; Klinkhammer et al., 1983; Elderfield, 1988; Piepgras and Jacobsen, 1992). In contrast to the HREE enriched pattern typical of seawater, dissolved riverine REE patterns are typically MREE enriched (e.g. Sholkovitz et al., 1999, Stolpe et al., 2013). Additionally, suspended riverine and estuarine particulates have a flat (shale-like) REE pattern or a MREE enriched pattern (e.g. Sholkovitz et al., 1999; Sholkovitz and Szymczak, 2000; Censi et al., 2007, Stolpe et al., 2013). Similar HREE depletions have also been reported in bottom sediments from estuarine settings (e.g. Censi et al., 2007) and riverbeds (Sholkovitz, 1999). These HREE depletions have been attributed to the preferential settling of larger grain sizes that carry HREE enriched heavy minerals (Sholkovitz et al., 1999). Fractionation of the REEs certainly influences these elements during transport, but there is still a fundamental discrepancy between the REE patterns of REE sources to the ocean and the REE pattern of seawater. This discrepancy between the oceanographic REE signature and that of the sources is at the heart of our knowledge gap in REE geochemistry.

Given the importance of a benthic source to the ocean's REE balance, the REE patterns in pore fluid will be important for constraining the significance of particle-fluid interactions for controlling REEs. Pore fluid REE patterns are a function of the competition between REEs being introduced into the fluid phase (from a sedimentary

source) and the REEs being removed from solution (Haley et al., 2004). REE sources and sinks may act preferentially on specific REEs and result in fractionation. Precipitation of phosphate bearing minerals (e.g. Koeppenkastrop and De Carlo, 1993; Kuss et al. 2001), degradation of organic material, organic matter coatings (Byrne and Kim, 1990), weathering of REE rich phosphates (e.g. Censi et al. 2007), and volcanic ash (Schacht et al., 2010) have all been shown to exert influence over pore fluid REE distributions and these processes can each have specific REE signatures. Existing data from pore fluids show that REE patterns fit into one of three general categories (Elderfield and Sholkovitz 1987; Sholkovitz et al., 1989; Haley et al., 2004; Schacht et al., 2010; Kim et al., 2012): (1) those with a constant (“linear”) but moderate increase in PAAS-normalized REEs across the series from light to heavy, (2) those having a middle REE (MREE, including Eu, Gd, Tb, and Dy) enrichment or “bulge,” or (3) those with a marked HREE enrichment – much like seawater (Haley et al., 2004). REE patterns in anoxic pore fluids tend to be characterized by a MREE “bulge” pattern in the ferruginous zone (Haley et al., 2004; Kim et al., 2012). Deeper anoxic pore fluids within the sulfidic and methanogenic zones have linear REE patterns or are HREE enriched (Kim et al., 2012). The HREE enriched pattern is consistent with preferential complexation of HREEs after REE release from organic matter degradation (Goldberg et al., 1963; Byrne and Sholkovitz, 1996; Haley et al., 2004). The REE pattern observed in pore fluid is a result of the combined source and sink terms acting on these fluids. Therefore, the pore fluid REE pattern can be used to identify the mechanistic influences on pore fluid REE geochemistry if the fractionation caused by the source or sink is known.

Identifying the mechanistic influences on pore fluid REE patterns has been limited by the scarcity of pore fluid REE data. Understanding these mechanisms is essential to constraining the fluid-particle interactions that would generate a marine sedimentary REE source. Here, we present pore fluid REE profiles collected from eight sites across the continental margin of Oregon and California (USA). Our sites are continental margin environments with site locations above, within, and below the eastern North Pacific's oxygen minimum zone. These sites provide additional data to constrain how diagenesis influences REE distributions and allow us to estimate the flux of dissolved REEs to the ocean from marine sediments.

2.2 Study Sites and methods

2.2.1 Study Sites

Pore fluid was collected from eight sites in the eastern North Pacific along the Oregon and California margin (**Figure 2.1, Appendix Table 2.A1**). Samples were collected over the course of three cruises: in September 2007 (Stations 1, 2, 3, and 6), October 2012 (HH500, HH1200, and HH3000), and July 2013 (HH200, same location as Station 2). The sites off the Oregon margin are divided into shelf sites (Station 1, open diamond; Station 2, open triangle; and HH200, closed triangle) and slope sites (HH500, closed diamond; HH1200, closed circle; and HH3000, closed square). Together these six sites form a shallow (105 m) to deep (3060 m) east-west transect near the mouth of the Umpqua River (Oregon). Despite the general proximity to the Umpqua River, the shelf sites do not represent the river's depositional center as this locality is well defined by previous work and is south of our sites as indicated by reactive iron and manganese

contents, δC_{org} , C:N, and ligand measurements (Hastings et al., 2012; Roy et al., 2013); therefore, these sites are representative of the more general continental shelf setting along this margin (e.g., Hastings et al., 2012; McManus et al., 2012; Roy et al., 2013), which is influenced by both autochthonous and riverine inputs. Both California margin sites (Station 3, open circle and Station 6, open square **Figure 2.1**) are shelf sites (water depths ~ 100 m), adjacent to the mouth of the Eel River (California). Closed symbols indicate sites visited in October 2012 and July 2013, open symbols are those sites visited in September 2007 that had adequate sample volumes for REE analyses (McManus et al., 2012).

The sediments of the Oregon-California margin generally have a large terrestrial influence and are characterized by relatively high C_{org} (1 to 2 wt %) and relatively low $CaCO_3$ ($<0.5\%$) (Lyle et al., 2000; Roy et al., 2013; Hastings et al., 2012). Sedimentation is seasonally variable, with the annual period of high sediment deposition typically falling from October to March (Kniskern et al., 2011). The Eel River and the Umpqua River have many contrasting geologic and discharge characteristics. There is an order-of-magnitude greater sediment discharge from the Eel River compared to the Umpqua ($\sim 18 \times 10^9$ kg versus $\sim 1.4 \times 10^9$ kg, respectively; Wheatcroft and Sommerfield, 2005) and higher sedimentation rates near the Eel River sites compared to near the Umpqua River slope sites. Previous studies from the Oregon-California margin indicate sedimentation rates between 0.2 - 1.4 cm yr^{-1} on the shallow shelf near the Eel River (Sommerfield and Nittrouer, 1999) and sedimentation rates between 1.1 to 2.4 mm yr^{-1} at our Umpqua River shelf sites (Station 1 and Station 2, HH200; McManus et al., 2012; also see Wheatcroft et al., 2013). Additionally, high discharge events are less frequent in the Umpqua River

than the Eel River (Goñi et al., 2013). The Eel drainage basin consists largely of marine sedimentary rocks (sandstones and shales) in contrast to the Umpqua drainage basin, which consists of the sedimentary Tyee Formation (siltstones, sandstones) and volcanics (<http://www.nationalatlas.gov/>; Kniskern et al., 2011 and sources therein). The Umpqua River's suspended particulate organic matter is dominated by biogenic sources compared to the Eel River which has significant petrogenic derived organic matter, which is highly diluted by suspended mineral particulates (Goñi et al., 2013). In the shallower reaches of the continental margin, sand content can be quite high (Kulm et al., 1975) with content up to 40% documented on the shallow (~100 m) shelf near the Umpqua and amounts of sand decreasing off shore (<20% by 200 m water depth, Kulm et al., 1975). In the same study, the amount of clay was shown to increase from less than 20% in 100 m water depth to up to 40% by 200 m (Kulm et al., 1975). In terms of clay mineral abundances, the Umpqua and nearby rivers have higher smectite/illite ratios (2.3-3.1) than the Eel river (0.3 - 0.8; VanLaningham et al., 2008).

The Northeast Pacific oxygen minimum zone occurs between the depths of 600 and 900 m along the Oregon shelf (**Figure 2.2a**). Bottom depth for each coring site is indicated on the water column oxygen profile from site HH3000 (**Figure 2.2**). Slope sites (HH500, HH1200, and HH3000) are located below the water column thermocline (**Figure 2.2b**) and halocline (**Figure 2.2c**). The dissolved oxygen, temperature, and salinity profiles observed at all the Oregon transit sites would be indistinguishable from each other if overlain on the scale of **Figure 2**.

2.2.2 Sampling and Pore fluid extraction

Unfiltered and filtered water column samples were collected from 12 depths at HH1200 and HH3000 and five depths at HH500 (**Appendix Table 2.A2**). For unfiltered samples, seawater was collected directly from the Standard PVC Niskin bottle into an acid cleaned cubitainer. Niskin bottles were not cleaned prior to deployment. For filtered samples, the Niskin bottles were pressurized using N₂, which facilitated filtration of seawater using in-line “Disposal A” 0.45 µm filters with a white acrylic copolymer coating over a non-woven substrate (Geotech Environmental item 73050004) during direct transfer into acid cleaned cubitainers. All samples were acidified to pH ≤2.5 using 12 M HCl.

Sediment cores were collected using a multi-corer (Barnett et al., 1994). Pore fluid samples were extracted only from cores that appeared on visual inspection to be intact and of similar integrity. Clarity of the water at the interface, the lack of slope of the sediment surface, core seal, and gaps in the sediment along the core liner were used as visual guides to evaluate core integrity following recovery. Additionally, cores with macrofauna present (e.g. sea urchins) were generally excluded, although on occasion we encountered these organisms during core processing and they were discarded. The selected cores were sectioned in an anoxic glove bag, and sediment intervals transferred into 85 mL centrifuge tubes, and centrifuged at 10,000 – 12,000 rpm for 15 minutes. Pore fluid was syphoned off the top of each tube in a second anoxic glove bag and filtered using PALL® acrodisc syringe filters with a 0.45µm Supor® membrane. When processing samples from the HH200, HH500, HH1200, and HH3000 sites, corresponding intervals from multiple cores were combined after filtering to create large volume pore fluid samples (for isotope analyses not reported here). These samples were acidified to

pH ~2 and kept refrigerated until analysis. Samples from HH200, HH500, HH1200, and HH3000 were typically analyzed within a month of collection. Smaller volume individual core samples were collected from Stations 1, 2, 3 and 6 using the same centrifuge technique (Severmann et al., 2010), and were analyzed in 2012. We also collected samples for REE concentration measurements using Rhizon pore fluid sampling devices; however, we found that these samplers remove more than half of HREEs from solution during collection and can introduce a substantial LREE blank (see **Appendix 2.2A**) and cannot be used for REE determinations.

2.2.3 Analytical Methods

2.2.3.1 REE separation

The rare earth elements were separated from 10 mL samples of the pore fluid or seawater using a column with 2 mL of BioRad Analytical Grade Chelex® 100 resin (100-200 mesh, sodium form CAT#142-2832). These columns were optimized for REE yield (>80% with calibration standards) and effective Ba removal. Before separations, the resin was cleaned with 10 mL of 3M HNO₃ and conditioned with 10 mL of chelation concentration reagent 2.0 M ammonium acetate (pH 5.4 ± 0.1, Dionex or Thermo Scientific). For samples that did not have 10 mL available, the maximum volume available was loaded onto the column. Each sample was buffered with 100 µL of the 2.0 M ammonium acetate immediately prior to column loading to bring the sample from pH 2 to pH 5. Following the sample addition, 15 mL of 2.0 M ammonium acetate was eluted prior to collecting the REEs in 12 mL of 3 M HNO₃ (final pH 1 to 2). Calibration standards, including blanks, made using a known amount of REE in 10 mL of a NaCl (0.6 M) and Ba (95 µM) solution, were also run through the columns. The resulting

solutions were used for the standard curve on the ICP-MS. The consistency of our standard curve was verified by seawater sample NBP95R10, which has greater Ba concentrations, and therefore greater Ba oxide interference potential than our pore fluid samples. The REE fraction was analyzed using a Thermo VG ExCell quadrupole ICP-MS at the W.M. Keck Laboratory for Plasma Mass Spectrometry (Oregon State University). The ICP-MS was tuned to minimize oxide formation (<3%) in the plasma stream. The isotopes monitored as well as the ICP-MS running parameters are given in **Appendix Table 2.A8**. A seawater sample (NBP95R10) collected from the Bransfield Strait in the Southern Ocean (62° 46'S, 59° 24'W, 1300 m water depth) was used as an in-house consistency standard (no calibrated seawater or pore fluid REE standards are available). This chromatography technique is accurate to $\pm 1\sigma$ values ranging from 0.2 to 4 pM for REEs in NBP95R10 (**Appendix Table 2.A2**). The limit of detection (**Appendix Table 2.A3**) was below the procedural blank (4.2 pM La, 6.8 pM Ce, 0.8 pM Pr, 3.5 pM Nd, 0.5 pM Sm, 0.7 pM Eu, 0.3 pM Gd, 0.1 pM Tb, 0.3 pM Dy, 0.1 pM Ho, 0.2 pM Er, 0.05 pM Tm, 0.1 pM Yb, and 0.3 pM Lu) for all REEs. However, pore fluid samples from Station 2 interacted differently on the chelex columns, and Ba counts were elevated (100,000 instead of <3,000) during analysis. Therefore we chose to not include the corresponding Eu data because we cannot be certain that these analyses were not affected by a barium oxide interference during ICP-MS analysis.

2.3 Results

2.3.1 Water Column REEs

Water column samples from the Oregon transit show that REE concentrations are low in surface waters (13 - 20 pM Nd, 0.7 - 0.8 pM Tb, 2.8 - 4.7 pM Yb) and increase with depth, characteristic of a nutrient concentration profile (**Figure 2.3, Appendix Table 2.A2**). Only Nd is shown in **Figure 3** as all the REE profiles are similar in shape. Our sites exhibit a shallow (~250 m) subsurface REE minimum, but we do not have adequate resolution to confidently identify this feature. However, we note a similar feature in prior work at the Peru-Chile upwelling margin where REE concentrations at 250 m water depth were less than half of the surface concentrations (Jeandel et al., 2013). Other locations with a similar feature include the ocean-margin boundary off Japan where REE minima occurred at ~100 m water depth (Zhang and Nozaki, 1998) and in the Bay of Bengal where a REE minima was observed between ~100 m and 400 m water depth (Singh et al., 2012). The shallow REE minimum off Oregon and California is similar in depth (250 m) and magnitude (30 to 50% lower at minimum than surface water concentrations) to the Chile upwelling margin minimum and the minimum observed in the Bay of Bengal. Additionally, surface water concentrations (13 - 20 pM Nd) measured off Oregon and California are comparable to the Chile margin (site UPX 26.6-27.5 pmol/kg Nd, Jeandel et al., 2013) and the Bay of Bengal surface waters (22-46 pmol/kg Nd, Singh et al., 2012). The concentration profiles at HH1200 and HH3000 are similar within the upper 600 m. Additionally the bottom waters at these sites have the highest and most variable (22-43 pM Nd, 0.9-1.8 pM Tb, 7.8-9.4 pM Yb at HH1200; 12.0-38.0 pM Nd, 0.8-1.9 pM Tb, and 3.0-13.3 pM Yb at HH3000) dissolved REE concentrations

(**Figure 2.3**). The near-bottom concentrations for both the HH1200 and HH3000 sites approach 40 pM Nd and 2 pM Tb. There is a greater variation in bottom water HREE concentrations than there is in either LREE concentrations or MREE concentrations between sites HH3000 and HH1200 (13.3 pM Yb, 9.4 pM Yb respectively). The difference in the water column REE profile below 600 m at sites HH1200 and HH3000 occurs because HH1200 has a similar change in concentration from 600 m to the bottom as HH3000 has from 600m to the bottom (18 to 40 pM Nd, 1 to 2 pM Tb, 4 to ~10 pM Yb) but the increase in concentration at HH1200 occurs within 600 m of water column instead of 2400 m of water column at HH3000 (**Figure 2.3**).

2.3.2 Pore fluid profiles

The sedimentary environments of the Oregon shelf sites (Station 1, Station 2, and HH200) are geochemically more homogeneous with respect to the REE concentrations than the Oregon margin slope sites (HH500, HH1200, HH3000). The sediment-water exchange at the deeper slope sites (HH1200 and HH3000) is likely diffusion controlled whereas the shelf sites (Station 1, Station 2, HH200) are likely influenced by bioirrigation and other advective factors (Severmann et al., 2010; **see 2.4.2.1**). The shelf sites (Station 1, Station 2, and HH200) are characterized as having ferruginous pore fluids (values typically between 50 and 250 μM , **Figure 2.4a and b**) indicative of anoxic sediments. In contrast, the Fe profiles of the slope sites (HH500, HH1200, HH3000) change with site water depth (**Figure 2.4c**). Specifically, the maximum concentration of Fe is greater with decreasing site water depth (10 $\mu\text{mol/L}$ at HH3000, 35 $\mu\text{mol/L}$ at HH1200, and 70 $\mu\text{mol/L}$ at HH500). Additionally, the first appearance of Fe occurs deeper within the core at HH3000 (12 cm) than at the shallower sites (2.5 cm at HH500, 3.7 cm at HH1200)

(**Figure 2.4c**). California margin sites (Station 3, Station 6) have dissolved iron concentrations up to twice the levels at any of the other sites (**Figure 2.4b**). Despite this difference in concentration, the shallow appearance of dissolved Fe at Station 3 and Station 6 resembles the Fe profiles of the Oregon shelf sites (HH200, Station 1, Station 2; **Figure 2.4a**). Overall, the sites in this study represent a range of geochemical conditions in the pore fluids as indicated by dissolved Fe profiles.

A range of pore fluid REE concentration profiles also exists between the Oregon shelf (Station 1, Station 2, HH200), Oregon slope sites (HH500, HH1200, HH3000), and California shelf (Station 3, Station 6) sites (**Figure 2.4**). At each site, all pore fluid REE concentration profiles have similar trends, but the concentrations vary among the REEs (**Figure 2.4, Appendix Table 2.A3**). For Oregon shelf sites HH200 and Station 1, REE concentration profiles generally maintain uniform down-core distributions with low REE concentrations (< 400 pM Nd, <15 pM Tb, and <30 pM Yb; **Figure 2.4a**). Station 2 is the only Oregon shelf site without a uniform low REE concentration. Instead, Station 2 has a deep REE concentration maximum (10.6 cm) with high REE concentrations (2250 pM Nd, 60 pM Tb, 100 pM Yb). The deeper sites (HH500, HH1200, and HH3000) have more REE pore fluid profile variation down-core and generally higher REE concentrations (maximum pore fluid concentrations HH500: 475 pM Nd, 13 pM Tb, 25 pM Yb; HH1200: 500 pM Nd, 12 pM Tb, 35 pM Yb; HH3000: 790 pM Nd, 24 pM Tb, 62 pM Yb) (**Figure 2.4c**). California shelf sites (Stations 3 and 6) resemble the Oregon slope sites (HH500, HH1200, and HH3000), having a shallow (~ 5 cm), subsurface REE concentration maximum (850 pM Nd, 15 pM Tb, and 48 pM Yb at Station 3; and 1200

pM Nd, 29 pM Tb, and 58 pM Yb at Station 6) and a decrease in concentration with depth (**Figure 2.4b**).

2.4 Discussion

2.4.1 Water column REEs

For comparative purposes water column samples are normalized both to Post-Archean Australian Shale (PAAS) (**Figure 2.5a-c**) as well as to Oregon Bulk Sediment (ORBS) and the Pr concentration (**Figure 2.5d-f**). ORBS is an average of sediment digests from HH500, HH1200, HH3000. Here we present the REE values for ORBS that we use for normalization (**appendix Table 2.A4; appendix text 2.1A**), but leave further discussion of these bulk sediment data (**appendix Table 2.A5**) to a future publication. While the PAAS normalization is more common in the literature, the ORBS normalization provides a comparison to the local sediment source, which is important for our purposes. The double normalization using both shale and Pr concentration is applied so that the pattern variability in the lower absolute concentration samples can be compared to the patterns in the higher concentration samples. Normalization to either PAAS or ORBS removes the naturally occurring odd-even pattern in the abundance of the lanthanides (Byrne and Sholkovitz, 1996) (**Figure 2.5**).

Increasing REE concentrations with water depth (**section 2.3.1**) are accompanied by the HREE enrichment of the normalized water column REE patterns as expected for seawater (**Figure 2.5**) (Elderfield and Greaves, 1982; Klinkhammer 1983; Piepgras and Jacobsen, 1992; Bertram and Elderfield, 1993; German et al., 1995). The deep-water samples from HH3000 are the most HREE enriched patterns of the sites in this study

(**Figure 2.5f**). Additionally, the greatest variation in PAAS normalized patterns coincides with site HH3000, with patterns showing the most change in terms of HREEs from the shallow water to the deep water (**Figure 2.5c**). Interestingly, and as discussed in section 2.4.2.3, the deepest water column sample at HH3000 approaches the pattern of the pore fluids, and is the only sample to differ significantly from the trend of increasing HREE/LREE with increasing water depth (**Figure 2.5c, f**).

2.4.2 Pore Fluid REEs

2.4.2.1 Variability Amongst Shelf Profiles

All the Oregon shelf sites (Station 1, Station 2, HH200) appeared similar geochemically when sampled. They had bottom water O₂ from 65 to 80 µmol/L and exhibited dissolved Fe maxima in the uppermost 15 cm of the sediment column. However, the pore fluid from Station 2 was found to have much higher REE concentrations, especially at ~10 cm depth (**Figure 2.4a**). The REE patterns (**Figure 2.6b**) as well as the iron profile (**Figure 2.4a**) from Station 2 pore fluids provide evidence that the high REE concentrations at Station 2 (**Figure 2.4a**) are not a sampling artifact. With HH200 and Station 2 being positioned at approximately the same geographic location and having similar geochemical conditions, the change between high REE concentrations at Station 2 (maximum: 2248 pM Nd, 56 pM Tb, 98 pM Yb; 2007) and the low REE concentrations at HH200 (HH200 maximum: 400 pM Nd, 12 pM Tb, 22 pM Yb; 2013) suggests there could be processes causing variation in REE release from the shelf.

Spatial differences, including the patchiness of sediment distribution on the shelf, as well as temporal variability have implications as to the presence of a shelf source of REEs to the ocean. Variability in pore fluid chemical profiles has been observed in other

shallow pore fluid profiles (e.g. Sholkovitz et al., 1989; Berelson et al., 2013) and possible factors include dissolved and particulate riverine REE concentrations and patterns that may change seasonally (e.g. Shiller 2002; Stolpe et al., 2013), seasonal delivery of organic carbon (e.g. Graf et al., 1983; Berelson et al., 2003), upwelling variability, bioirrigation of the sediments, or discontinuous burial creating hiatuses in sediment accumulation and differing downcore sediment properties. Additionally, the HH200 REE profile is an average profile at the site, combining the pore fluids of several cores and this average is not available at Station 2, where REE profiles are from a single core.

The mechanisms behind the observed shelf variability require further study, but the observed difference in REE concentrations between 2007 (Station 2) and 2013 (HH200) could have implications regarding the presence and magnitude of a shelf sedimentary source flux. If this variability between 2007 and 2013 is a consequence of advective pore fluid transport in particular (e.g., Severmann et al., 2010) our data would provide only a minimum estimate of the source flux (**see section 2.4.3**) for these shallow sites.

2.4.2.2 REEs and Fe

The relationship between the REE cycling in pore fluids and Fe is not straightforward. REE maximum concentrations in the pore fluids do not align with the presence of dissolved Fe (**see section 2.3.2**). Nor do the REE maximum concentrations in the pore fluids align with the presence of dissolved Si or Mn (**Appendix Figure 2.A4**). The most basic interpretation of the differences in Fe and REE profiles is that Fe and REEs are not as simply related as previously thought (e.g. Haley et al., 2004). The

abundance of REEs is much less than the abundance of Fe, meaning that the REEs could be sensitive to a small change in Fe concentration, potentially below the limit of Fe detection. Another possibility is that Fe and REEs are both reacting to changes in a third variable such as pH or a complexing agent (e.g. Bau et al., 2013). The influence of Fe cycling on the REEs cannot be fully discerned with our data set; however, Fe is nevertheless likely to be important in the cycling of marine REEs (Haley et al., 2004; Bau et al., 2013; Haley et al., 2013).

The complex relationship between Fe and REEs may be one of the reasons no observable difference in pore water REE behavior was observed in our sites above, within, and below the oxygen minimum zone. We expect to see elevated REE concentrations with MREE enriched patterns because of the reduction of Fe-oxides in anoxic sediments (Haley et al., 2004). However, the highest levels of dissolved Fe occur in our shallow sites (HH200, Station 1, and Station 2 **Figure 2.4**) above the oxygen minimum zone, and decrease from HH500 to HH1200 to HH3000. Additionally, the highest REE concentrations occur at HH3000 (exception Station 2), below the oxygen minimum zone. HH500 and HH1200 show no distinct REE behavior associated with the overlying oxygen minimum zone. Instead, these sites appear to fit into a trend of REE profile changes from shallow to deep sites that contradicts our expectations for REE behavior related to the oxygen minimum zone and further supports the complex relationship between the REEs and Fe. Additionally, this suggests the overlying water column does not have a direct influence on pore water dynamics, possibly a result of seawater REE concentrations being at least an order of magnitude lower than pore water

REE concentrations. Collectively, these observations suggest that iron cycling and bottom water oxygen are not dominant drivers of REE behavior in these sediments.

2.4.2.3 REE cycling

Sediment pore fluid REE concentrations are one to two orders of magnitude higher than in the overlying water column. This observation is not unique to this study (e.g. Sholkovitz et al., 1989; Haley et al., 2004; Bayon et al., 2011) and implies that the upper sedimentary package, via the pore fluids, is an important source of dissolved REEs to the ocean (e.g. Haley et al., 2004; Schacht et al., 2010). We observe two distinguishable pore fluid REE patterns, a HREE depleted pattern (red symbols in **Figure 2.6**) and a MREE and HREE enriched pattern (blue symbols in **Figure 2.6**). We interpret the HREE depleted pattern (red symbols in inset **Figure 2.6**) to be the primary diagenetic source to the pore fluids because this pattern consistently occurs at the same depth as the REE concentration maximum for all sites. The HREE depleted pattern also characterizes almost all pore fluid samples for the shallower sites (HH200, HH500, and Station 2). The HREE depleted pattern is flat across the LREEs and MREEs and begins to deviate from a straight line for the HREEs, meaning that the main difference between the primary source sediment (ORBS) and the pore fluids is in the relative abundance of HREEs. The HREE depletion (i.e., normalized values < 1) suggests that the HREEs are not as readily released from the sediments compared to the LREEs. The dominance of this HREE depleted pattern in shallow site (HH200, HH500, Station 2) pore fluids and at the depth of the maximum REE concentration at all sites implies that fractionation of the REEs continues to occur after the initial release of REEs into the pore fluid. Therefore, the source pattern is only observed in pore fluid intervals experiencing the greatest REE release from

sediments (“source depth”) or in pore fluids that are well mixed. As the REEs diffuse away from the source depth, both upwards and downwards, the patterns become increasingly enriched in MREEs and in HREEs (blue symbols in **Figure 2.6**). One possibility for this change in pattern is that the LREEs are preferentially retained within the sediment either through secondary adsorption or precipitation reactions. Consistent with the idea of LREE retention, Caetano et al. (2009) observed preferential LREE retention in a sedimentary layer that was enriched in Fe-oxyhydroxides. Another factor that could cause the HREE enrichment away from the source is the preferential complexation of HREEs as they are released. This complexation then prevents the HREEs from coming back out of solution as they diffuse away from the source. A combination of LREE adsorption and HREE complexation can explain the increasing HREE enrichment away from the source observed in pore fluid patterns.

The comparison of REE behavior among sites can further our understanding of the mechanisms controlling the cycling of REEs, and subsequently the flux of dissolved REEs from the sediments. Of the sites in this study, California shelf sites (Station 3, Station 6) have more similarities with the Oregon slope sites than with the Oregon shelf sites in general. Station 3 and Station 6 both have the characteristic HREE depleted source patterns at the depth corresponding to the maximum concentration of REEs in pore fluid (**Figure 2.6c,d**). Additionally, similar to Oregon slope sites HH1200 and HH3000 (**Figure 2.6g, h**), a HREE enriched REE pattern occurs away from the source at both sites.

Comparison of the HREE enrichment away from the source at each site also contributes to our understanding of the mechanisms controlling REE cycling in pore

fluids. This HREE enrichment is more apparent at sites with a deeper source (i.e., HH3000), as the pore fluids from these deeper sites (i.e., HH3000) are generally more enriched in the HREEs compared to the shallower, shelf pore fluids (**Figure 2.6e-h**). The HREE enriched pattern in pore fluids at HH3000 begins to approach the REE pattern of seawater. This seawater-like HREE enrichment is not observed at the shallower sites (i.e. HH500, HH200). Ultimately, the REE pattern of seawater is a function of the fluxes of REEs into and out of the ocean and complexation/internal cycling of REEs within the ocean. Although there are small, but measureable, differences of REE patterns in seawater, the overall global consistency of the seawater REE pattern implies that internal processes do not have the potential to completely change the REE pattern of seawater. Therefore, a source with a more seawater like REE pattern is more logically consistent with less internal alteration.

Of the fluxes into the ocean, the riverine REE source pattern is highly variable (e.g. Shiller 2002; Stolpe et al., 2013; Sholkovitz et al., 1999; Stolpe et al., 2013) and is modified significantly through estuaries (e.g. Sholkovitz, 1995; Sholkovitz and Szymczak, 2000; Åström et al., 2012). REEs in submarine groundwater discharge can have HREE enrichment, similar to the pattern of seawater (Johannesson et al., 2011). Our data show that pore fluids also can also have a HREE enrichment, similar to the pattern of seawater. This HREE enriched pattern, as seen at HH3000, may imply that deep ocean pore fluids are an important REE source to the ocean. This possibility is further supported by the HREE enrichment in HH3000 bottom water sample that deviates from the trend observed in other deep water samples at HH3000 (**Figure 2.5**). This deviation results in a REE

pattern of HH3000 bottom water that approaches the REE pattern of the upper pore fluids at HH3000 (see **section 2.4.1**).

The fundamental point from these pore fluid pattern observations is that deeper sites (HH1200 and HH3000) have REE patterns that begin to appear more like seawater compared to the shallower sites (Station 1, HH200, HH500). The shallower sites (Station 1, HH200, and HH500) maintain a HREE depletion similar to the sedimentary (pore fluid) source pattern. The pore fluids at HH1200 and HH3000 demonstrate that even though the REE pattern at the pore fluid concentration maximum does not resemble the oceanic deep-water REE pattern, the REE pattern of the diffusive flux could resemble seawater more closely because of fractionation processes preferentially taking up the LREE or preferentially releasing HREEs as the REEs are transported through the pore fluids.

2.4.3 Diffusive Flux from the pore fluids

Data from this as well as other studies (Elderfield and Sholkovitz, 1987; Sholkovitz et al., 1989; Sholkovitz, 1992; Haley et al., 2003; Arsouze et al., 2009) provides evidence that there is a large sediment (pore fluid) source of REE to the oceans. Moreover, the pore fluid REE concentrations at slope sites are at least an order of magnitude greater than the concentrations found in the overlying water column (**Figure 2.7**). Even a small addition of REEs from the sediments, when extrapolated over the area of the seafloor, has the potential to significantly influence the oceanic budget of REEs. Additionally, while the bottom water REE concentrations are small relative to the pore fluid concentrations, these bottom water REEs are higher than the rest of the overlying water column, particularly at HH1200 and HH3000 (**Figure 2.3**) indicating that the source of REEs to the water is from below.

We calculated the diffusive flux of REEs to the overlying water column for the Oregon slope sites (HH500, HH1200, and HH3000) that can be supported by the pore water gradients. Calculations were not attempted at the shallower sites (Station 1, Station 2, and HH200) because these sites are likely influenced by non-diffusive processes and high levels of benthic faunal activity (discussed in **2.4.2.1**) rendering these calculations inappropriate for estimating sediment-water exchange rates (Archer and Devol, 1992; Elrod et al., 2004; Pakhomova et al., 2007). For slope sites (HH500, HH1200, HH3000) the concentration gradient of each REE in pore fluid was fit using the equation

$$C_z = C_d - (C_d - C_0)\exp(\alpha z) \quad (1)$$

where C_z is the concentration at depth, z , C_d is the concentration at infinite depth or for our purposes the approximate concentration at the source, C_0 is the concentration at the sediment-water boundary, α is the attenuation coefficient, and z is core depth in cm. This nomenclature follows that previously published for biogenic silica dissolution fluxes across the sediment water boundary (e.g., McManus et al., 1995). Fluxes across the sediment-water interface were calculated by combining Fick's first law with equation (1) resulting in the expression:

$$J = \emptyset D_s \alpha (C_z - C_0) \quad (2)$$

where J is the flux, $\emptyset$ the estimated core top porosity and D_s the sediment diffusion coefficient corrected for tortuosity. Molecular diffusion coefficients (D) for La^{3+} at 0°C, 18°C, and 25°C and Yb^{3+} at 25°C (Li and Gregory, 1974) were used to estimate D for all REEs. D for Yb^{3+} was assumed to follow the same linear relationship between D and temperature displayed by La^{3+} allowing D values at 4°C for both elements to be calculated using the equation $D = 1 \times 10^{-7}(T) + 3 \times 10^{-6}$. A linear extrapolation from La^{3+}

through Yb^{3+} resulted in the equation $Y = -1.61 \times 10^{-8}(R) + 3.42 \times 10^{-6}$ where R is between 1 and 14. D for each REE was assumed to be equally spaced, therefore, La was assigned $R = 1$ and Lu $R = 14$. The values for D calculated from a linear extrapolation were the same as the D values calculated using ionic radius (not shown). These calculations result in lower values of D for the HREEs than the LREEs (**Appendix Table 2.A6**). Complexation and adsorption of REEs was not accounted for in values of D since both processes are poorly constrained in pore fluids. D_s was estimated from the relation $D_s = D/(\phi F)$ with ϕ the porosity of the surface sediments (assumed = 0.9) and F the formation factor. F was calculated using Archie's Law $F = \phi^{-n}$ ($n = 2.5$ for fine grained sediments; Andrews and Bennett 1981, Ullman and Aller, 1982). The resulting calculated fluxes (black symbols) for each REE were then normalized to ORBS and PAAS (**Figure 2.8**). Values for C_z , C_0 , α , and $\partial C/\partial z$ as well as for all REE calculated fluxes are summarized in **Appendix Table 2.A6**.

The profile fits could bias the flux estimates at HH500 and HH1200 because of low sampling resolution above the source depth. For example, the depth resolution at HH500 only allowed for flux calculations assuming linear concentration gradients in the REEs. HH3000 had the most data above the source depth, implying that the model fits for HH3000 are the most reliable. The calculated fluxes become systematically more HREE enriched from HH500 to HH1200 to HH3000 (**Figure 2.8**) to the extent that at HH3000 the flux is HREE enriched relative to the bulk sediment (light grey symbols). The similarity of the HREE enriched flux pattern to that of the HREE enriched water column is consistent with the idea that the flux from sedimentary pore fluids of the deep ocean potentially has a significant influence on marine REEs.

Because site HH3000 exhibits a flux pattern most like seawater, and for instructive purposes, we extrapolated the flux observed at HH3000 to provide a back-of-the-envelope estimate of the potential global contributions of REEs from the sediment (through the pore fluids) to the oceanic budget (**Table 2.1, Appendix 2.5A**). This extrapolation gives a global sediment flux surprisingly similar to model budget requirements (Tachikawa et al. 2003; Arsouze et al., 2009) ranging between a conservative estimate of $18 \times 10^6 \text{ mol Nd yr}^{-1}$ and a liberal estimate of $110 \times 10^6 \text{ mol Nd yr}^{-1}$ (**Table 2.1**). Any value in this range suggests that the benthic flux of REEs to the ocean is large, likely larger than the riverine input. A more definite estimate of the global sediment contributions of REEs will require further investigation of the mechanisms, applicable water depths, and role of sediment type in controlling the flux of REEs. We recommend for such work efforts to improve down-core sample resolution and to access flux mechanisms at shallow sites.

2.5 Conclusions and Summary

Pore fluid REE concentrations were measured at eight sites along the Oregon and California margin, adding to the limited number of pore fluid REE data to date. The dissimilar dissolved Fe and REE pore fluid profiles suggest that the relationship between the REEs and Fe is more complicated than discussed in Haley et al. (2004). There is a clear REE pore fluid concentration maximum at most sites. The mechanism that generates this sedimentary “source” of REEs remains poorly understood, but the measured REE concentrations in pore fluids are at least an order of magnitude greater than the concentrations in the overlying water column.

A HREE depleted REE pattern was characteristic of the pore fluid at the shallow sites (Station 2, HH200, HH500) and of the pore fluid at the dissolved concentration maximum at all sites. HREE enrichment was apparent in the REE pattern away from this maximum at deep sites HH1200 and HH3000. These observed differences among the REE patterns within the sediment package suggest significant alteration of the REEs as they diffuse through the sediment package. Patterns appear to co-vary with REE concentration suggesting that the processes influencing the REEs as they are mobilized and transported through the pore fluids systematically fractionate the REEs. Additionally, this fractionation may explain why the pore fluid REE patterns at deeper sites (HH1200 and HH3000) are a closer match to the REE pattern of seawater than the REE patterns in pore fluids at shallower sites (HH200, HH500, Station 1). These data, and the resulting calculated diffusive flux of Nd from deep sediments suggest that pore fluids could be the major source of REEs to the ocean, at flux levels adequate to meet the “missing” source required by recent isotopic modeling (Arsouze et al., 2009; Tachikawa et al., 2003), making the REE flux from the sediments larger than all other oceanic REE sources, consistent with previous suggestions (e.g. Haley et al., 2003). The role of shelf sediments as a REE source is less clear, but the potential of shelf sediment pore fluid to influence oceanic REEs cannot be discounted.

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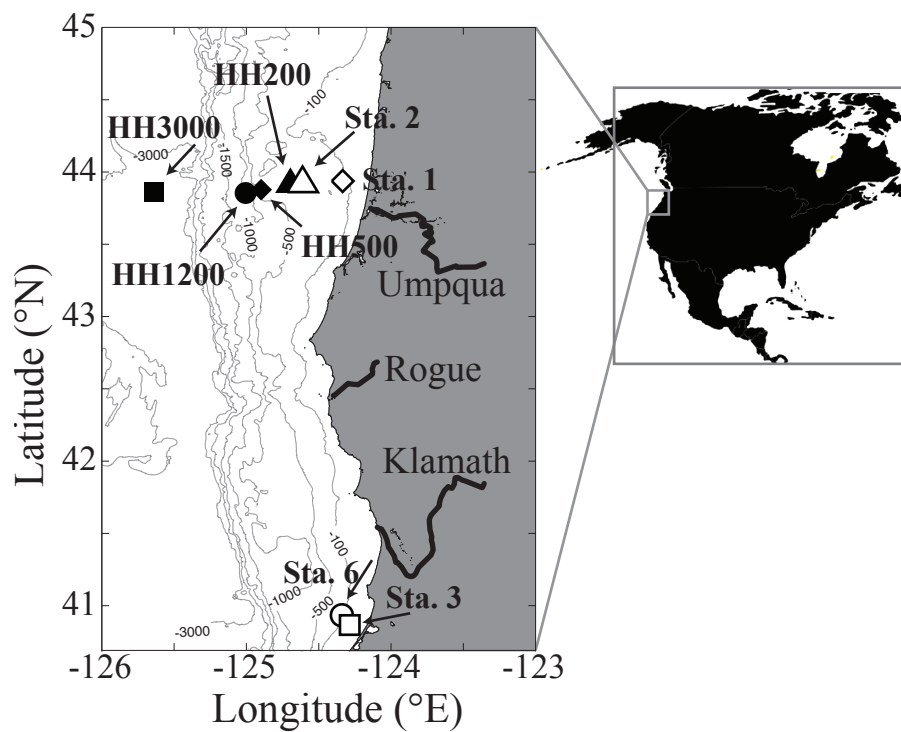
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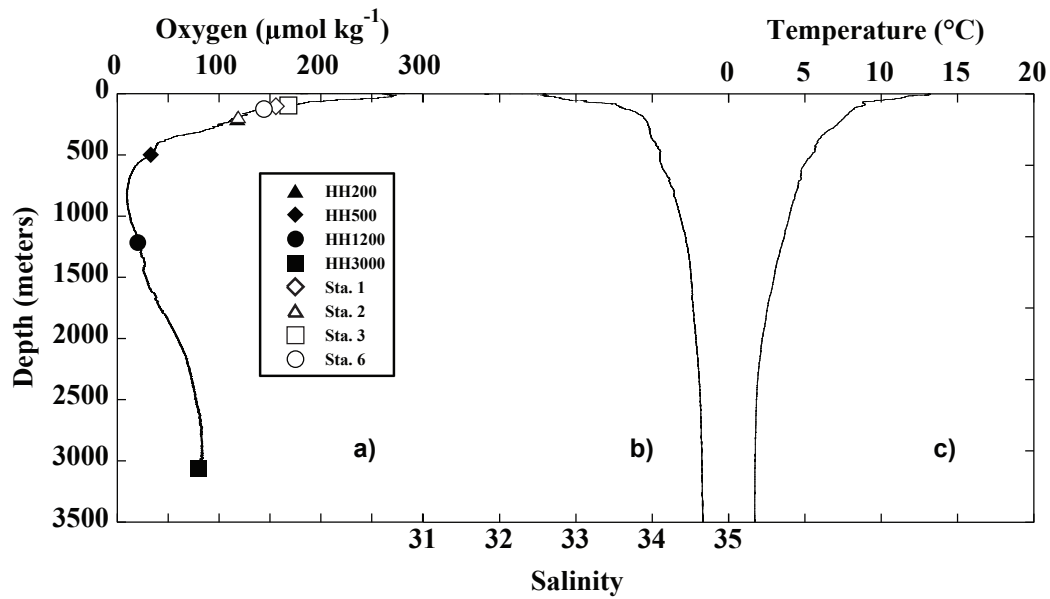
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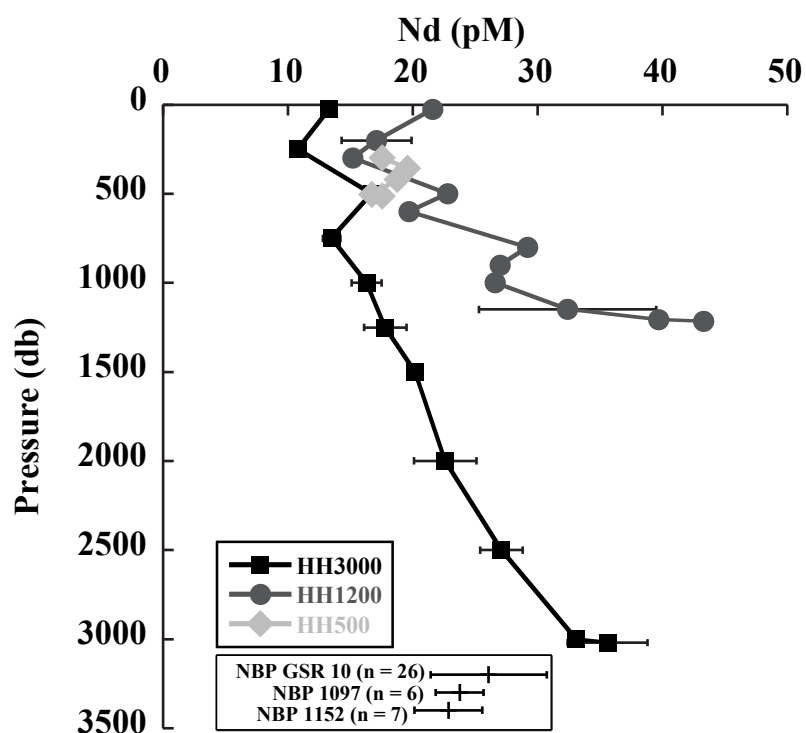
2.1 Site locations.

Filled symbols represent sites unique to this study and open symbols are sites where we have analyzed archived samples from prior expeditions (see text). Rivers are indicated in black and labeled. The Eel River flows into the southern edge of this map and is not shown.



2.2 Water column oxygen, temperature, and salinity.

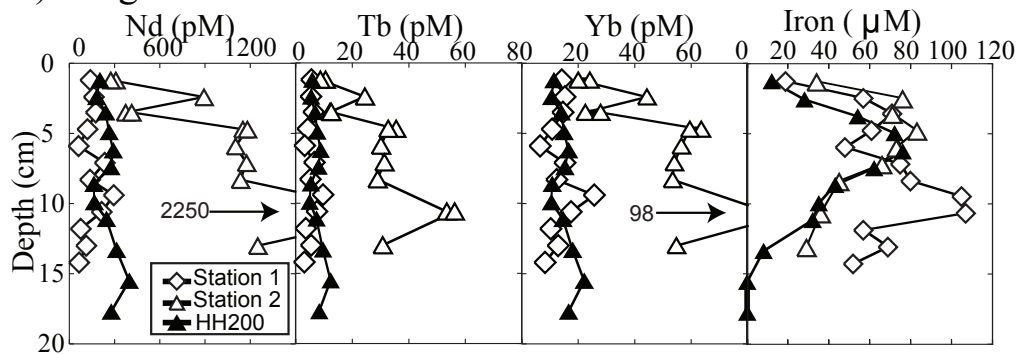
(a) Dissolved oxygen, (b) Salinity, and (c) Temperature as a function of water depth. Profile data are taken from the HH3000 study site. Symbols for other locations denote sampling depths, and the symbols are placed along the oxygen profile for illustrative purposes, see **Appendix Table 2.A1** for bottom water oxygen values.



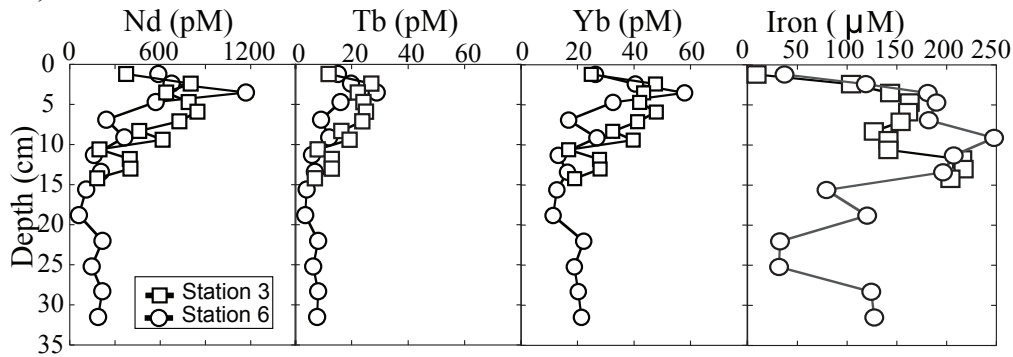
2.3 Water column Nd concentration.

Water column Nd concentration plotted as a function of water depth for Oregon slope sites. Uncertainties are ± 1 s based on sample replicates. Our internal standards, “NBP” samples are placed in the box at the base of the figure with their average concentration ± 1 s. Samples for the upper water column at HH500 were not collected. NBP samples are large volume filtered seawater samples collected from the Bransfield Strait in 1995 and acidified to pH 2.5 from water depths of 1310 m (NBPGSR10), 1152 m (NBP 1152), and 1097 m (NBP 1097).

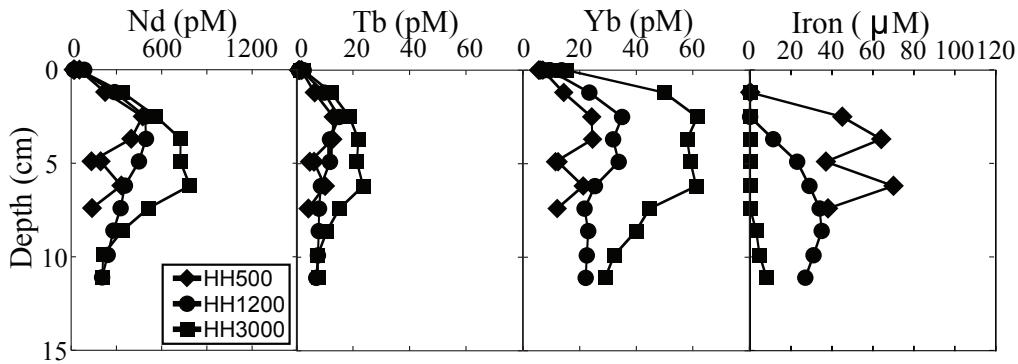
a) Oregon Shelf



b) California Shelf

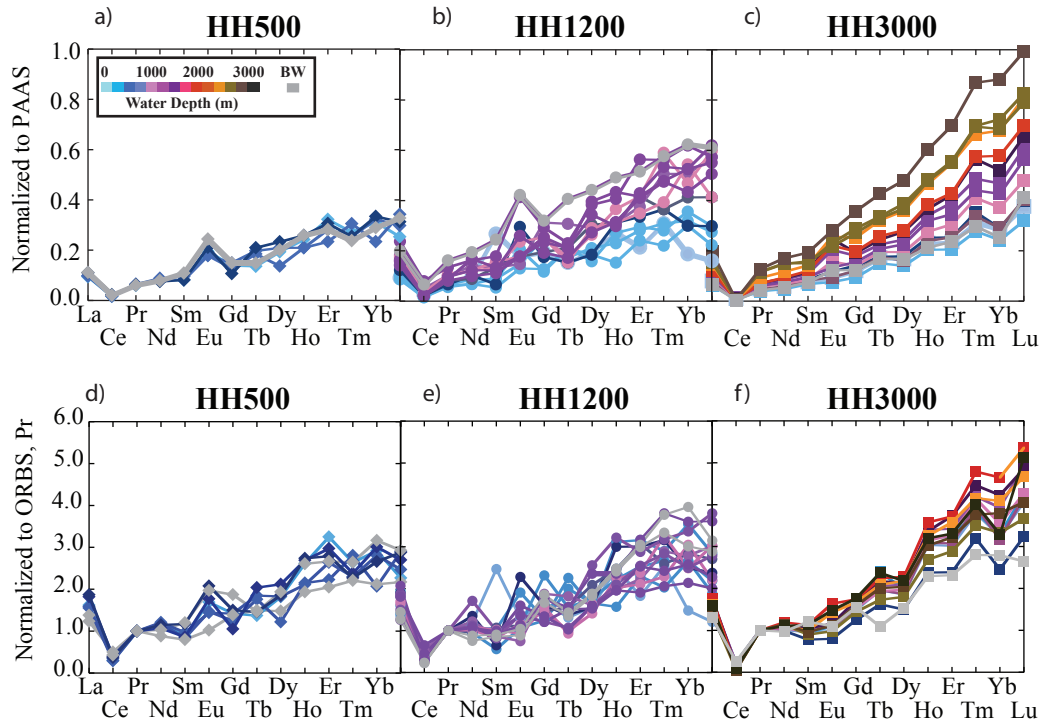


c) Oregon Slope



2.4 Pore water profiles.

Dissolved rare earth element (Nd, Tb, and Yb) and iron plotted against sediment depth in pore fluids from (a) the Oregon shelf, (b) the California shelf, and (c) the Oregon slope. For station 2, Nd concentrations peak at 2250 pM (not shown) and Yb concentrations peak at 98 pM (not shown).



2.5 Water column REE patterns

(a – c) Water column profile rare earth elements normalized to PAAS (values after Nance and Taylor 1976)

grouped according to the stations. The data is color-coded to capture the water depth information (see legend). (d – e) Water column profile rare earth elements for the same samples as plotted in (a – c) but

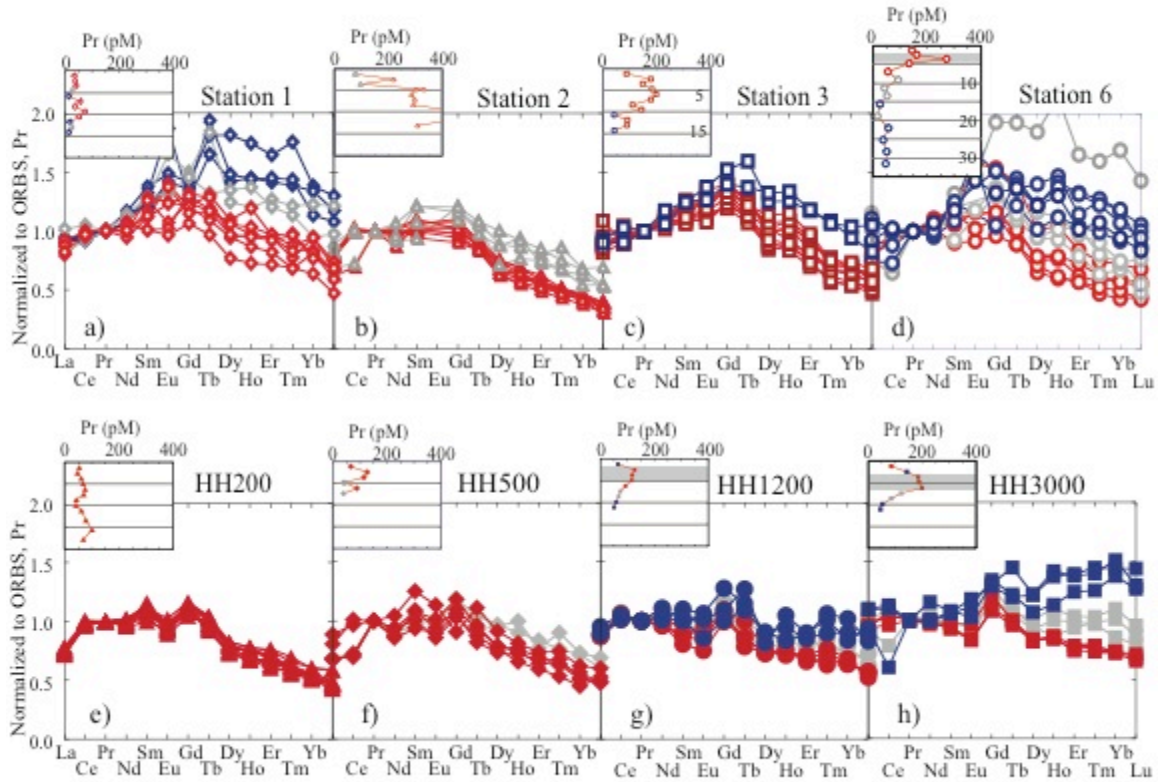
with the normalization now calculated for ORBS and Pr. Bottom water is shown in black (gray in color

version) for all plots. PAAS values used La: 273.6; Ce: 570.9; Pr: 63.2; Nd: 221.9; Sm: 35.2; Eu: 7.2; Gd:

29.9; Tb: 4.5; Dy: 27.1; Ho: 6.1; Er: 17.3; Tm: 2.4; Yb: 15.4; Lu: 2.5. ORBS values used La: 17.12; Ce:

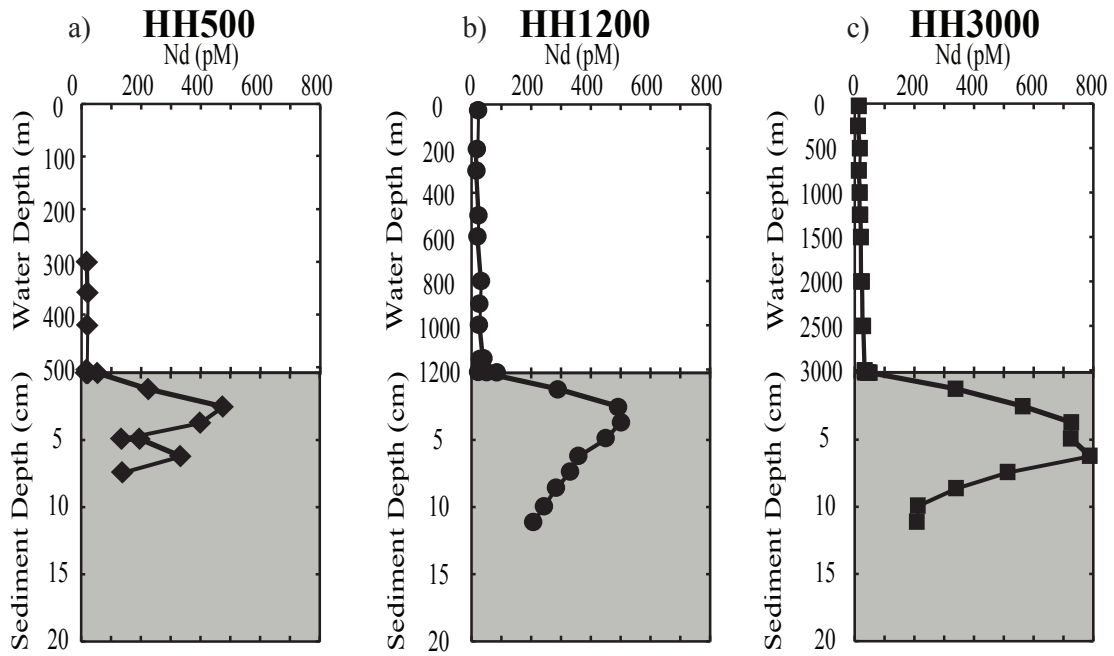
33.61; Pr: 4.03; Nd: 16.10; Sm: 3.43; Eu: 0.89; Gd: 3.14; Tb: 0.48; Dy: 3.08; Ho: 0.60; Er: 1.81; Tm: 0.26,

Yb: 1.72; Lu 0.30.



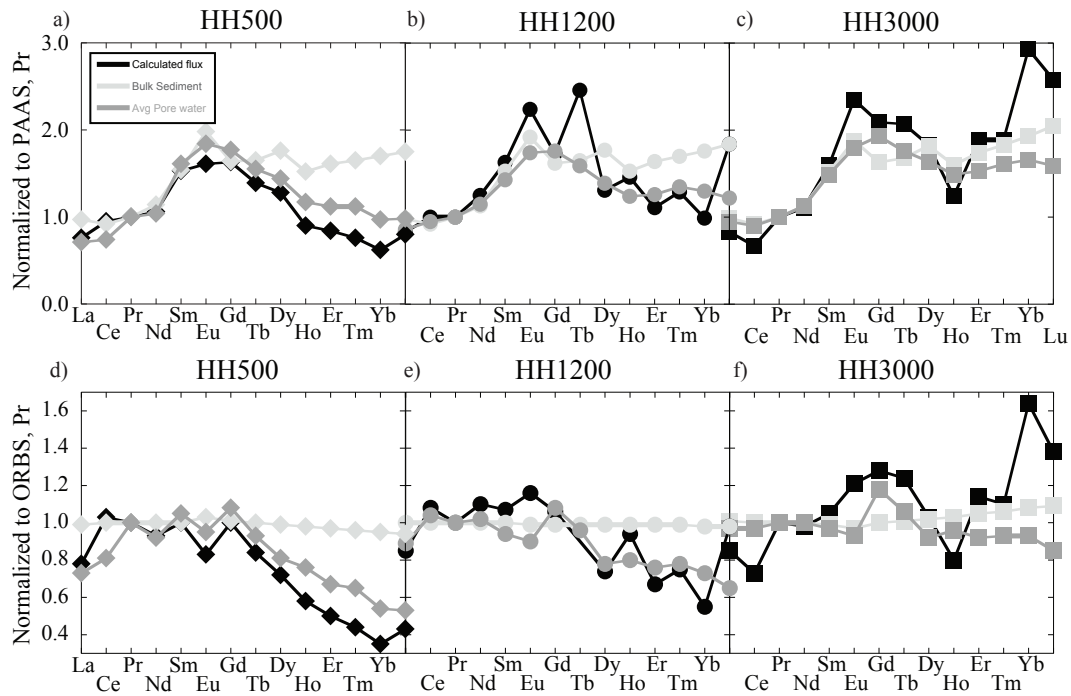
2.6 Pore water REE patterns

Pore fluid REE patterns normalized to ORBS and Pr for **(a)** Station 1, **(b)** Station 2, **(c)** Station 3, **(d)** Station 6, **(e)** HH200, **(f)** HH500, **(g)** HH1200, and **(h)** HH3000. Each pattern represents a different depth interval from the site. Patterns that have a lower HREE:LREE than ORBS are plotted in red and patterns with the highest HREE:LREE are in blue. Intermediate patterns are in light gray. Inset Pr profile for each site with color corresponding to pattern line for each depth. Thick gray bars in inset represent zone of maximum concentration for sites HH1200 and HH3000, gray lines mark every 5 cm of core depth in the inset Pr profile.



2.7 Water column pore fluid composite Nd profile

Water column and pore water Nd plotted as a function of water depth for (a) HH500, (b) HH1200, and (c) HH3000. The gray box indicates sediment and 1σ error bars are smaller than symbol size. Note that the sediment depth scale (gray area) and the water column depth portion of the scale differ.



2.8 REE flux patterns

(a) HH500 calculated flux patterns normalized to PAAS and Pr, **(b)** HH1200 calculated flux patterns normalized to PAAS and Pr, **(c)** HH3000 calculated flux patterns normalized to PAAS and Pr, **(d)** HH500 calculated flux patterns normalized to ORBS and Pr, **(e)** HH1200 calculated flux patterns normalized to ORBS and Pr, **(f)** HH3000 calculated flux patterns normalized to PAAS and Pr. Bulk sediment shown is by site and is not ORBS. Pore water average is also site specific. The REE pattern of the calculated flux is shown in black, the average pore water REE pattern in gray and the bulk sediment REE pattern in light gray. Symbols are site specific.

Oceanic Nd Source Fluxes		Flux out of Deep Sediments ($10^6 \text{ mol Nd yr}^{-1}$)			
Source	$10^6 \text{ mol Nd yr}^{-1}$	Area (10^6 km^2)	Full Area	No Calcareous	Only Pelagic
Rivers	1.8	151.5 Abyssal plains/hills	48	37	18
Atmospheric	0.7	170.8 plus continental rise	54	40	21
Sediment Dissolution modeled as missing	76	289.6 plus oceanic rise & ridge	92	64	35
Submarine Groundwater Discharge	29-81	344.8 plus continental slope & shelf	110	73	42

2.1 Source Comparison

Oceanic Nd source fluxes and extrapolated neodymium flux out of the deep sediments. The calculated flux is similar to the missing flux from models. The missing sediment source, riverine source, and atmospheric source are taken from Arsouze et al. 2009. Submarine groundwater discharges are from Johannesson and Burdige 2007. Seafloor areas and province are from Menard and Smith 1966. Sediment coverage estimated from Berger 1976. All flux values shown are based on an extrapolation using the flux from site HH3000 ($32 \text{ pmol cm}^{-2} \text{ yr}^{-1}$), additional flux extrapolations using the flux from site HH500 ($13 \text{ pmol cm}^{-2} \text{ yr}^{-1}$) are provided in **Appendix table 2.A7**. Details of flux extrapolation are provided in **Appendix 2.A5** and complete list of flux calculations in **Appendix tables 2.A6 and 2.A7**.

2.A Appendix

Tables 1-3 present site descriptions (1), REE concentrations in seawater (2) and REE concentrations in pore fluids (3) and are discussed in the main text.

2.A1 Oregon Bulk Sediment (ORBS)

ORBS is the average REE pattern of the total sediment digests from sites HH500, HH1200, and HH3000 (**Appendix Table 2.A4**). Sediments from HH200, HH500, HH1200, and HH3000 were digested in a mixture of HNO₃, HCl and HF using a CEM Corp MARS-5 microwave following the procedures of Muratli et al. (2012) and analyzed for REEs on the Thermo VG ExCell quadrupole ICP-MS at the W.M. Keck Laboratory. The sediment intervals analyzed correspond to the same depth intervals as the pore fluids. The REEs in these sediments are largely invariant (**Appendix Table 2.A5**). The patterns from all measured intervals at each site were averaged into a site average REE pattern, and then the three average site profiles were averaged to obtain ORBS (**Appendix Table 2.A4**). The REE pattern of ORBS normalized to PAAS is shown in **Appendix Figure 2.A1**.

2.A2 Rhizons and Rare Earth Elements

Laboratory experiments with REE enriched seawater were run to test the impact of rhizons on the extraction of REEs from pore fluids. For both tests, a known REE spike (0.15 ng (**Figure 2.A2 a**) and 0.05 ng (**Figure 2.A2 b**)) was added to a filtered, unacidified surface seawater sample from the Gulf of Mexico. Syringes and Rhizons

used in this experiment were the same type as the ones used at sea for pore water collection. The spiked solution was pulled through a Rhizon and analyzed for REE concentrations. Additionally, the spiked solution was collected in a syringe and analyzed for REE concentrations without passing through a Rhizon to establish a syringe blank.

Results from the Rhizon tests were variable. In the higher concentration experiments, the cleaned Rhizon showed LREE blanks as high as ~4x the loaded concentration (**Figure 2.A2 a**) and the unclean Rhizon up to ~2x the spike concentration. MREE and HREE depletion (>50%) was observed with both clean and uncleaned (new) Rhizons. However, one of the uncleaned Rhizon tests displayed no MREE or HREE depletion, highlighting the erratic nature of the problem with Rhizons. These results imply that Rhizons should probably not be used to collect samples for REE concentration determination. All results presented in this manuscript are from pore water samples collected using centrifuge techniques (as described in **2.2.2**).

2.A3 Chelex Columns and Seafast II

REE concentrations were analyzed after being separated from the seawater matrix either through the use of Chelex-resin columns or an ESI seaFAST II system. Samples were run by both methods to check the reproducibility between methods (**Figure 2.A3**). Repeatability between methods can be seen with both pore water and seawater samples. The deviation of the Oct-Chelex interval samples (solid lines) is due to the poor preservation of HREEs in solution at pH 2.5 as discussed below. When the same samples were processed using Chelex at the time of seaFAST II analysis (July Chelex) the results from each method were in agreement.

2.A4 Acidification and Rare Earth Element Preservation

Pore water and seawater samples from HH200, HH500, HH1200, and HH3000 were acidified to pH 2.5 at the time of collection and analyzed for rare earth element concentrations within one month of collection. This degree of acidification appears adequate for maintaining rare earth elements in solution for seawater samples, however a lower pH is needed for pore water fluids. For example, the HH1200 pore fluids were run again 9 months after collection and showed up to a 60% loss of heavy rare earth elements from solution (**Figure 2.A3**). In some cases, loss was also observed in the middle rare earths starting at Sm. Ce was the only element showing a concentration increase (30-40% in pore water) over the same 9 month time span. The rest of the light rare earth elements did not show any change. These REE concentration changes in pore water make a significant impact on the shape of the pattern of the rare earth elements when normalized to PAAS (**Figure 2.A3 b**).

BIF samples were acidified to pH 1.7 and analyzed for rare earth element concentrations. The REE patterns from BIF II sites 1, 2, 3, and 6 fall within the observed range of pore water patterns from HH200, HH500, HH1200, and HH3000. The agreement among the BIF II patterns (samples preserved at pH 1.7) and the samples run shortly after collection suggests that pH 1.7 is adequate to preserve the HREEs in solution and these patterns are assumed accurate but further testing is needed to confirm that no MREE or HREE loss occurs at pH 1.7 in pore water. It is clear that as samples are stored for prolonged periods at higher pH (~2.5) they may be subject to HREE loss from solution. We do not know to what degree our samples may have been affected by

REE removal from solution, but the general agreement and consistency among our results suggest that this effect is minor in our data set.

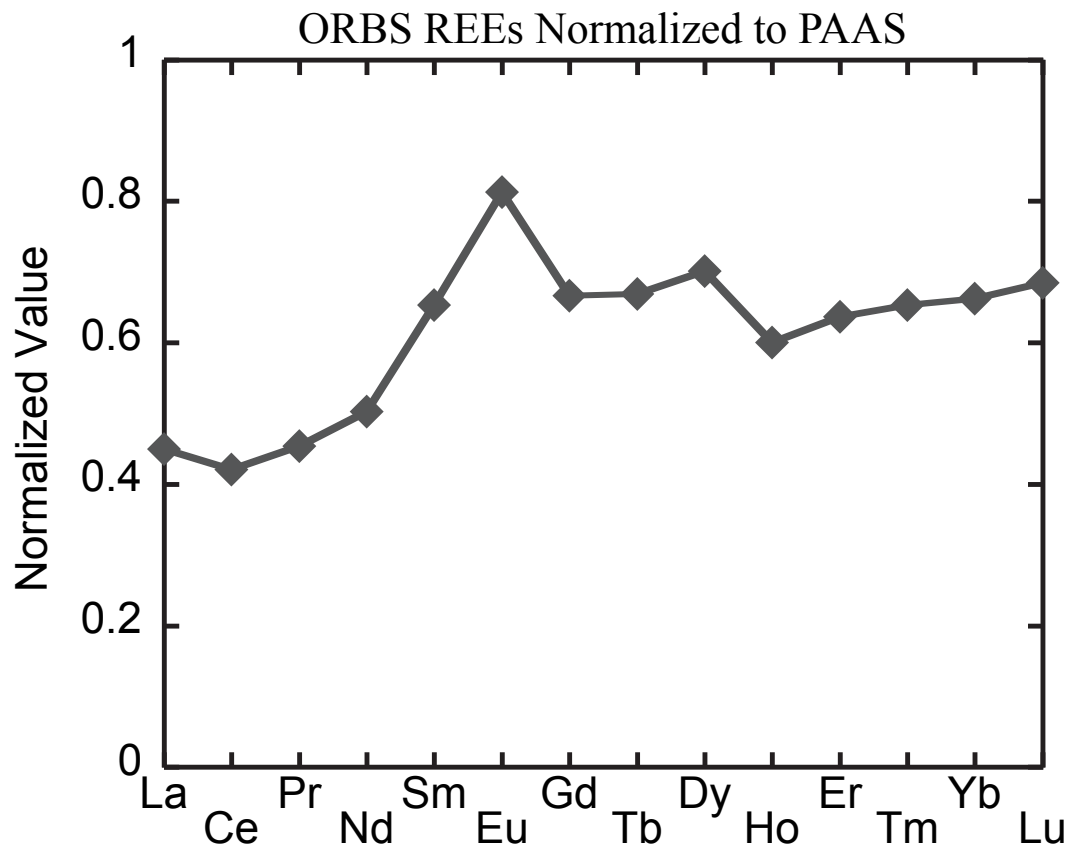
2.A5 Flux calculations

To better understand the implications of the calculated flux at HH3000, we extrapolated the HH3000 flux (section **2.4.3**) to larger areas of the ocean using province and sediment type restrictions. Province areas (Menard and Smith, 1966) considered were the abyssal hills and plains (mainly between 3000 and 6000 km water depth), the continental rise (mainly between 2000 and 5000 km water depth), the oceanic rise and ridge (mainly between 2000 and 6000 km water depth), and the continental slope and shelf (mainly shallower than 2000 km water depth) (Menard and Smith, 1966; **Table 2.1, Appendix Table 2.A6, Appendix Table 2.A7**). To provide a more conservative estimate, we applied sediment restrictions to constrain these areas. We removed the area of the ocean floor covered by calcareous ooze (because of the low Nd abundance in carbonate sediments; e.g. Parekh et al., 1977; Elderfield et al., 1981; Shaw and Wasserburg, 1985). by assuming an average carbonate compensation depth (CCD) of 5000 m, so that 50% of OCBN and 20% of RISE could not be calcareous. The remaining areas were considered to be 47% calcareous (Berger, 1976). For our most conservative estimate, we constrained the province areas with a pelagic sediment requirement, calculating fluxes based on 38% of the original province areas (Berger, 1976) for a rough estimate of the flux possible from only pelagic sediments (**Table 2.1, Appendix Table 2.A6, Appendix Table 2.A7**).

From these extrapolations, the sedimentary source of dissolved REE appears to be a significant contributor to the global REE budget. While we base these extrapolations on our best-constrained flux estimate (HH3000, flux of $\sim 32 \text{ pmol cm}^{-2} \text{ yr}^{-1}$) this flux value is similar to the flux estimated at HH1200 ($38 \text{ pmol cm}^{-2} \text{ yr}^{-1}$) and the same order of magnitude as the flux estimated at HH500 ($13 \text{ pmol cm}^{-2} \text{ yr}^{-1}$)(**Appendix Table 2.A6**). Because of the sampling resolution, we used a linear concentration-depth gradient at HH500; the same linear slope applied to HH1200 and HH3000 resulted in similarly lower fluxes at these sites ($14 \text{ pmol cm}^{-2} \text{ yr}^{-1}$, $13 \text{ pmol cm}^{-2} \text{ yr}^{-1}$ respectively, **Appendix Table 2.A6**). Importantly, the range of our calculated flux estimates (Appendix Table 7) is relatively small ($8 \text{ to } 110 \times 10^6 \text{ mol Nd yr}^{-1}$) considering the high uncertainty in these global extrapolations.

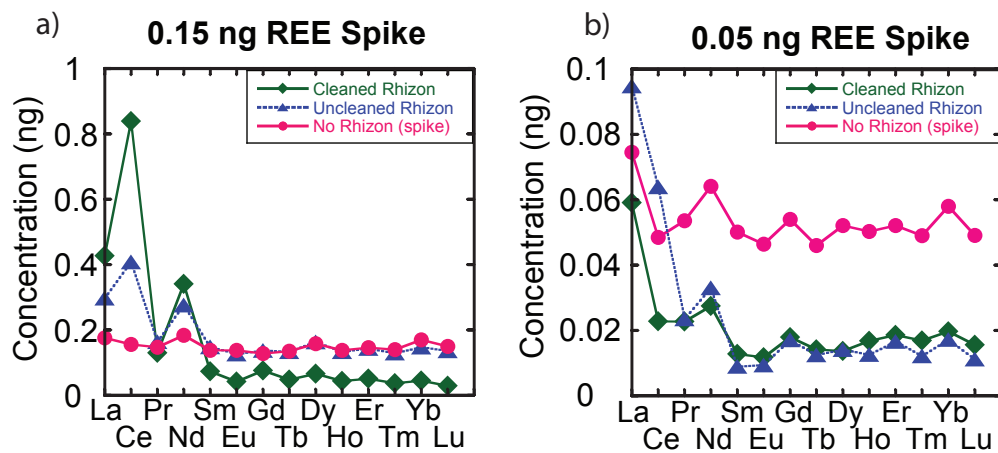
2A References

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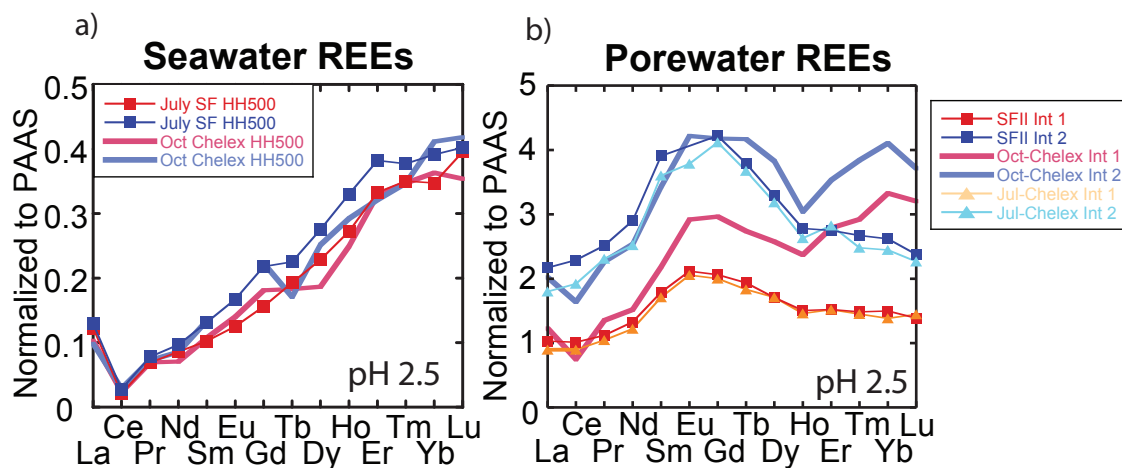
2.A1 ORBS REE normalized to PAAS

REE pattern of Oregon Bulk Sediment (ORBS) normalized to PAAS.



2.A2 Rhizon REEs

Results of rhizon yield test with known REE spike. **(a)** REEs measured after **(a)** a 0.15ng REE spike and **(b)** a 0.05ng REE spike was passed through a clean rhizon (green diamonds), uncleaned rhizon (blue triangle), and the control, no rhizon (pink circle).



2.A3 REE Preservation

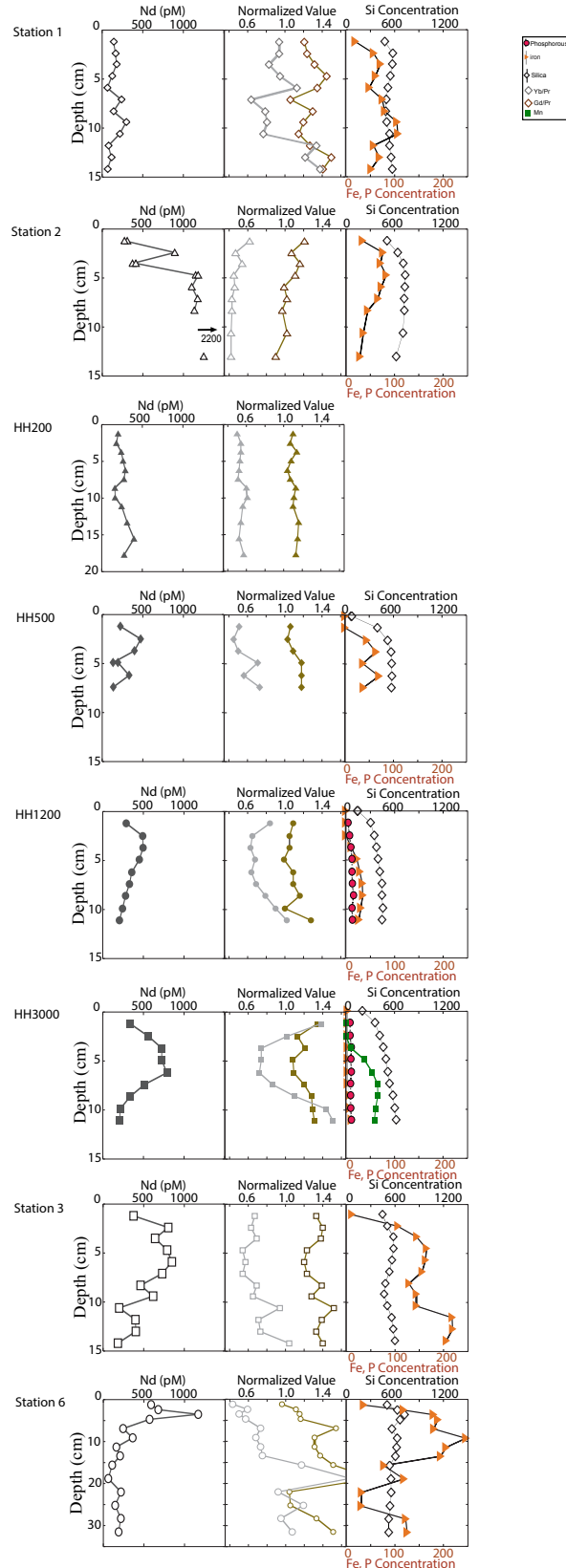
Comparison of REEs measured using Chelex column chromatography and REEs measured using the ESI SeaFast II system in the Keck Laboratory at Oregon State University. Chelex columns were measured in October (solid line) and July (triangles), SeaFast II measurements were only taken in July (squares). All samples represented here were stored at pH 2.5 **(a)** Seawater values were reproducible between methods and remained constant between sample times. **(b)** Pore water values were reproducible between methods but changed over time indicating that pH 2.5 is not low enough for REE preservation in pore water samples.

2.A4 Additional Pore Fluid Profiles

Nd, Si (open black diamond), P (pink circle), Mn (green square), Fe (orange triangle), Yb:Pr and Gd:Pr profiles for all sites, as available. Mn data was below detection at sites HH200, HH500, and HH1200. Mn data for stations 1, 2, 3, and 6 is provided in

Appendix Table 3 but is not shown here, as it would be indistinguishable from zero on the given scale. Nd and REE ratio symbols vary by site to match **Figure 4**; Yb:Pr shown

in gray, Gd/Pr in black. All REE ratio calculations made on ORBS-normalized REE values.



Supplemental Table Captions (*tables online only*)

2.A1 Site Descriptions

Water depth, cruise ID, sampling date, latitude, longitude, and bottom oxygen for each site. Bottom water oxygen for HH200, HH500, HH1200, and HH3000 from CTD measurement; bottom water oxygen for Stations 1, 2, 3, and 6 are from discrete measurements.

2.A2 Oregon Slope Water Column REEs

Water column REE concentrations in pM for HH500, HH1200, and HH3000. Samples above 300 m at HH500 were not collected. The mean REE concentrations of NBPGR10 (27 measurements) and procedural blank are reported with 1σ error.

2.A3 Pore water centrifuge results

Fe and Mn concentrations for all sites reported in $\mu\text{mol/L}$. REE concentrations for all sites reported in pM. Si and P concentrations reported in $\mu\text{mol/L}$ where available. Depth 0.0 is bottom water collected from niskin bottle attached to multicorer. A “*” next to 0.0 denotes an unfiltered sample, and “**” denotes a water sample collected on an unsuccessful core deployment with likely sediment disturbance.

2.A4 Oregon Bulk Sediment (ORBS)

REE values for ORBS reported in $\mu\text{g REE per g sediment}$.

2.A5 Sediment Digest REEs

REE concentrations in sediment digested in a mixture of HNO_3 , HCl and HF (procedures of Muratli et al. 2012) from the Oregon slope sites (HH500, HH1200, HH3000) reported in $\mu\text{g REE per g sediment}$.

2.A6 REE flux by site

a) Fitting parameters for non-linear diffusion calculations at HH1200 and HH3000. M1 is equivalent to the concentration at the depth of the maximum elemental concentration, M2 is the concentration in the bottom water, and M3 is the attenuation coefficient of concentration with depth. The χ^2 and r values for each fit are provided. Fluxes are calculated by equation $y = C_z - (C_z - C_0) \times \exp(\alpha x)$ using both D and D_s . The D_s based flux is also presented as a value normalized to PAAS. **b)** Linear concentration gradients ($\delta C/\delta z$) for each element at all three sites calculated from the depth of maximum concentration to the bottom water. Fluxes are calculated as $F = -D(\delta C/\delta z)$ and $F = -D_s(\delta C/\delta z)$ for each site. Negative flux values represent diffusion from the pore fluids into the bottom waters. **c)** Estimate of error for the Nd flux from HH3000 based on fitting parameters and error from **(a)**. Porosity and diffusion coefficients remained unchanged. The error introduced by the value of the gradient ($C_z - C_0$) had the least influence on the overall flux results, and the greatest deviation from the value reported in **(a)** resulted from a maximum error on both α and the gradient.

2.A7 Diffusive Flux Estimates

Nd flux from the pore fluids into the overlying water reported in $\text{mol Nd yr}^{-1} \times 10^6$. All fluxes are calculated based on a flux out of the sediments of $31.8 \text{ pmol Nd cm}^{-2} \text{ yr}^{-1}$ and of $13.1 \text{ pmol Nd cm}^{-2} \text{ yr}^{-1}$. Depth, province, and basin divisions and areas from Menard and Smith (1966). Sediment type coverage areas from Open University (1989) with calculations as described in Appendix A.5.

2.A8 ICP-MS Settings

Characteristics and settings for the ICP-MS used for REE concentration analysis including isotopes monitored and data acquisition settings.

Chapter 3: Bottoms up: sedimentary control of the deep North Pacific Ocean's ϵNd signature

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ABSTRACT

The ability to reconstruct past ocean currents is essential for determining ocean circulation's role in global heat transport and climate change. Our understanding of the relationship between circulation and climate in the past allows us to predict the impact of future climate-driven circulation changes. One proposed tracer of past ocean circulation is the neodymium isotope composition (ϵNd) of ancient water masses. However, ambiguities in what governs the ϵNd distribution in the modern ocean hamper interpretations of this tracer. Here we present ϵNd values for marine pore fluids, sediments, and the overlying water column for three sites in the North Pacific. We find that ocean bottom water ϵNd ($\epsilon\text{Nd}_{\text{BW}}$) in the northeast Pacific lies between the value expected for the water mass (-3.3) and the measured ϵNd of sediment pore fluid ($\epsilon\text{Nd}_{\text{PW}}$; -1.8). Moreover, $\epsilon\text{Nd}_{\text{PW}}$ resembles the ϵNd of the sediment. Combined, these findings are consistent with recent assessments that sediment pore fluids may be a major source of rare earth elements to the ocean and suggest that the benthic flux of Nd from pore fluids exerts the primary control over the deep ocean distribution of ϵNd .

3.1 Introduction

Neodymium isotopes are used as a tool in reconstructing ocean circulation. The neodymium isotopic value (ϵNd) is defined as $[(^{143}\text{Nd}_{\text{sample}}/^{144}\text{Nd}_{\text{sample}}) / (^{143}\text{Nd}_{\text{CHUR}}/^{144}\text{Nd}_{\text{CHUR}}) - 1] \times 10^4$ whereas CHUR is the chondritic uniform reserve, used as an average Earth value ($^{143}\text{Nd}/^{144}\text{Nd} = 0.512638$) (Jacobsen and Wasserburg, 1980). Utilizing ϵNd to reconstruct ocean circulation is based on the fundamental assumption that changes in ϵNd reflect conservative mixing of water masses (Frank, 2002). However, this assumption has been called into question because the marine budget for ϵNd is unbalanced (Tachikawa et al., 2003; van de Flierdt et al., 2004; Arsouze et al. 2009) and because water mass ϵNd ($\epsilon\text{Nd}_{\text{WM}}$) appears to be altered by non-conservative processes in marginal settings or “boundary exchange” (Lacan and Jeandel, 2005; Carter et al., 2012; Grasse et al., 2012; Grenier et al., 2013; Haley et al., 2014; Stichel et al., 2015). In addition, global ocean circulation models incorporating ϵNd distributions suggest that there is a “missing” source of dissolved Nd that contributes up to ~95% of the Nd in the ocean (Arsouze et al., 2009). Pore fluid concentration profiles indicate that this missing source could be a benthic flux of Nd from sedimentary pore fluids (Sholkovitz et al., 1989; Haley et al., 2004; Abbott et al., 2015). If so, how does this benthic flux of Nd impact the distribution of ϵNd in the ocean and the use of ϵNd in paleoclimate reconstructions? To answer this question we examine the ϵNd of the pore fluids, which represent a benthic source of Nd that is significant to the marine Nd budget (Abbott et al., 2015).

3.2 Methods

We collected 20 L water column, ~1L sediment pore fluid, and sediment samples from three sites off the Oregon margin in October 2012 and July 2013 (**Figure 3.1**, detailed description in Abbott et al., 2015). Briefly, water column samples were collected using Standard PVC Niskin bottles that were pressurized with N₂ upon recovery to filter the sample using in-line “Disposal A” 0.45 µm filters (Geotech Environmental Equipment item 73050004). All water column samples were acidified to pH ≤2.5 using ultrapure 12 M HCl. Pore fluid was collected using centrifuged sediments from multiple cores and the centrifuged sediments were then digested in a mixture of HNO₃, HCl and HF using a CEM Corp MARS-5 microwave (Muratli et al., 2012; Abbott et al., 2015).

Water and sediment digests were analyzed for Nd concentrations on the Thermo VG ExCell quadrupole ICP-MS at the W.M. Keck Collaboratory for Plasma Spectrometry (Oregon State University). A large volume seawater sample (NBP95R10) collected from the Bransfield Strait in the Southern Ocean (62° 46’S, 59° 24’W) at a water depth of 1300 m was used as an in-house consistency standard (mean 24.8 pM Nd, 1σ = 4 pM, procedural blank 3.5 pM Nd) as no calibrated seawater standards are available. All isotopic analyses were performed on the Nu Plasma ICP-MS multi collector in the Keck Collaboratory at Oregon State University with ¹⁴⁴Nd on the axial cup internally normalized for mass bias to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. The JNdi-1 standard was used for normalization to ¹⁴³Nd/¹⁴⁴Nd = 0.512115 with a 2σ uncertainty of ± 0.000011, n = 166 (reference value 0.512115 ± 0.000007 Tanaka et al., 2000). Specpure, a Nd element quadrupole standard, was used as an in house reproducibility standard with ¹⁴³Nd/¹⁴⁴Nd = 0.511205 with a 2σ uncertainty of ± 0.000014, n = 147.

3.3 Results and Discussion

We find water column Nd concentrations to range between 10 pM and 40 pM (**Figure 3.2a**) and ϵNd to range between -1.2 and -3.2 (**Figure 3.2b**). Using potential temperature and salinity data we interpret our sites at 1200 and 3000 m depth sites to represent mixing between North Pacific Intermediate Water (NPIW, ~ 240 m depth) and Pacific Deep Water (PDW, ~ 3000 m depth, **Figure 3.2b**). Based on these water mass identifications and the published ϵNd of NPIW and PDW (Haley et al., 2014), the water column ϵNd profile is predicted to decrease with depth from -3 toward -3.5 (**Figure 3.2b**). Instead, the observed ϵNd appears to remain constant with depth below the surface, at -2.5 at 1200 m and at -2.3 at 3000 m (**Figure 3.3**). The deviation between the observed and the expected ocean bottom water ($\epsilon\text{Nd}_{\text{BW}}$) is greatest ($\Delta\epsilon\text{Nd}_{\text{exp-obs}} = 1.0$) in bottom water at our 3000 m site, coinciding with the largest benthic flux of Nd to the ocean (**Figure 3.3**, Abbott et al., 2015). The $\epsilon\text{Nd}_{\text{obs}}$ deviates toward the ϵNd of pore fluids ($\epsilon\text{Nd}_{\text{PW}}$), with $\epsilon\text{Nd}_{\text{obs}}$ being less radiogenic than predicted (**Figure 3.3**). The average pore fluid ϵNd value ($\epsilon\text{Nd}_{\text{PW}}$) at each site is nearly constant down core and is -0.2 at 200 m; -1.5 at 1200 m (excluding 1.2 cm and 2.4 cm); and -1.8 at 3000 m (**Figure 3.3**). These values are offset from PDW values (-3.5), and instead must be generated from the bulk sedimentary solid phase (**Figure 3.3**). Regardless of the mechanism of generation, our measured $\epsilon\text{Nd}_{\text{PW}}$ demonstrate that pore fluids can produce an isotopically distinct flux term.

We argue that the overlying water column ϵNd profile is controlled by the benthic Nd flux from the pore fluids and that the influence of this flux on water column ϵNd can be described as:

$$\epsilon\text{Nd}_{\text{WM}} = \int_{t=0}^{t=T} f([\text{Nd}]_{\text{WM}}, F_{\text{Nd}}, \Delta\epsilon\text{Nd}_{\text{Flux-WM}}) (1)$$

where $\epsilon\text{Nd}_{\text{WM}}$ is a function of the concentration of Nd in the water mass ($[\text{Nd}]_{\text{WM}}$; at time $t = 0$), the magnitude of the benthic flux (F_{Nd}), and the difference between the observed $\epsilon\text{Nd}_{\text{WM}}$ (at $t = 0$) and ϵNd of the benthic flux ($\Delta\epsilon\text{Nd}_{\text{Flux-WM}}$) integrated over the time of exposure to the flux (T). In this model, a surface water mass has low initial $[\text{Nd}]_{\text{WM}}$ and initial $\epsilon\text{Nd}_{\text{WM}}$ that resembles the regional riverine dissolved load. If this water mass does not contact the sediments, F_{Nd} is negligible, limiting changes in $\epsilon\text{Nd}_{\text{WM}}$ to only water column processes. However, if the water mass is exposed to a sedimentary source of Nd, then $\epsilon\text{Nd}_{\text{WM}}$ is possibly altered. The potential for alteration grows with increases in either the ratio of F_{Nd} to $[\text{Nd}]_{\text{WM}}$ (i.e., piston velocity) or the difference between the ϵNd of the flux relative to ϵNd of the water mass ($\Delta\epsilon\text{Nd}_{\text{Flux-WM}}$, where $\epsilon\text{Nd}_{\text{Flux}}$ is assumed equivalent to $\epsilon\text{Nd}_{\text{pw}}$). This model implies that a short exposure time of a water mass to the sediment with a high F_{Nd} or a large $\Delta\epsilon\text{Nd}_{\text{Flux-WM}}$ is able to readily alter the $\epsilon\text{Nd}_{\text{WM}}$ at timescales observed in the modern ocean (**Figure 3.4**). Alternatively, an infinitely long exposure to a zero flux, or a region with a small $\Delta\epsilon\text{Nd}_{\text{Flux-WM}}$ will not alter $\epsilon\text{Nd}_{\text{WM}}$. Essentially, our model based on observations from the North Pacific suggests that the deep-water distribution of ϵNd is primarily dependent on F_{Nd} , $\Delta\epsilon\text{Nd}_{\text{Flux-WM}}$, and exposure time to the benthic flux.

Our model provides a mechanism to explain deep-water ϵNd alteration in the North Pacific in the absence of modern deep-water formation. Specifically, the benthic

flux of Nd from sedimentary pore fluids can alter bottom water ϵNd to resemble a local sedimentary ϵNd signature. This alteration of bottom water ϵNd is most noticeable in regions with distinct weathering provenances. For instance, the benthic flux of Nd from the Amazon River depocenter may explain the resemblance of deep Caribbean water ϵNd ($\epsilon\text{Nd}\approx-9.2$) to the ϵNd of the Amazon River ($\epsilon\text{Nd}\approx-9$; Osborne et al., 2014) instead of the ϵNd of the Antarctic Intermediate Water (AAIW) ($\epsilon\text{Nd}\approx-11$). In general, biogenic phases will have an ϵNd that resembles surface water (Akagi et al., 2014), meaning $\Delta\epsilon\text{Nd}_{\text{Flux-WM}}$ in regions of dominantly biogenic sediments will not alter $\epsilon\text{Nd}_{\text{BW}}$ in homogenous water columns, such as the Southern Ocean (Stichel et al., 2012), but may alter $\epsilon\text{Nd}_{\text{BW}}$ in regions where $\epsilon\text{Nd}_{\text{Surface}}$ is different than $\epsilon\text{Nd}_{\text{BW}}$, such as in the North Pacific (Akagi et al., 2014). Moreover, low concentrations of Nd in calcareous sediments minimize the ability of these sediments to change $\epsilon\text{Nd}_{\text{WM}}$ (Parekh et al., 1977; Elderfield et al., 1981; Shaw and Wasserburg, 1985). The variation in F_{Nd} and $\Delta\epsilon\text{Nd}_{\text{Flux-WM}}$ (**Figure 3.3**) within our small study region highlights the need for further investigation of the reactions that govern the isotope composition and magnitude of the benthic flux throughout the global ocean.

Our benthic source model is consistent with Nd observations in the modern ocean. For instance, large vertical Nd concentration gradients in the Pacific (Lacan et al., 2012) are consistent with long-term exposure of old bottom water to a substantial benthic flux. Furthermore, the addition of Nd with a pore fluid ϵNd signature to bottom water would shift the ϵNd of the bottom water toward more radiogenic values, consistent with deviation of observed bottom water ϵNd from the predicted bottom water ϵNd at our sites (**Figure 3.3**). To produce this deviation only requires a small proportion of the dissolved

Nd in pore fluids to be transferred to the overlying water column (see Equation 2 below). In contrast, producing the observed bottom water Nd concentrations and ϵNd with only vertical water column processes is implausible because of the high mass transfer that would be required to create the observed as much as one 1 unit shift in ϵNd , consistent with previous findings (Lacan and Jeandel, 2005; Arsouze et al., 2009; Carter et al., 2012; Grasse et al., 2012; Grenier et al., 2013).

Our model shifts the dominant oceanic source of Nd from a series of surface point sources (i.e., rivers) to a diffuse sedimentary source. Is this hypothesis consistent with the temporal and spatial scales of ϵNd variability seen in the ocean? To address this question we use the concept of piston velocity to reflect the ability of the flux to influence the overlying water column. Piston velocity is typically used with respect to gases, but more broadly piston velocity is a calculation that treats the flux as proportional to the contrast in concentrations (Kump et al., 2005). Here we define piston velocity as the ratio of the magnitude of the flux and the Nd concentration in the overlying water mass ($F_{\text{Nd}}/[\text{Nd}]_{\text{BW}}$). The calculated piston velocities range from 860 cm yr^{-1} at 3000 m to 360 cm yr^{-1} at 1200 m to 140 cm yr^{-1} at 200 m.

The piston velocity should be related to the observed offset between $\epsilon\text{Nd}_{\text{BW}}$ and $\epsilon\text{Nd}_{\text{Flux}}$ if our calculated piston velocities are indicative of the ability of the benthic flux to alter $\epsilon\text{Nd}_{\text{BW}}$. Accordingly, we find an inverse relationship between the magnitude of the difference between the measured $\epsilon\text{Nd}_{\text{Flux}}$ and $\epsilon\text{Nd}_{\text{BW}}$ ($\Delta\epsilon\text{Nd}$) and the piston velocity at our sites (Equation 2). Specifically:

$$|\Delta\epsilon\text{Nd}| = 73 \times \text{PV}^{-0.9} \quad (2)$$

where PV is piston velocity (in cm yr^{-1})/ Equation 2 demonstrates that as piston velocities increase the flux will exert more control over the resulting $\epsilon\text{Nd}_{\text{BW}}$, i.e., $\Delta\epsilon\text{Nd}$ approaches zero. Conversely, as piston velocities decrease the flux has no potential to alter the bottom water ϵNd . The relationship between $\Delta\epsilon\text{Nd}$ and PV may provide a constraint on the degree of change to the ϵNd signature of a bottom water mass that is not related to conservative water mass mixing for paleocirculation because this relationship allows us to estimate the sediment-water exchange rate, provided $\Delta\epsilon\text{Nd}$ and $[\text{Nd}]_{\text{BW}}$ are known, or to estimate the $\Delta\epsilon\text{Nd}$ if the piston velocity is known. Estimates cannot be made in regions where either $\Delta\epsilon\text{Nd}$ or PV is zero, and our calculations do not account for exposure time. For the latter caveat, we can model the sensitivity of the response of $\epsilon\text{Nd}_{\text{WM}}$ to a predicted flux (Equation 2) over a range of exposure times; predicting $\epsilon\text{Nd}_{\text{WM}}$ over 500 years for 6 scenarios representing a range of conditions in the modern ocean (**Figure 3.4**). In all scenarios, $\epsilon\text{Nd}_{\text{Flux}} = -5$ and $\epsilon\text{Nd}_{\text{BW}} = 0$. The model results demonstrate that low fluxes require a longer exposure time to alter $\epsilon\text{Nd}_{\text{WM}}$ and have a lower ability to cause alteration (**Figure 3.4**). Conversely, high fluxes can result in fairly rapid shifts to $\epsilon\text{Nd}_{\text{WM}}$, regardless of initial Nd concentration (**Figure 3.4**). For example, scenario 1 results in a 1.5 ϵNd shift in ~50 years; the same change in ϵNd requires ~185 years in scenario 2, ~230 years in scenario 3, and more than 500 years in scenarios 4, 5, and 6 (**Figure 3.4**). All scenarios assume a water mass thickness of 2000 m. This sensitivity test demonstrates that the timescales associated with an influence of the benthic flux of Nd on the ϵNd distribution in the deep ocean is commensurate with modern observations (average mixing time of the deep ocean of 1500 years; Broecker and Peng, 1982).

We can go one step further and apply the piston velocity over the height of the overlying water mass to calculate the time required for the benthic flux to change the $\epsilon\text{Nd}_{\text{WM}}$ by calculating the “response time” (τ_{response}). We calculate the response time of a given water mass to the benthic flux of Nd for our model (Equation 3)

$$\tau_{\text{response}} = ([\text{Nd}]_{\text{WM}} \times H \times A) / (F_{\text{Nd}} \times A) \quad (3)$$

where H is the thickness of the water mass (2500 m at 3000 m site; 1000 m at 1200 m site; 200 m at 200 m site), $[\text{Nd}]_{\text{WM}}$ is the average concentration of Nd in the water mass, F_{Nd} is the magnitude of the flux, and A is the area. These τ_{response} calculations allow us to isolate and only consider the water mass in contact with the sedimentary source, assuming steady state. We find τ_{response} to be ~300 years at both our 1200 m and 3000 m site, consistent with the observed basin scale ϵNd variability seen in deep water (Tachikawa et al., 1999).

Our ϵNd data and benthic flux model support ϵNd as a useful tracer of ocean circulation. However, our model adds complexity to interpretations of the ϵNd data. We propose that ϵNd retains a memory of its flow path (Equation 1), as seen in our data by the alteration of more radiogenic Pacific Deep Water with a less radiogenic benthic flux (**Figure 3.3**). This memory means that past changes in circulation, such as shifts in the location of deep-water formation and current velocity, are recorded by ϵNd in part because they change the exposure time to benthic fluxes. For example, sluggish deep-water formation may alter $\epsilon\text{Nd}_{\text{BW}}$ simply due to increased exposure time of bottom water to the benthic flux. Additionally, factors such as sediment distribution and composition changes (Scher and Martin, 2004; Fagel and Hilaire-Marcel, 2006; Franzese et al., 2006) may alter $\epsilon\text{Nd}_{\text{BW}}$ with no concurrent change in circulation. We suggest that ϵNd is a more

precise tracer of circulation because these factors can be determined and provide additional constraints for reconstructions.

In conclusion, we suggest that marine sediments are a dominant source of Nd to the ocean and that this benthic source likely controls the Pacific Ocean's deep-water ϵNd distribution. We assert that the ϵNd signature of a water mass is determined by a combination of the circulation path and the exposure time to sedimentary fluxes, advancing our ability to interpret ϵNd as a robust tracer of circulation. We suggest the influence of boundary exchange through a large benthic flux may continue to alter the ϵNd signature of a water mass in the deep sea. This model presents a revised way to examine the oceanic Nd budget and suggests future ϵNd studies are needed to test this model in the abyssal Pacific and other major ocean basins.

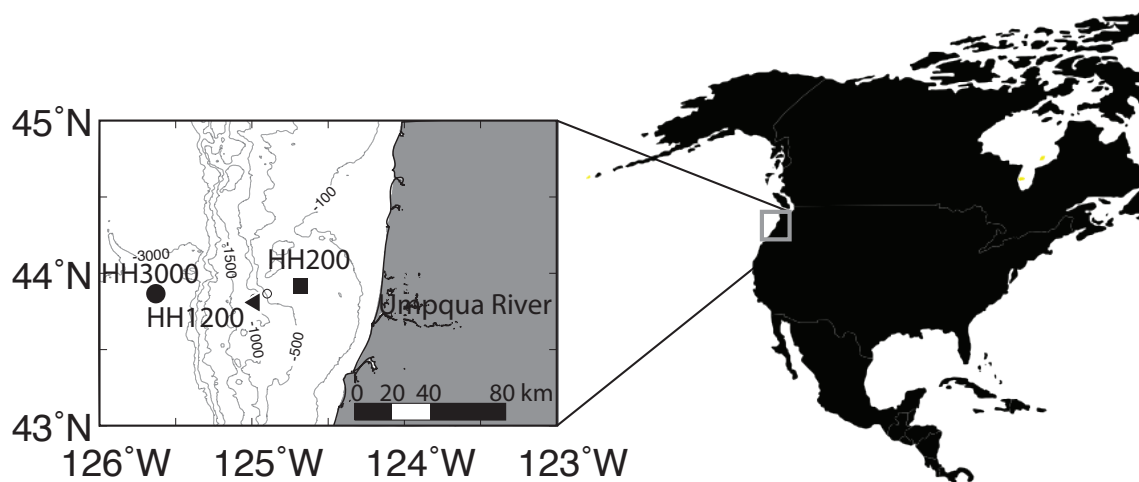
Acknowledgments

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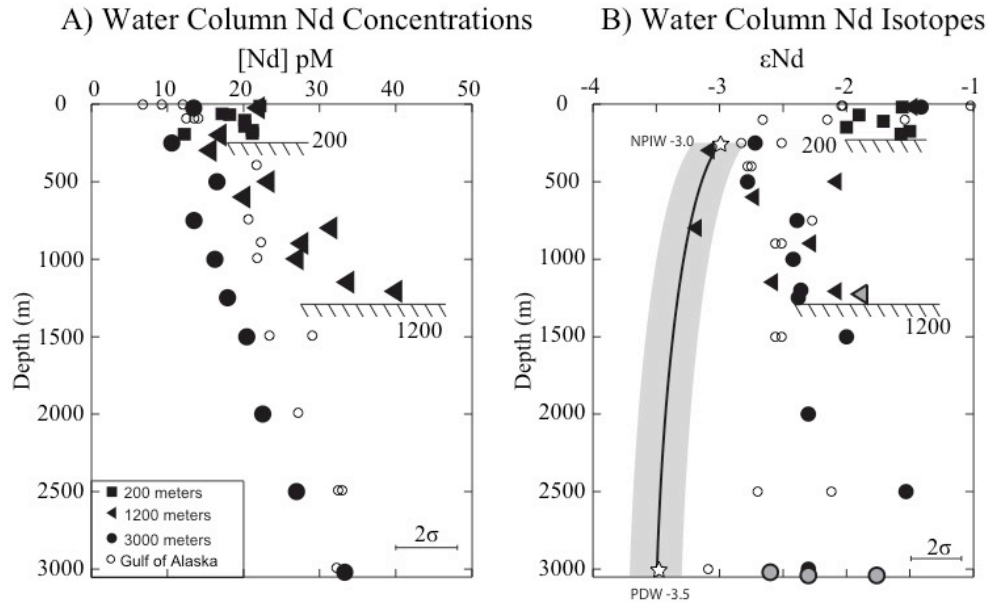
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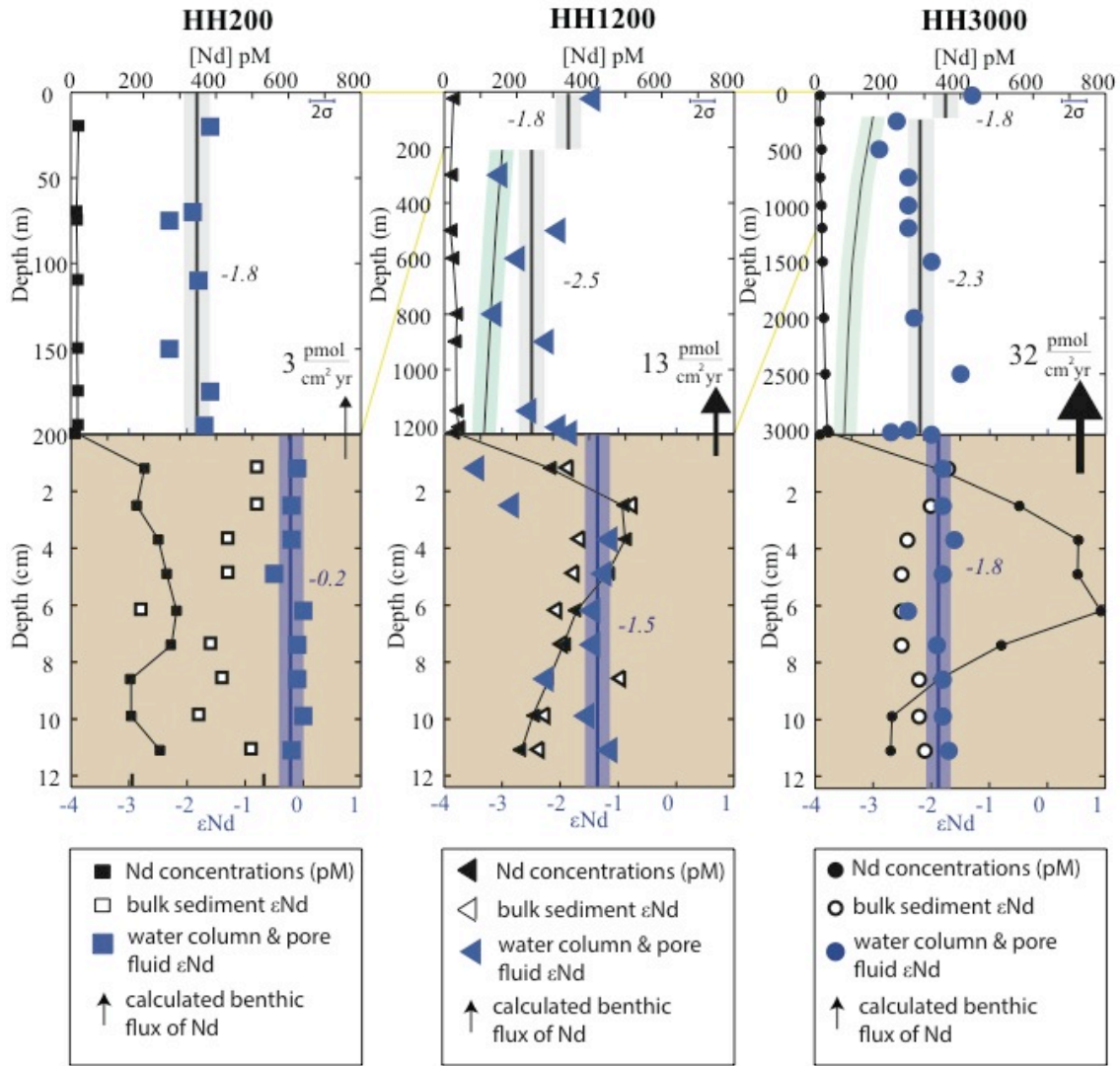
3.1. Site locations on a map of the eastern North Pacific

Sites are indicated by site-specific symbols (200 m site by a square, 1200 m site by a triangle, and 3000 m site by a circle).



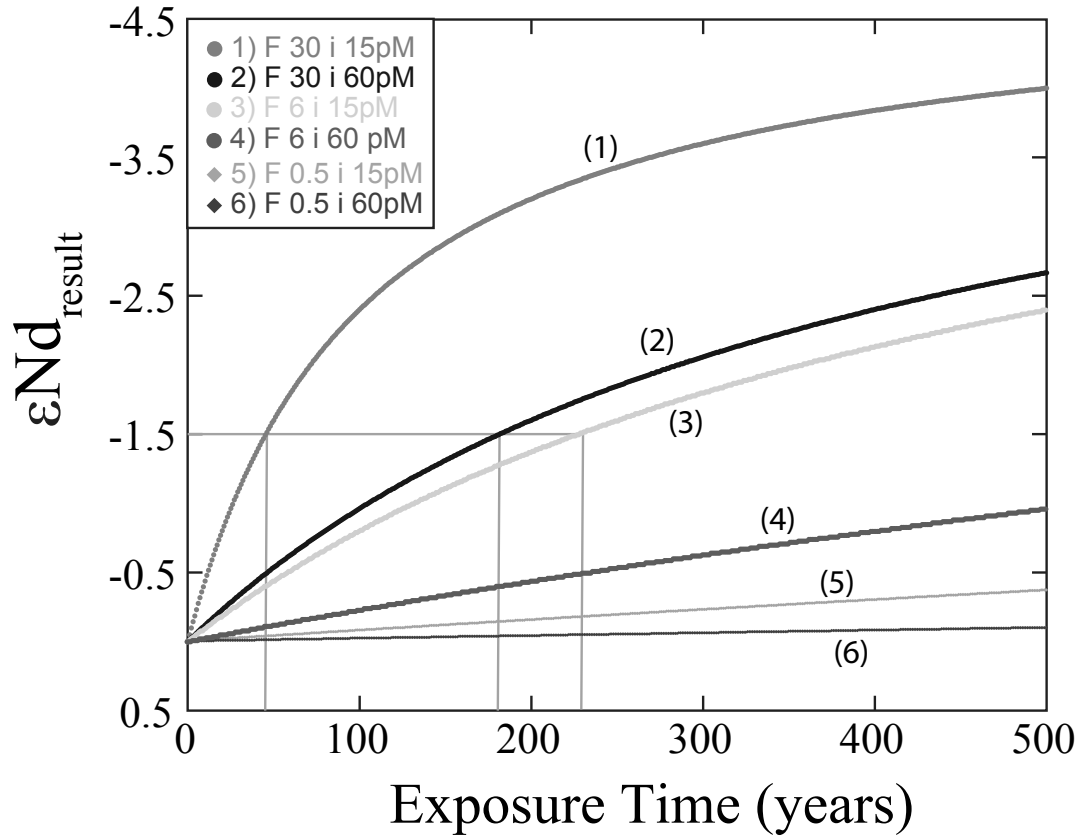
3.2. Water column Nd and εNd

Profiles of water column A) Nd concentrations and B) εNd plotted as a function of depth. The black line (B) represents the εNd profile expected based on water mass mixing between North Pacific Intermediate Water (NPIW) and Pacific Deep Water (PDW) with 2σ error indicated by gray shading. NPIW and PDW are indicated by black stars and labeled. Bottom water samples are indicated by gray filled symbols. Data from the Gulf of Alaska (Haley et al., 2014) are shown for comparison. The depth of the sediment-water interface is indicated for the 200 m and 1200 m site. Concentration data for 1200 m and 3000 m is from Abbott et al. (2015). Error bars (2σ) are provided for concentration and isotopic data.



3.3. Composite dissolved Nd concentration and ϵ Nd profiles

Composite dissolved Nd concentration and ϵ Nd profiles plotted as a function of water depth or sediment depth. Vertical bars represent the mean ϵ Nd of the water column (gray) and pore fluids (blue). The shaded vertical bars show 2σ error of the mean dissolved ϵ Nd for the water column (gray) and pore fluids (blue). The green lines represent the expected water column ϵ Nd profile from Figure 2. Concentration data for 1200 m and 3000 m is from Abbott et al. (2015). Mean observed ϵ Nd are *italicized*. Error bars (2σ) are provided for isotopic data, error bars for concentrations are smaller than the marker size.



3.4 Resulting ϵNd_{WM} for six modeled flux scenarios

The scenarios are 1) $30 \text{ pmol cm}^{-2} \text{ yr}^{-1}$ flux with 15 pM initial $[Nd]_{WM}$; 2) $30 \text{ pmol cm}^{-2} \text{ yr}^{-1}$ flux with 60 pM initial $[Nd]_{WM}$; 3) $6 \text{ pmol cm}^{-2} \text{ yr}^{-1}$ flux with 15 pM initial $[Nd]_{WM}$; 4) $6 \text{ pmol cm}^{-2} \text{ yr}^{-1}$ flux with 60 pM initial $[Nd]_{WM}$; 5) $0.5 \text{ pmol cm}^{-2} \text{ yr}^{-1}$ flux with 15 pM initial $[Nd]_{WM}$; 6) $0.5 \text{ pmol cm}^{-2} \text{ yr}^{-1}$ flux with 60 pM initial $[Nd]_{WM}$. For these scenarios, we used $\epsilon Nd_{BW} = 0$ and the $\epsilon Nd_{Flux} = -5$. Grey boxes illustrate the exposure time it takes a water mass to reach $\epsilon Nd_{BW} = -1.5$; only half of the scenarios reach $\epsilon Nd_{BW} = -1.5$ in 500 years.

3A Appendix

3.A1 Additional Methods

3.A1.1 Sample Preparation

Iron coprecipitation techniques were used to preconcentrate seawater and pore water REEs (modified from Stichel et al., 2012). Briefly, 1 mL clean ~1.0 M ferric chloride solution was added to each 20 L seawater sample and each 1 L of pore water followed by enough ultra-pure ammonia hydroxide to raise the pH of the water to 8. The water was syphoned away after iron flocculation was complete (typically 24 to 72 hours) and the remaining iron floc was rinsed with MQ water at least 3 times. Samples were then refluxed in distilled concentrated HCl and HNO₃ in a 1:1 solution for 24 to 78 hours, dried down completely and redissolved in ultrapure 6 M HCl (Stichel et al., 2012). Diethyl ether back extractions removed ~90% of the Fe from the solution. The samples were dried after ether back extractions to eliminate any remaining ether before being brought up in 1 mL 6M HCl.

Sediment, water column, and pore fluid samples were run through a series of ion exchange columns to isolate the Nd fraction for isotopic analysis. AG-1X8 resin was used first to remove Fe from the solution and therefore increase the yield and efficiency of the remaining columns. The resin was cleaned with 6 mL 6M HNO₃, 6 mL MQ, and conditioned with 6 mL 6M HCl before the sample was loaded in 1 mL 6M HCl as collection began and eluted with an additional 5 mL 6M HCl (modified from Scholz et al., 2014). Next, cation exchange columns (1.8 mL AG50-8X HCl form resin) removed major cations. Neodymium was further isolated from other lanthanides using Ln Spec resin (modified from Pin and Zalduegui, 1997). Each column was loaded with 2 mL of 50-100 µm mesh Ln resin (Eichrom® part LN-B50-5) and cleaned with 4 mL 6M HCl

and 6 mL MQ. The column was then conditioned in 4 mL 0.1M HCl before the 0.5 mL sample was loaded in 0.1M HCl, and then eluted with 15 mL 0.1M HCL and 0.25M HCl.

3.A1.2 Flux Calculations

The benthic flux of Nd from each of our sites was calculated using the concentration gradient in the pore fluids (Abbott et al., 2015). The benthic fluxes at our sites (between 2.6 and 31 $\text{pmol cm}^{-2} \text{yr}^{-1}$) are in agreement with benthic flux estimates from pore fluid (between 2.8 and 36 $\text{pmol cm}^{-2} \text{yr}^{-1}$) and benthic chamber (2.1 $\text{pmol cm}^{-2} \text{yr}^{-1}$) flux calculations from the California margin (Haley and Klinkhammer, 2003). We estimated the benthic flux of Nd at our 200 m site using a linear fit with a molecular diffusion coefficient (D) value of 2.3×10^{-6} even though the presence of macrofauna at this site likely interferes with diffusive processes (Abbott et al., 2015). Flux calculations at our sites did not take into account the concentration of Nd in the bottom water, allowing us to maintain the independence of piston velocity in identifying the relationship between piston velocity and $\Delta \epsilon \text{Nd}$ (equation 2). However, for illustrative purposes, we also calculate the flux across the sediment-water interface including the bottom water. These calculations are based on only the bottom water Nd concentration and the upper most (1.2 cm) pore fluid Nd concentration after the calculation by Haley and Klinkhammer (2003). The resulting fluxes still increase from our 200 m site (16 $\text{pmol cm}^{-2} \text{yr}^{-1}$) to our 1200 m site (22 $\text{pmol cm}^{-2} \text{yr}^{-1}$) to our 3000 m site (26 $\text{pmol cm}^{-2} \text{yr}^{-1}$).

3.A1.3 Exposure Time Model

We modeled the sensitivity of the $\epsilon \text{Nd}_{\text{WM}}$ response to the benthic flux over time. Specifically, the model demonstrates how exposure time can limit $\epsilon \text{Nd}_{\text{WM}}$ alteration. The

fundamental constraint is whether the observed spatial variation in water column ϵNd values is consistent with our measured benthic flux values. For this model, we define:

$$\epsilon\text{Nd}_{\text{BW}}(t) = \epsilon\text{Nd}_{\text{BW}}(t=0) \times ([\text{Nd}]_{\text{BW}, t=0} / [\text{Nd}]_{\text{BW}, t=t}) + \epsilon\text{Nd}_{\text{Flux}}(t=0) \times ([\text{Nd}]_{\text{Flux}, t=0} / [\text{Nd}]_{\text{BW}, t=t}) \quad (4)$$

and

$$[\text{Nd}]_{\text{C}} = F \times t \times p \quad (5)$$

Where $[\text{Nd}]_{\text{C}}$ is the cumulative concentration of Nd that is derived from the benthic input, F is the flux, t is time, and p is the limit imposed on the amount of Nd as a fraction of the flux that can be added to the bottom water ($0 \leq p \leq 1$). We present the simplest of these models in the main text: a 500 year simulation for 6 scenarios, each with $\epsilon\text{Nd}_{\text{Flux}} = -5$ and $\epsilon\text{Nd}_{\text{BW}} = 0$, in which the amount of Nd added is equal to the cumulative flux (i.e., $p=1$, **Figure 3.4**). The model presented is not at steady state as there is no loss term included to conserve bottom water Nd concentrations. However, by adjusting p we can numerically conserve the Nd concentration in the water mass, and bring the model towards steady state. While conservation of concentration is possible, a realistic sink needs to be constrained both isotopically and in terms of the pattern of REEs. The constraint of the sink is tangential to the characterization of the source of Nd from the benthic flux. For this reason, we do not present the results of the steady state model. For the model presented (**Figure 3.4**) we use a constant water mass height of 2000 m for all 6 scenarios when calculating the amount of Nd in the bottom water (concentration (pmol cm^{-3}) $\times$ height (cm)). The model can be adjusted to the parameters at each site (e.g. water column height, $\epsilon\text{Nd}_{\text{Flux}}$, and $\epsilon\text{Nd}_{\text{BW}}$) and can be adjusted for a balance between source and sink (i.e. steady state, p approaches 0). Currently, presenting

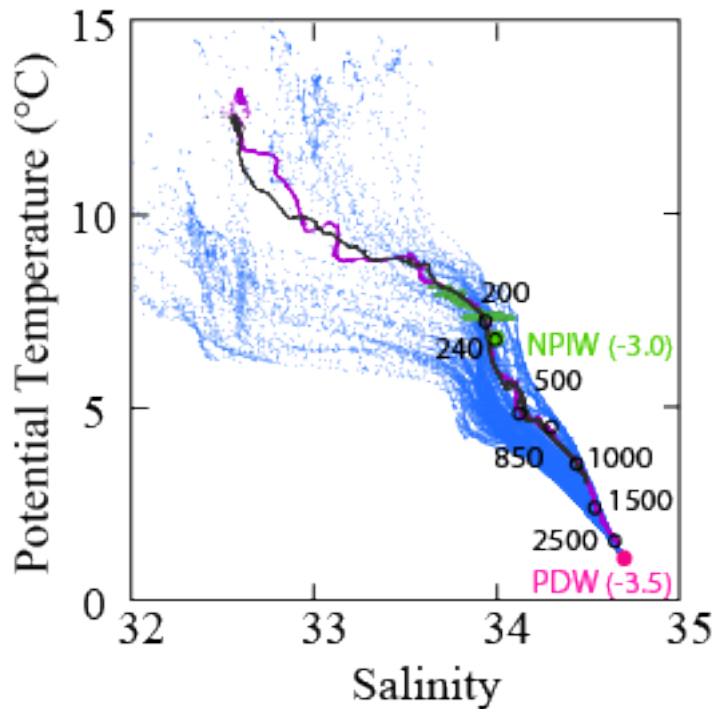
the results of this site specific model are unwarranted given that the pore fluid ϵNd data presented here are the first of their kind and limited to sites on the Oregon margin. The purpose of the model at this stage is to conceptualize the influence of the benthic flux and the simplest model (presented) demonstrates how ϵNd might change in a water mass as it is exposed to a Nd flux from below. While the simplest model provides a crude estimate for the benthic processes that determine bottom water ϵNd in the North Pacific, more complex models will need to be implemented to fully describe these processes.

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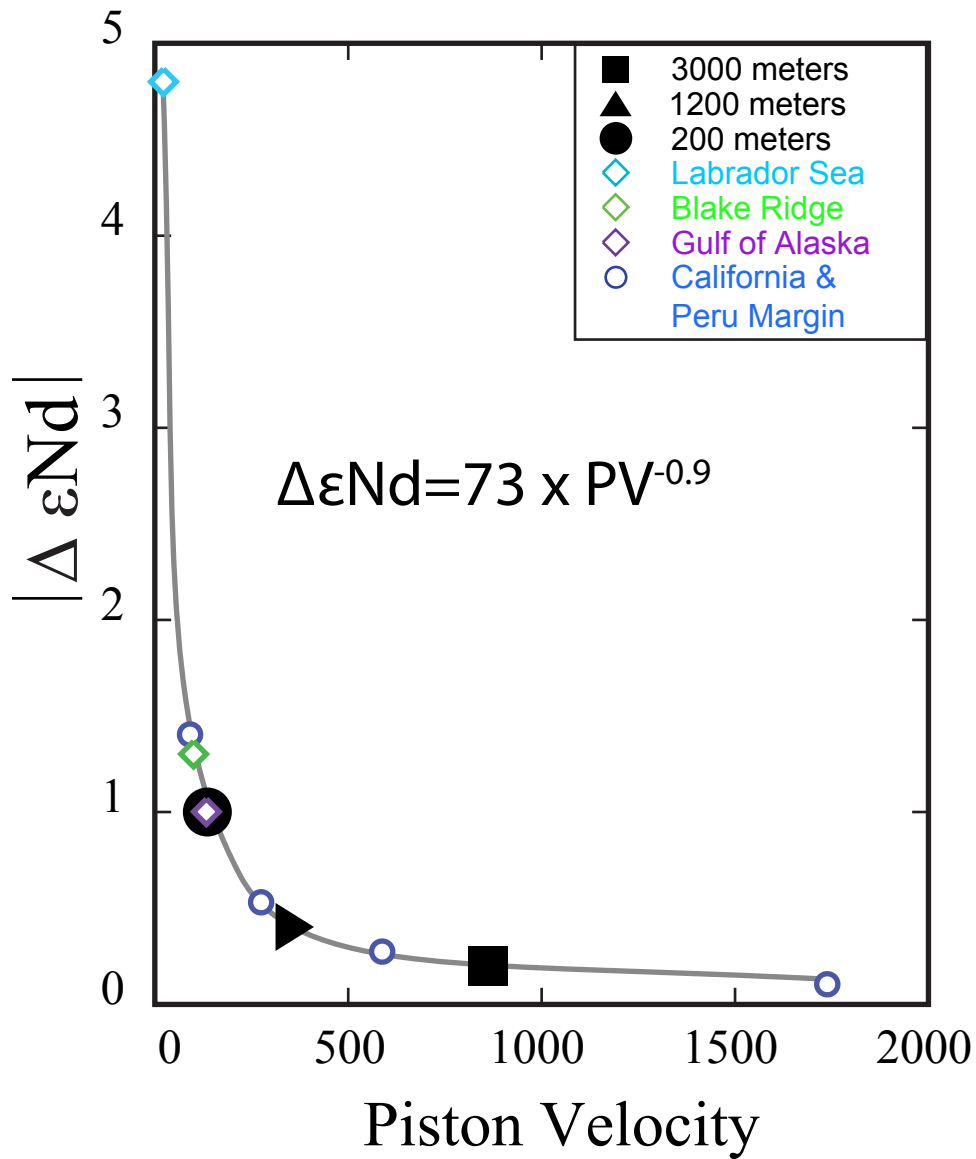
Start Appendix 3 (MS #2) Figures Here

Appendix Figure Captions



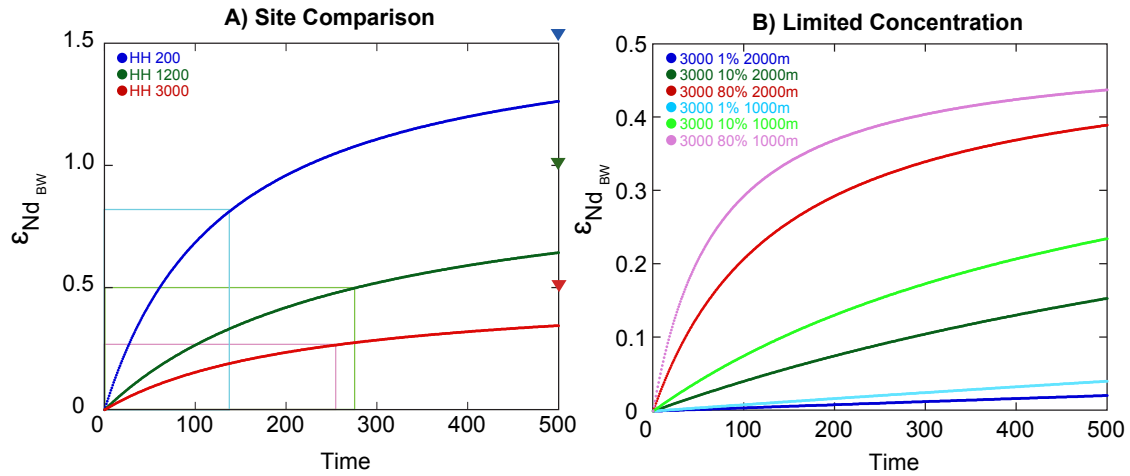
3.A1 T-S Plot

Temperature plotted as a function of salinity for 200 m (green), 1200 m (black), and 3000 m (purple) sites. Blue dots are WOCE data for the eastern North Pacific (Schlitzer, R., Ocean Data View, <http://odv.awi.de>). Select water column depths are labeled (in meters, open circles) on the plot. Major water mass cores for North Pacific Intermediate Water (NPIW, green) and Pacific Deep Water (PDW, pink) are identified with solid circles. Water mass temperature and salinity data is from Talley et al. (2011) and the ϵNd of the water masses (labeled in parenthesis) is from Haley et al. (2014).



3.A2 $|\Delta \epsilon_{Nd}|$ plotted as a function of piston velocity (PV)

The relationship between $|\Delta \epsilon_{Nd}|$ and piston velocity is described as $|\Delta \epsilon_{Nd}| = 73 \times PV^{-0.9}$. This relationship shows that $\epsilon_{Nd_{BW}}$ is not altered to resemble $\epsilon_{Nd_{BW}}$ when the piston velocity approaches zero allowing $\Delta \epsilon_{Nd}$ to retain higher values. Alternatively, $|\Delta \epsilon_{Nd}|$ will approach zero as piston velocities increase. Filled symbols are sites where both $\Delta \epsilon_{Nd}$ and piston velocity are based on field measurements. Open diamonds are calculated piston velocities based on measured $\Delta \epsilon_{Nd}$ and $[Nd]_{BW}$. Open circles are calculated $\Delta \epsilon_{Nd}$ based on published pore water fluxes and $[Nd]_{BW}$ (Haley and Klinkhammer, 2003).



3.A3 Modeled flux scenarios

A) Resulting $\epsilon_{Nd_{WM}}$ for modeled flux scenarios representing observations at our 200 m (blue), 1200 m (green), and 3000 m sites (red). Triangles on the right axis indicate the $\epsilon_{Nd_{FLUX}}$ for each site. The boxes indicate the time needed for the $\epsilon_{Nd_{WM}}$ to an $\epsilon_{Nd_{WM}}$ half way between the initial $\epsilon_{Nd_{WM}}$ and $\epsilon_{Nd_{FLUX}}$. B) Resulting $\epsilon_{Nd_{WM}}$ for modeled flux scenarios limited increases in bottom water Nd concentration of 1% (blue), 10% (green), and 80% (red) of the flux for a 2000 m water column (dark) and a 1000 m water column (light) for observed conditions at our 3000 m site.

3.A1. Estimating Flux from Changes in Epsilon

Site	$ \Delta\epsilon\text{Nd} $	$\epsilon\text{Nd}_{\text{Flux}}$	$\epsilon\text{Nd}_{\text{BW}}$	F_{Nd} pmol cm ⁻² yr ⁻¹	$[\text{Nd}]_{\text{BW}}$ pM	piston velocity cm yr ⁻¹
HH3000 ¹	0.2	-1.8	-2.0	31.0	36	861
HH1200 ¹	0.4	-1.5	-1.9	13.0	36	361
HH200 ¹	1.0	-0.2	-1.2	2.6	19	137
Labrador Sea ^{2,3}	4.8	-13.5	-18.3	0.4	20	22
Blake Ridge ⁴	1.3	-12.2	-13.5	6.2	62	99
N. Pacific GOA ⁵	1.0	-2.1	-3.1	5.8	43	134
Peru, MC84 ⁶	0.5	n/a	n/a	7.7	29	266
800 m site, CA ⁶	0.3	n/a	n/a	19.9	34	585
1600 m site, CA ⁶	1.4	n/a	n/a	2.8	33	85
3400 m site, CA ⁶	0.1	n/a	n/a	36.0	23	1565

1 This Study

2 Vance and Burton 1999

3 Piepgras and Wasserburg 1987

4 Gutjahr et al. 2008

5 Haley et al., 2014

6 Haley and Klinkhammer 2003

Bold & Italic= calculated this study

3.A1 Flux and $\Delta\epsilon\text{Nd}$

Results from equation 3 estimates of flux and $\Delta\epsilon\text{Nd}$ from sites where either the pore water flux and the bottom water Nd concentration or the $\Delta\epsilon\text{Nd}$ is published compared to sites in this study. The calculated component is in bold italics.

3.A2. Sites

Cruise	Site	Water Depth (m)	Latitude	Longitude	Oxygen ($\mu\text{mol/L}$)	Date
OC1307a	HH200	202m	43.917	124.68	71	Jul-13
OC1210a	HH1200	1216m	43.083	124.983	20	Oct-12
	HH3000	3060m	43.867	125.633	82	Oct-12

3.A2 Site descriptions and site locations

Latitude and longitude are in decimal degrees.

Supplemental Table Captions (*tables online only*)

3.A3 Water Column Profiles

Neodymium concentrations and ϵNd profiles for HH200, HH500, HH1200, and HH3000. Mean and standard deviation for NBP-GSR 10 is also provided

3.A4 Pore Fluid and Sediment Neodymium

Neodymium concentrations and ϵNd profiles for HH200, HH1200, and HH3000 pore fluid and bulk sediment.

Chapter 4: The impact of sedimentary coatings on the diagenetic Nd flux

April N. Abbott, Brian A. Haley, James McManus

Abstract

Understanding the connection between ocean circulation and climate through time is an important component of refining climate models. One method employed to reconstruct ocean circulation patterns is the neodymium isotope composition of authigenic coatings recovered from marine sediments. These coatings are interpreted as a record of the neodymium isotope signature of bottom water through time, thus variations in the recovered signature are interpreted as changes in ocean circulation. However, recent pore fluid studies present evidence of significant post depositional neodymium cycling within the upper portions of the marine sediment package that drives a benthic flux of neodymium to the ocean. Internal cycling within the upper sediment package calls for a closer examination of the relationship between the neodymium signature recorded in authigenic coating and the overlying neodymium signature of the seawater. To examine the mechanisms controlling the benthic flux of Nd and the relationship between the composition of the authigenic coating and that of the pore fluid we examined the upper sediment column at three sites on the Oregon margin in the northeast Pacific Ocean. We compare the neodymium concentrations and isotope compositions from total sediment digests, pore fluid, and sediment leachates. We find that the leachable components (average weak leachate: $2 \mu\text{g Nd g}^{-1}$; average strong leachate $5 \mu\text{g Nd g}^{-1}$) account for about half of the Nd in the total sediment (average $15 \mu\text{g Nd g}^{-1}$), therefore representing a significant reservoir of reactive Nd within the sediment package. Despite having 1 to 2 orders of magnitude greater Nd concentration than the bottom water, the pore fluid is still $<0.0006\%$ of the total Nd reservoir in the upper sediment column. We propose a conceptual model to describe the benthic flux in which the amount of reactive

coating in the sediment is a key factor in determining the magnitude of the sedimentary source of Nd. With this model, we argue that sediment diagenesis determines the ϵ_{Nd} of the pore fluid, which in turn determines the ϵ_{Nd} of the bottom water. To achieve mass balance in our model, we find it necessary to invoke the presence of radiogenic (+10) trace mineral. When present, a disproportional influence of this trace mineral on the ϵ_{Nd} of the pore fluids in less evolved sediments can complicate interpretations of the ϵ_{Nd} of the reactive coatings. However, in regions with more evolved sediments and a large benthic flux there will be an apparent agreement between the ϵ_{Nd} of the recovered coatings driving the flux and the ϵ_{Nd} of the bottom water resulting from the flux.

Keywords

Neodymium, diagenesis, benthic flux, oxide coatings

Highlights

- The benthic flux of Nd is a function of sediment diagenesis.
- Sediment diagenesis determines pore fluid ϵ_{Nd} , which determines bottom water ϵ_{Nd} .
- Authigenic phases drive diagenesis since they are a large, reactive, Nd reservoir.
- Trace minerals can influence the pore fluid ϵ_{Nd} resulting from diagenesis.

4.1 Introduction

The neodymium isotope composition (ϵNd) of seawater has been employed as a tracer of past ocean circulation (e.g. Frank 2002; Goldstein and Hemming, 2003). The neodymium isotope value is reported as ϵNd , defined as $[(^{143}\text{Nd}_{\text{sample}}/^{144}\text{Nd}_{\text{sample}})/(^{143}\text{Nd}_{\text{CHUR}}/^{144}\text{Nd}_{\text{CHUR}})-1] \times 10^4$ where CHUR is the Chondritic Uniform Reserve, used as an average earth value ($^{143}\text{Nd}/^{144}\text{Nd}=0.512638$; Jacobsen and Wasserburg, 1980; Wasserburg et al., 1981). The ϵNd of bottom water is thought to be recorded in marine sedimentary authigenic phases, including Fe or Mn (oxy)hydroxides. The changes in the ϵNd of these authigenic phases over time are therefore interpreted as shifts in global ocean circulation (e.g. Colin et al., 2010; Haley et al., 2008; Piotrowski et al., 2004, 2005; Rutberg et al., 2000). Consequently, the interpretation of ϵNd as a paleoproxy is dependent on a quasi-conservative behavior of Nd throughout the global ocean (Tachikawa et al., 2003) and the ability to dependably recover bottom water ϵNd from the sediment record.

The main source of Nd to the ocean has conventionally been assumed to be riverine dissolved load, with a minor contribution from atmospheric deposition (e.g. Jones et al., 1994; Elderfield et al., 1990). However, dynamically coupled ocean-atmosphere models indicate that this budget of Nd does not account for 95% of the Nd in the ocean (Arsouze et al., 2009). These models suggest that the dissolved riverine flux is inconsequential to the overall distribution of ϵNd throughout the global ocean. However, the particulate flux to the ocean is nearly 100 times that of the dissolved Nd flux (Oelkers et al., 2011). Jeandel et al. (2015) propose that dissolution in the water column of less than 3% of this annual particulate load can account for the “missing” Nd in the ocean.

Instead, we have proposed that the role of the particles is post depositional Nd release driven by sediment diagenesis (Abbott et al., 2015). This idea is levered upon other 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., 2007; Haley and Klinkhammer, 2004; Jeandel et al., 2007; Lacan and Jeandel 2001, 2004a, b, c, 2005a, b; Wilson et al., 2013), and that the benthic flux may determine the ϵ_{Nd} distribution of the deep ocean (Abbott et al., 2015a,b).

The influence of the benthic flux on the bottom water ϵ_{Nd} is dependent on the magnitude and ϵ_{Nd} value of the flux (Abbott et al., 2015b). However, the way in which the sediments determine pore fluid ϵ_{Nd} is largely unconstrained. Understanding the relationship between the sediments and the pore fluid may allow us to predict the ϵ_{Nd} flux based on existing data sets. Here, we begin to constrain the factors and processes that control the magnitude and ϵ_{Nd} signature of the benthic flux.

4.2 Methods

Sediment cores were collected from three sites in the eastern North Pacific (**Figure 4.1**) in October 2012 (HH1200 and HH3000) and July 2013 (HH200) (Abbott et al., 2015). 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 (Abbott et al., 2015).

Detailed core collection techniques are published elsewhere (Abbott et al., 2015a). Briefly, cores were collected using a multi-corer (Barnett et al., 1994) capable of collecting up to 8 cores per deployment. Cores were sectioned in an anoxic (N₂) glove bag into intervals operationally defined as the amount of sediment required to fill an 85 mL centrifuge vial. On average, these intervals represent 1.2 cm of depth in the core. After sectioning, the samples were centrifuged at between 10,000 and 12,000 rpm for 15 minutes. Pore fluid was then filtered during syphoning using acid-clean syringes and PALL® acrodisc syringe filters with a 0.45µm Supor® membrane. Pore fluids from each subsequent interval were combined into large volume samples (250-750 ml) and acidified to pH ≤2.0 using ~11 M HCl while at sea. The sediment in the centrifuge tube was frozen after pore fluid removal, and remained frozen until they were freeze dried. A single core was used for total sediment digests, CNS analysis, grain size, and chemical leaching as described below.

Centrifuged sediments were digested in a mixture of HNO₃, HCl and HF using a CEM Corp MARS-5 microwave following the procedures of Muratli et al. (2012). We measured total carbon on a PerkinElmer Series 11 CNHSO Analyzer and inorganic carbon on a UCI Inc. Coulometrics CMS130 Coulometer. Organic carbon is calculated as the difference between the total carbon and organic carbon pools. Sediment grain size distributions for the freeze-dried total sediment and leached sediments from HH200, HH1200, and HH3000 were measured on a Beckman Coulter LS 13 320 multi-wavelength Laser Diffraction Particle size Analyzer at Oregon State University. Beckman Coulter® LS Control G15 and Latron 300 LS were analyzed at the beginning of each run and validated against Beckman Coulter® precision guidelines. An in-house

bimodal control (250 and 550 μm) was also analyzed during each run. Bulk sediment samples were loaded with dispersant and sonicated before analysis. Leached sediment samples were also loaded with dispersant but were not sonicated prior to analysis. Measurements are reported in 116 size bins between 0.4 and 1822 μm for each sample (**Appendix Table 4.A1**).

Two sequential leachates were collected from the centrifuged sediments. Subsamples of the freeze-dried sediment from the centrifuge tubes was weighed (2-3 g dry weight) and transferred to acid-rinsed Falcon [®] Blue Max 50 mL modified polystyrene conical tubes. The leaching procedure began with three MQ rinses shaken by hand for one minute, centrifuged for 15 minutes, and then decanted. Next, a 20 mL ~0.25 M acetic acid leach solution (250 mL MQ, 41 g sodium acetate, and 210 g glacial acetic acid; pH 3.5-4) was shaken for 2 hours, centrifuged for 20 min, and 60% of the leachate was collected and stored in a clean Teflon vial (acid leachable). Following the weak leach and three more MQ rinses (same as above), a ~50 mM hydroxylamine leach solution (250 mL MQ, 1.73 g 50 μM hydroxylamine hydrochloride, 75.062 g >99.9% pure glacial acetic acid and 10 g 0.25 N sodium hydroxide; pH 3.5-4) was agitated for 2 hours, centrifuged for 20 min, and 60% of the leachate was collected and stored in clean Teflon (reducible). All leachate samples were dried completely, re-dissolved in concentrated distilled HNO_3 , and dried again before re-dissolution in 6 M HCl before analysis.

Leachate and total digest solutions were analyzed on the Thermo VG ExCell quadrupole 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 digests are reported as ng REE per g dry sediment.

Total digest, leachate, and seawater samples were run through a series of columns to isolate the Sr and Nd fractions for isotopic 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 6M HNO₃, 6 mL MQ, and then conditioned with 6 mL 6M HCl. Samples were centrifuged for 5 minutes at 13400 rpm and then loaded in 1 mL 6M HCl. Collection of the sample began when the sample was loaded. After the 1 mL elution was complete, any particles remaining in the centrifuge tube were transferred into the column. To complete sample collection, an additional 5 mL of 6M HCl was eluted. The collected solution was dried completely, redissolved in 1M 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 HCl, and conditioned with 6 mL of 1M HCl before the sample was loaded. Samples were eluted with 3 mL of 1M HCl, 6 mL of MQ, and 4 mL of 2M HNO₃ and then the Sr fraction was collected in 7 mL of 2M HNO₃. After the collection of the Sr fraction, the REE fraction was collected in 10 mL of 6M HNO₃.

The Sr fraction was further purified using 50 µL Sr Spec Resin (Eichrom® part SR-B505, 50-100 µm). Resin was cleaned with 300 µL of H₂SO₄, MQ, and 3M HNO₃ before the 50 µL sample was loaded in 3M HNO₃, and eluted with 600 µL of 3M HNO₃. Sr was then collected in 500 µL 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 internal standard, EMD, which yielded a mean $^{87}\text{Sr}/^{86}\text{Sr} = 0.708185$ with a 2σ standard deviation of ± 0.000051 . National Bureau of Standards reference material 987 (NBS-987) is measured for these analysis at $^{87}\text{Sr}/^{86}\text{Sr} = 0.710245$ with a 2σ standard deviation of ± 0.000052 normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. NBS-987 and EMD were analyzed, at minimum, after every 6 samples and analyzed in replicate at the beginning and end of every batch run.

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 by the Nu Plasma multi-collector ICP-MS for $^{144}\text{Nd}/^{143}\text{Nd}$. Sm and Ba were monitored during analysis to detect oxide interference. Precision was determined by repeated analysis of SpecPure yielding a mean $^{144}\text{Nd}/^{143}\text{Nd} = 0.511205$ with a 2σ standard deviation of ± 0.000014 . JNdi-1 was measured for these analysis at $^{144}\text{Nd}/^{143}\text{Nd} = 0.512115$ 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.

4.3 Results

4.3.1 Pore Fluid

Pore fluids are MREE enriched relative to PAAS at all sites and HREE enriched at HH3000 (**Figure 4.2**, Abbott et al., 2015a). The maximum concentration of Nd in the

pore fluid increases in magnitude and occurs deeper within the sediment column from HH200 to HH1200 to HH3000 (**Figure 4.3**, Abbott et al 2015a, b). This trend does not correlate directly to Fe, Mn, Li, or P in the pore fluids (**Figure 4.3; Appendix Table 4.A2**). The highest concentration of dissolved Fe ($\sim 80 \mu\text{M}$) occurs at HH200 and the lowest ($<10 \mu\text{M}$) occurs at HH3000 (**Figure 4.3**) with dissolved Fe reaching an intermediate concentration of $35 \mu\text{M}$ at HH1200. Dissolved Mn is below detection at HH200 and HH1200, but reaches concentrations of $50 \mu\text{M}$ at HH3000. The pore fluid Li concentration profile at HH3000 has a steeper decrease with depth than observed in the pore fluid Li concentration profile at HH1200 (**Figure 4.3**). Li data is unavailable for pore fluids from HH200. Dissolved P is higher at HH1200 than at HH3000. Specifically, at HH1200 P increases downcore from $\sim 4 \mu\text{M}$ in near surface pore fluids to $\sim 16 \mu\text{M}$ at 8 cm while P generally remains between 6 and $8 \mu\text{M}$ throughout the measured pore fluids at HH3000 with the lowest ($\sim 6 \mu\text{M}$) occurring in the upper most pore fluids.

With the exception of the upper two data point from HH1200, the ϵNd of the pore fluids is relatively constant at each site (**Figure 4.3**) and becomes less radiogenic from HH200 (average ϵNd -0.2) to HH1200 (average ϵNd -1.5) to HH3000 (average ϵNd -1.8; **Figure 4.3**; Abbott et al., 2015b). Deviations from the site average pore fluid ϵNd are largely restricted to the HH1200. We do not interpret these deviations in our model and instead focus on the average pore fluid ϵNd 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.

4.3.2 Solid Phase

Total sediment digest chemical characteristics among our sites are similar. There is a narrow range in REE patterns for the total sediment digests among sites that is MREE

and HREE enriched relative to PAAS (**Figure 4.2**, Abbott et al., 2015a) At all sites, bulk ϵ_{Nd} ranges between 0.0 and -2.5 (**Figure 4.4**). The concentration of Nd in the digest shows little variation within each core, but Nd concentrations becomes more enriched from 200 m (average $14 \mu\text{g g}^{-1}$) to 1200 m (average $16 \mu\text{g g}^{-1}$) to 3000 m (average $17 \mu\text{g g}^{-1}$). Particulate organic carbon content averages between 1.7% and 2.0% at all sites, with a slight downcore decrease present at 1200 m (**Figure 4.4**). Fe concentration is lowest at 200 m (<5%) and greatest at 1200 m (5-8%; (**Appendix Table 4.A3**). Mn concentrations are constant at ~450 ppm down-core at both 200 m and 1200 m (**Figure 4.4**). However, Mn concentrations reach almost 3600 ppm in the surface sediments at 3000 m before decreasing to ~680 ppm at 7 cm (**Appendix Table 4.A3**). Ca decreases from HH200 ($1.6 \pm 0.03\%$) to HH1200 ($1.4 \pm 0.15\%$) to HH3000 ($1.0 \pm 0.08\%$). The $^{87}\text{Sr}/^{86}\text{Sr}$ of the sediment digests becomes increasingly more radiogenic with increasing water depth, specifically the average $^{87}\text{Sr}/^{86}\text{Sr}$ at HH200 (0.707565) < HH1200 (0.708156) < HH3000 (0.709773) (**Figure 4.4**). This 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 sediment digests at HH3000 have Sr isotopic values more radiogenic than seawater (**Figure 4.4, Figure 4.5**).

The mineralogy of the marine sediment was similar among all sites (**Appendix Figure 4.A1**). All samples consisted of quartz, albite, a white mica (illite or muscovite) and a chlorite mineral (clinochlore). The only difference observed between pre-leach and post-leach sediments was the presence of crystalline halite in the pre-leach sediments, likely formed during sample drying.

Grain size distributions were consistent downcore at each site for both pre- and post-leach measurements (**Appendix Table 4.A1**). Pre-leach and post-leach distributions are largely bimodal. The primary peak is at $\sim 85 \mu\text{m}$ at HH200 and $\sim 180 \mu\text{m}$ 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 4.6**). The post-leach distributions are bimodal, with the smallest overall mean at HH3000 ($\sim 20 \mu\text{m}$) and larger at both HH200 ($\sim 110 \mu\text{m}$) and HH1200 ($\sim 140 \mu\text{m}$; **Figure 4.6**). The primary grain size peak is the smallest at HH3000 ($\sim 5 \mu\text{m}$) and increases at HH1200 ($\sim 15 \mu\text{m}$) and HH3000 ($\sim 20 \mu\text{m}$).

4.3.3 Leachates

The acid leachable solution becomes less radiogenic from HH200 ($\epsilon\text{Nd} -1.1$) and HH1200 ($\epsilon\text{Nd} -1.2$) to HH3000 ($\epsilon\text{Nd} -1.9$, **Figure 4.6**). The Fe in this leachate is on average higher at HH200 ($87\text{-}141 \mu\text{g mL}^{-1}$) than at HH1200 ($66\text{-}135 \mu\text{g mL}^{-1}$) and is lowest at HH3000 ($53\text{-}66 \mu\text{g mL}^{-1}$, **Appendix Table 4.A4**; **Figure 4.7**).

The reducible leachate has an average ϵNd between -0.6 and -0.9 at all sites with a maximum ϵNd of 0.0 and a minimum ϵNd of -1.7 (**Figure 4.6**; **Appendix Table 5**). The ϵNd of this leachate is consistent 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 ($\epsilon\text{Nd} -1.2$ at 1.2 cm ; $\epsilon\text{Nd} -0.1$ at 9.8 cm) and the reducible leachate at HH3000 m is less radiogenic with depth ($\epsilon\text{Nd} -0.3$ at 1.2 cm ; -1.7 at 9.8 cm ; **Figure 4.7**). Unlike in the acid leachable solution, the minimum ($136 \mu\text{g mL}^{-1}$) and maximum

values ($429 \mu\text{g mL}^{-1}$) of Fe in the reducible leachate both occur at HH3000 (**Appendix Table 4.A4; Figure 4.7**).

At all locations, the ϵNd of both leachates is more radiogenic than the total sediment (**Figure 4.7**). However, the acid leachable solution is most similar to the total sediment at HH3000. Additionally, the relationship of both leachates to the pore fluid varies among sites (**Figure 4.7**). The concentration of reactive Nd (sum of leachates) was between 55 and 70% of the Nd in the total sediment digest (average concentration per site $7.5\text{--}13.0 \mu\text{g Nd g}^{-1} \text{ sed}$; **Appendix Table 4.A6, Appendix Figure 4.A3**). Of the leachable Nd, 45% was recovered in the acid leachable solution and 55% in the reducible leachate. The concentration of Nd in both leachates increases with depth at all sites. The largest amount of reactive Nd was at HH3000 corresponding to the highest leachate Mn. Mn at HH3000 is one to three orders of magnitude higher than at HH200 or HH1200 (15 to $1500 \mu\text{g mL}^{-1}$ compared to 1.5 to $5.5 \mu\text{g mL}^{-1}$) for both leachates. The REE pattern of the acid leachable solution is indistinguishable from the REE pattern of the reducible leachate. The leachate REE pattern is MREE enriched and HREE depleted (**Figure 4.2**).

4.4 Discussion

4.4.1 Reservoirs of Neodymium in the Upper Sediment Column

4.4.1.1 Major reservoirs

We have shown previously that there is a flux of Nd from sediment pore fluids into bottom water (Abbott et al., 2015a). Furthermore, it was shown that this flux determines bottom water ϵNd (Abbott et al., 2015 b). The concentration of Nd in the pore fluid reservoir is simply too small to allow pore fluids to maintain a unique ϵNd signature.

Therefore, because the Nd concentration and the Nd isotopic signature of the pore fluids differ from bottom water, diagenetic processes must be controlling pore fluid ϵNd . The pore fluid Nd concentration (160-790 pM) is 1 to 2 orders of magnitude greater than bottom water (18-30 pM), meaning that the pore fluid can provide a large flux of Nd to the bottom water that is capable of altering bottom water ϵNd (Abbott et al., 2015a,b). However, compared to the total solid phase, the Nd in the pore fluid accounts for less than 0.0007% by volume (**Figure 4.6; Appendix Table 4.A7**).

Here we present a model that explains 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 4.8**). There are three main 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 it is similar in concentrations among all sites and does not covary with any of the Nd pools (**Figure 4.4**). Therefore, our model separates the total sediment into a lithogenic component and an authigenic component (**Figure 4.8**). While the lithogenic component is often considered refractory, substantial mineral dissolution has been observed to influence the surrounding fluid phase (Henry et al., 1994; Jeandel and Oelkers, 2015; Rosseau et al., 2015; Tachikawa et al., 1999). Because our measured authigenic component is operationally defined by the leaching procedure, we divide this reactive component into two phases: the reducible leachate, which is recovered in the hydroxylamine leach targeting metal oxides (e.g., Gutjahr et al., 2007) and an acid leachable solution which is recovered in the acetic acid leach. The idea that the different leaching reagents target different relative amounts of at least two reactive phases is

further supported by the Fe, Mn, and ϵNd characteristics measured in the leachates (**Figure 4.7**). Specifically, the Fe/Mn ratios are higher in the strong leachate and the ϵNd signatures are generally more radiogenic in the strong leachate.

The amount of authigenic phases in the sediments can be inferred from the grain size distributions (**Figure 4.6**). Specifically, the unexpectedly large pre-leach grain size distributions, and remaining large secondary peaks ($\sim 85\ \mu\text{m}$ at HH200, $\sim 490\ \mu\text{m}$ at HH1200 and $\sim 100\ \mu\text{m}$ at HH3000) in the post-leach distributions, are considered an artifact of coagulation of grains due to surface coatings. We therefore consider the difference between pre- and post-leach grain size distributions as a result of the amount of coating present. The greatest coating is evident at HH3000 where the shift between the pre- and post-leach grain size distributions is the greatest (**Figure 4.6**). The change in grain size distribution is the best indicator of the amount of coating present in the sediments from each site available due to the lack of a method for an accurate weight of the leachate. However, the largest change in grain size distribution at HH3000 does correspond to the highest percent of the total sediment Nd leachable at HH3000 (**Figure 4.6**). The steeper decrease with depth in pore fluid Li at HH3000 compared to HH1200 (**Figure 4.3**) is also consistent with authigenic mineral formation with the concentration of Li^+ by products of alteration (e.g., clay minerals; Stoffyn-Egli and Mackenzie, 1984 *and references therein*).

The ϵNd and Nd concentration of the operationally defined authigenic phases likely represents a combination of “true” authigenic phases and lithogenic contamination, together composing the “reactive” component. Because ϵNd serves as a tracer of the sedimentary source and because the Nd in the pore fluid only accounts for $<0.001\%$ of

the Nd by volume (**Figure 4.6**), we expect pore fluid ϵNd (**Figure 4.3**) to resemble the true authigenic component (**Figure 4.4**). However, the pore fluid does not resemble the ϵNd of the recovered leachates (**Figure 4.6**). Since pore fluid simply does not have enough Nd to maintain a unique signature, the leachates must not be representative of the true authigenic phases.

Sr is expected to behave differently than Nd, and indeed there is a more even distribution of Sr among phases but the $^{87}\text{Sr}/^{86}\text{Sr}$ are consistent with our diagenetic model for Nd. The pore fluid is still small compared to the solid phases, but does account for ~1% of the Sr in the upper sediment column by volume. On average, the Sr in the acid leachable solution is 45% of the Sr in the upper sediment column by volume. The remaining 54% of Sr is split evenly between the reducible leachate and the refractory phase. The $^{87}\text{Sr}/^{86}\text{Sr}$ of both leachates is between the $^{87}\text{Sr}/^{86}\text{Sr}$ of the pore fluid and the $^{87}\text{Sr}/^{86}\text{Sr}$ of the total sediment at all sites. As with ϵNd , the greatest deviation in leachate $^{87}\text{Sr}/^{86}\text{Sr}$ from pore fluid $^{87}\text{Sr}/^{86}\text{Sr}$ occurs at HH200 supporting our assertion that the leachates contain a contaminate phase (**Figure 4.5**).

We have measured the ϵNd and Nd concentration for the total sediment digest (**Figure 4.6**), the acid leachable and reducible leachates (**Figure 4.7**), the bottom water, and the pore fluid (**Figure 4.3**). We observe that the pore fluid is more radiogenic than the total digest, the reducible leachate, and the acid leachable solution at HH200 (**Figure 4.6**). Therefore, our model requires a more radiogenic source of ϵNd to be able to explain the pore fluid ϵNd . The initial bottom water chemistry of pore fluids cannot provide this radiogenic source because the amount of Nd in the bottom water is insignificant compared to the diagenetic influences of the total solid and the bottom water is not more

radiogenic than the pore fluids. Of the acid leachable, the reducible, and the lithogenic component, the lithogenic component is the only ϵNd not directly measured (**Table 4.1**). Because the concentration and isotopic composition must maintain a mass balance, we can calculate the ϵNd and Nd concentration for the lithogenic component to determine whether the total lithogenic component can provide the needed radiogenic source. We calculate the total lithogenic component as

$$\epsilon\text{Nd}_{Lith} = \frac{((\epsilon\text{Nd}_{Total} \times [\text{Nd}]_{Total}) - (\epsilon\text{Nd}_{React} \times [\text{Nd}]_{React}))}{[\text{Nd}]_{Lith}} \quad (1)$$

where the *Total* is the measured total sediment digest, *React* 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 ϵNd_{Lith} of -2 at HH200, -2.5 at HH1200, and -3.1 at HH3000 (**Table 4.1**), meaning that as a whole, the lithogenic component does not provide the needed radiogenic source. However, we know that the lithogenic component consists of multiple major mineral phases (quartz, albite, a white mica, and clinochlore; **Appendix Figure 4.A1**) raising the possibility of a preferential contribution from a single phase within the total lithogenic component. This suggestion that the contribution from each mineral in the total lithogenic component is not homogeneous is consistent with laboratory leaching experiments in which the ϵNd obtained was dependent on the fraction of the particles reacting with the leach solution (Wilson et al., 2013). But, because we observe no loss in these major mineral phases between pre-leach and post-leach samples, this preferential contribution either results in loss of one of the major mineral phases that is too small to detect or results from a minor mineral phase that is not detectable by XRD

analysis. Because the major mineral components of the lithogenic fraction remain constant among sites while ϵNd of the pore fluid does not remain constant, the radiogenic source is likely a reactive trace mineral.

4.4.1.2 Minor reservoirs

The radiogenic trace mineral provides the “unseen” radiogenic source required to explain the pore fluid ϵNd signature in the absence of any other measurable highly radiogenic lithogenic component. We assume that this trace mineral has an ϵNd of +10; a value within the range of ϵNd expected from the Depleted Western Terranes in the region including the Intermontane Belt, Coast Mountain Belt, Cascade Arc, and Vancouver Island (ϵNd 0 to +11; Carpentier et al., 2014). From a model perspective, the trace mineral reacts readily, resulting in a significant contribution to the pore fluid in less evolved shallow sediments (i.e. HH200) and a less significant contribution as the amount of trace mineral remaining in the total solid decreases with sediment evolution (**Figure 4.8**). This expected decrease in the reactive mineral is supported by more radiogenic total solid at HH200 ($\epsilon\text{Nd}_{\text{Total}}=-1.4$) compared to HH3000 ($\epsilon\text{Nd}_{\text{Total}}=-2.2$, **Figure 4.4, Table 4.1**) and consistent with the measured leachate $^{87}\text{Sr}/^{86}\text{Sr}$ deviating from pore fluid $^{87}\text{Sr}/^{86}\text{Sr}$ at HH200 more than at HH3000. Furthermore, the increase in $^{87}\text{Sr}/^{86}\text{Sr}$ from HH200 to HH3000 corresponding to a decrease in ϵNd is consistent with larger contributions from a trace end-member with depleted characteristics at HH200, shifting the Sr-Nd of the total sediment digest at HH200 (0.707565) towards the depleted western terranes (0.702000-0.706000; e.g. DePaolo and Wasserbug, 1976; Carpentier et al., 2014). REE patterns also support a greater contribution from the reactive trace mineral in the less evolved sediments at HH200. The REE patterns of pore fluids are LREE enriched

relative to the total sediment digest at HH200, suggesting a LREE enriched trace mineral (**Figure 4.2**). The similarity of the REE patterns of pore fluids and total sediment digest at HH3000 support the absence of this trace reactive mineral.

A change in total solid ϵNd of this magnitude requires $\sim 10\%$ loss of the total Nd between HH200 and HH3000 m from the trace phase, consistent with a lower contribution from the trace phases at HH1200 and HH3000 than at HH200 (equation 2, **Figure 4.8**). We determine $[\text{Nd}]_{\text{Trace}}$ as

$$\epsilon\text{Nd}_{3000} \times [\text{Nd}]_{3000} = (\epsilon\text{Nd}_{200} \times [\text{Nd}]_{200}) - (\epsilon\text{Nd}_{\text{Trace}} \times [\text{Nd}]_{\text{trace}}) \quad (2)$$

where the trace component is the difference between the measured values at HH200 and HH3000. Evidence for this radiogenic trace mineral exists in our bottom water from HH200. At HH200, we were able to measure the ϵNd signatures of a filtered bottom water sample and an unfiltered bottom water sample. The unfiltered bottom water sample represents a combination of the filtered bottom water and a leach of the particles in the water due to sample acidification. Specifically, at HH200 we observe that the ϵNd of the unfiltered bottom water ($\epsilon\text{Nd}_{\text{UBW}} = +0.7$) is more radiogenic than the ϵNd of the filtered bottom water ($\epsilon\text{Nd}_{\text{BW}} = -1.8$; **Table 4.1**). As the shallowest site, HH200 is the most likely to be influenced by the most reactive minerals because the initial release of Nd from suspended particulate matter is rapid (3 ± 1 weeks, Rousseau et al., 2015). The influence of the presence of particles in unfiltered bottom water provides a simple system to isolate the trace reservoir for our model. We assume that the acidification of the unfiltered bottom water only adds Nd from the reactive trace mineral. Admittedly, this is

an assumption we cannot verify but nevertheless we can calculate the amount of Nd from the trace mineral needed to produce the change in ϵNd between the unfiltered and filtered bottom water as:

$$\epsilon\text{Nd}_{UBW} \times [\text{Nd}]_{UBW} = \epsilon\text{Nd}_{\text{Trace}} \times [\text{Nd}]_{\text{Trace}} + \epsilon\text{Nd}_{BW} \times [\text{Nd}]_{BW} \quad (3)$$

resulting in a required 20% increase from the trace mineral ($\epsilon\text{Nd}_{\text{Trace}} = +10$) in the $[\text{Nd}]_{BW}$ to produce the observed shift in bottom water ϵNd , consistent with the observed ~20% increase in the concentration of Nd in the unfiltered sample relative to the filtered sample.

4.4.2 Fluxes between reservoirs

Now that we have constrained ϵNd and Nd concentration for each reservoir we can examine the interactions among these reservoirs that include the pore fluid, the acid, the reducible, the lithogenic component, and the reactive trace mineral (**Table 4.1**). Because the Nd in the pore fluid is <0.001% of the total Nd in the system, even a small exchange between the pore fluids and the authigenic or lithogenic reservoirs will dominate the pore fluid signal. In our model, the lithogenic component is allowed to release Nd to the pore fluids through diagenesis but it cannot acquire Nd from the pore fluids. In contrast, the authigenic phases are exchanging with the surrounding pore fluid (**Figure 4.8**). Because the authigenic phases are a large reservoir of Nd (~50% of the total solid) and because these authigenic phases readily exchange with the pore fluid, we propose that this exchange determines the concentration of Nd in the pore fluids. In turn, the exchange between the authigenic phases and the pore fluid determines the concentration gradient in the pore fluids and the resulting magnitude of the benthic Nd

flux. The amount of exchange is influenced by the amount of authigenic phases in the total sediment. For example, we observe the greatest pore fluid concentrations of Nd at HH3000 concurrent with the largest percent of authigenic phases as indicated by the largest shift in grain size distribution from pre- to post-leach of any of our sites (**Figure 4.6**). The total solid at HH3000 also has the largest fraction of leachable Nd (~50% of total sediment Nd; **Figure 4.6**). In contrast, at HH200 we observe the smallest pore fluid Nd concentrations (**Figure 4.3**) and a small shift in grain size distribution from pre- to post-leach sediment (**Figure 4.6**).

The dependence of the exchange on the amount of authigenic phases likely results from the exchange being a surface process. Specifically, this exchange depends on the surface area of the authigenic coatings relative to the volume of the total solid, consistent with findings on other processes such as dissolution (Schott et al., 2009, Schott et al., 2012). Therefore, the greater the size of the authigenic reservoir, the greater the capacity of the upper sediment column to sustain a benthic flux. The difference between the release and capture of Nd by the authigenic phases is a small but constant percentage of the reservoir meaning that this difference becomes more significant as the relative size of the authigenic reservoir increases. As a result, more Nd is left behind in the pore fluid reservoir resulting in a greater concentration maximum and greater flux when a larger authigenic reservoir is present.

4.4.2.1 Continuum of diagenetic evolution

There are clear differences in the size and flux from each reservoir among HH200, HH1200, and HH3000 and we consider these to represent a continuum in the diagenetic evolution of the sediments, with HH200 being the least evolved system (**Figure 4.8a**) and

HH3000 representing a more evolved system (**Figure 4.8b**). Our model describes this evolution of sediment diagenesis, with the amount of authigenic phases increasing and the amount of trace minerals decreasing as sediments become more evolved from HH200 to HH1200 to HH3000. While the trace mineral is too small to identify in total solid analyses, a contribution as small as 1% from an accessory mineral with $\epsilon\text{Nd} +10$ can create the offset from total sediment in pore fluid ϵNd observed at HH200 (**Figure 4.6**). A contribution from the reducible phases may buffer the change in pore fluid ϵNd because the ϵNd of the reducible leachate changes minimally among sites (**Figure 4.7**). For example, the ϵNd of the pore fluid at HH1200 resembles the ϵNd of the total solid at HH200, and the ϵNd of the pore fluid at HH3000 resembles ϵNd of the total solid at HH1200 (**Figure 4.6**).

4.4.3 Applicability to ϵNd distribution of the global ocean

Our diagenetic model provides a mechanism to explain the radiogenic ϵNd signatures in the deep Pacific Oceans that ocean general circulation models (OGCM) cannot reproduce when ϵNd is treated as a conservative tracer (Jones et al., 2008). These models generally can reasonably predict the Atlantic Ocean, but struggle with the Pacific (e.g. Jones et al., 2008; Arsouze et al., 2009). For instance, an OGCM requires a deep source of radiogenic Nd in the Pacific to predict ϵNd values similar to those observed (Jones et al., 2008; Arsouze et al., 2009). In our model, the ϵNd of the deep Pacific is determined by the ϵNd of the benthic flux. As seen at all of our sites, the ϵNd 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 ϵNd of the bottom water becomes more radiogenic. Once the Pacific Ocean is ‘corrected’ in this

model with the adjustment of the ϵ_{Nd} of the return flow from the Pacific Ocean to the Southern Ocean to observed values, the majority of the predicted ϵ_{Nd} values for the Southern Ocean were within 1 ϵ_{Nd} unit of observed values (Jones et al., 2008). No corrections or additional sources were required to predict North Atlantic Deep Water ϵ_{Nd} values that are consistent with observations (Jones et al., 2008) suggesting a smaller role for reactive trace minerals in the North Atlantic.

4.5 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 determine the ϵ_{Nd} distribution of bottom water. We find no simple relationship between diagenetic Nd enrichment and mineralogy or organic carbon degradation. The pore fluid Nd concentration maximum occurs above the appearance of dissolved Fe, suggesting that the diagenetic release of Nd is not simply driven by redox and that future work examining the pH sensitivity of this release is necessary. 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 solid phase. Within the total solid, the authigenic phases are a large and reactive reservoir of Nd. 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 evolved sediments at HH3000 therefore support the greatest pore

fluid Nd concentrations. The less evolved sediments at HH200 support smaller pore fluid Nd concentrations and have pore fluid ϵNd more susceptible to the presence of trace minerals. This model provides a foundation for identifying sediment characteristics that are likely to result in a large magnitude benthic flux or result in a benthic flux with an ϵNd influenced by trace minerals. The model also suggests that the only time the ϵNd of the recovered coatings will resemble the ϵNd of the bottom water will be when the benthic flux is large enough to exert control on the bottom water ϵNd signature.

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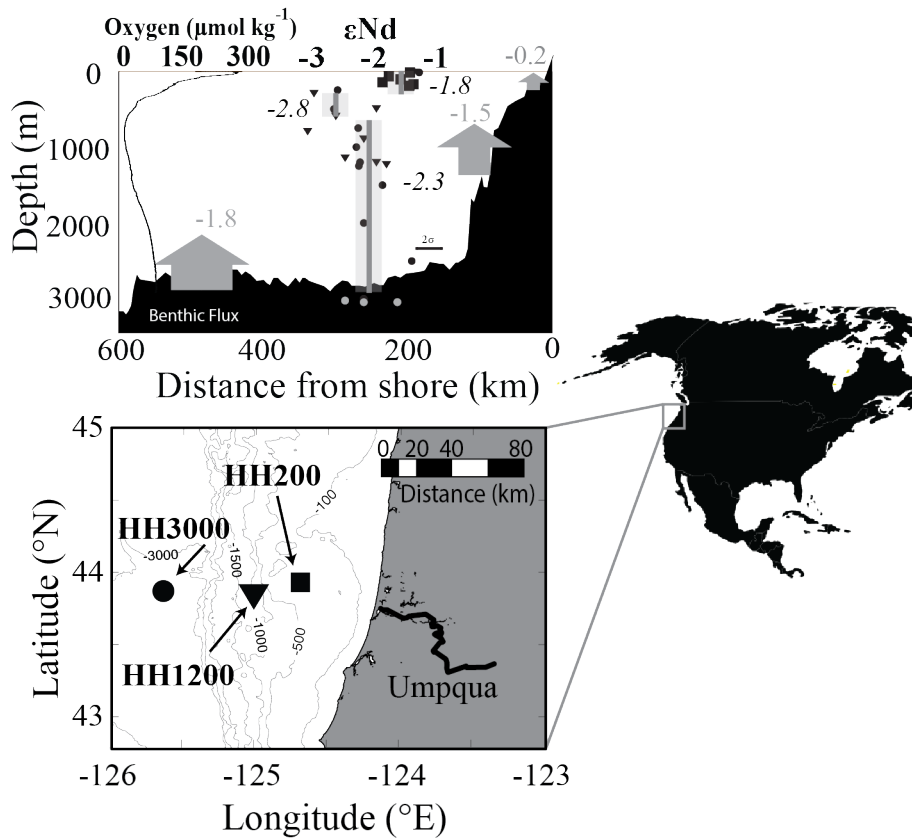
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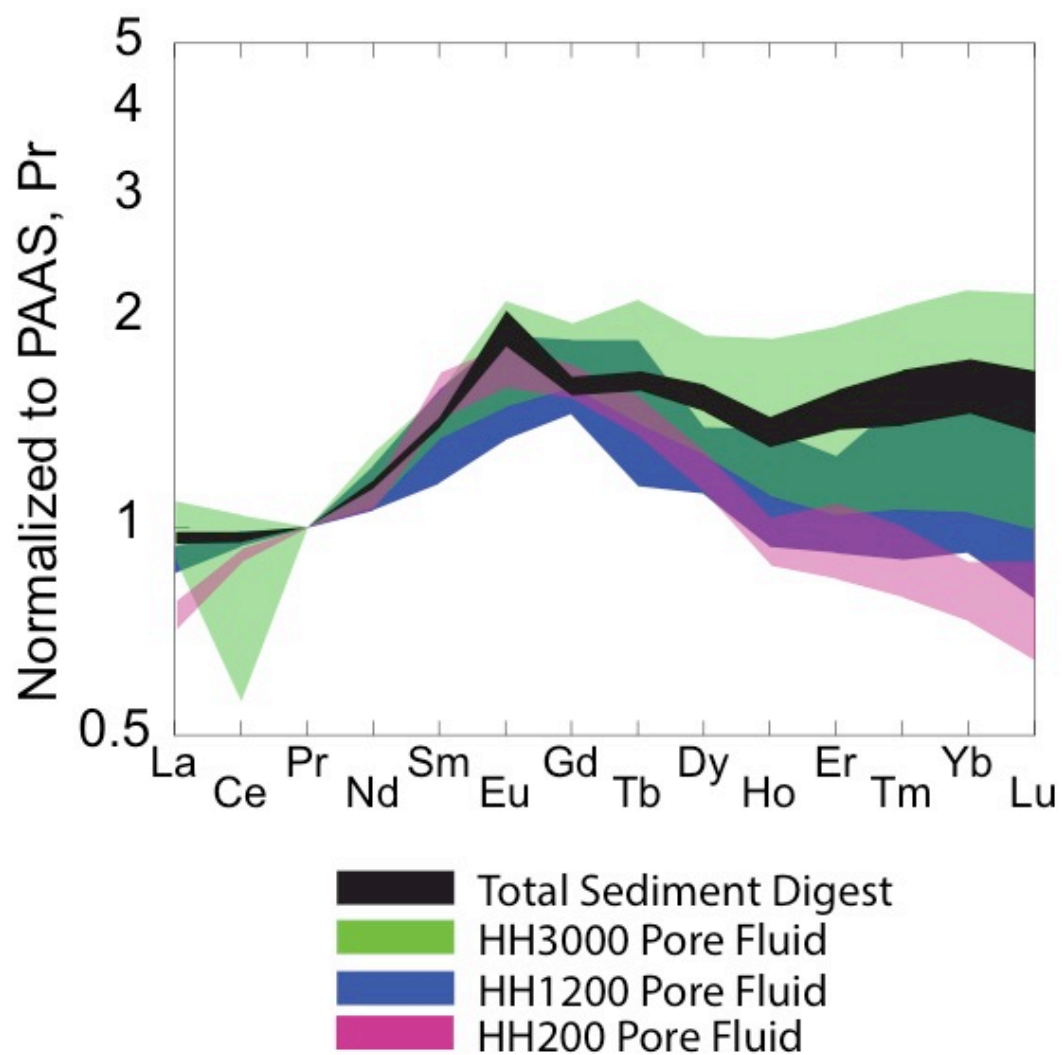
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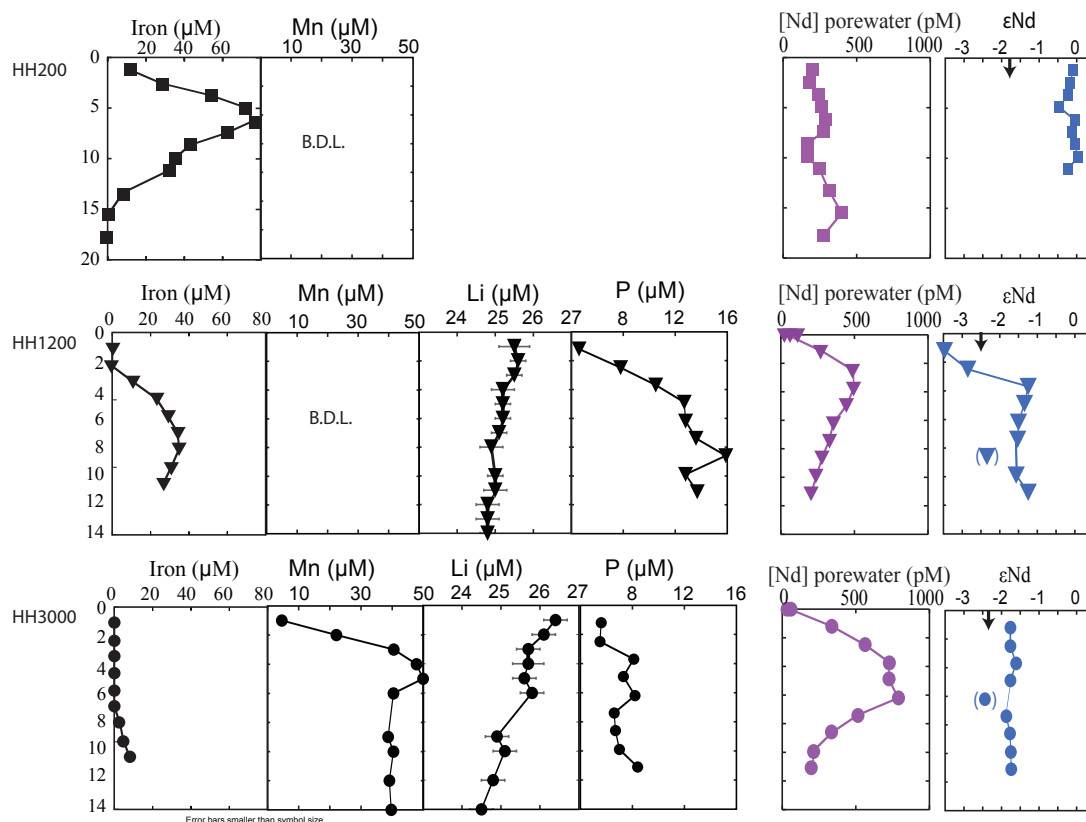
4.1 Study Sites.

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 ϵNd (right). The dissolved oxygen profile is only shown at 3000 m, as the profiles were indistinguishable among sites at this scale. ϵNd is shown for HH200 (squares), HH1200 (diamonds), and HH3000 (circles).



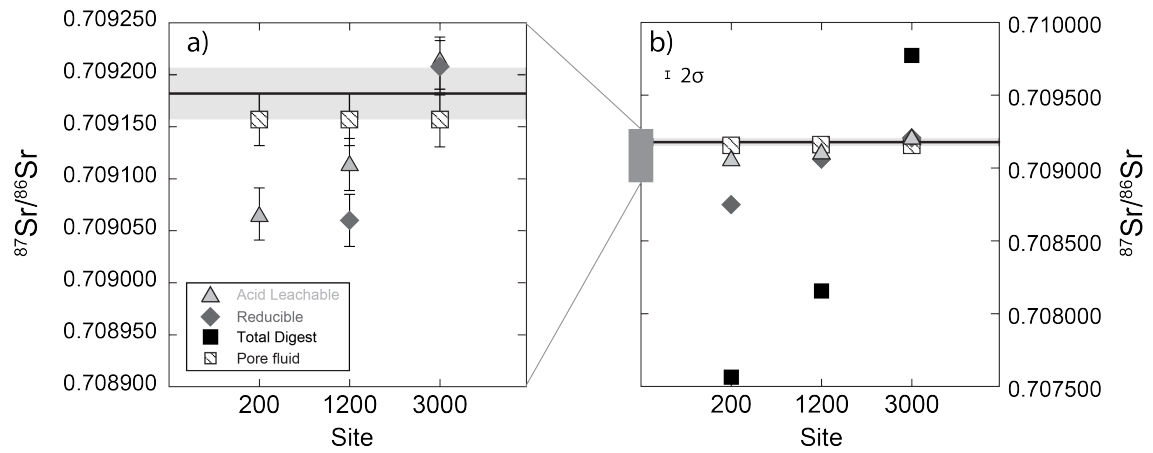
4.2 Rare Earth Element Patterns

REEs normalized to PAAS and Pr. Total sediment digest (black) represents the range in pattern from all sites. Pore fluid patterns are shown individually for HH200 (pink), HH1200 (blue), and HH3000 (green).



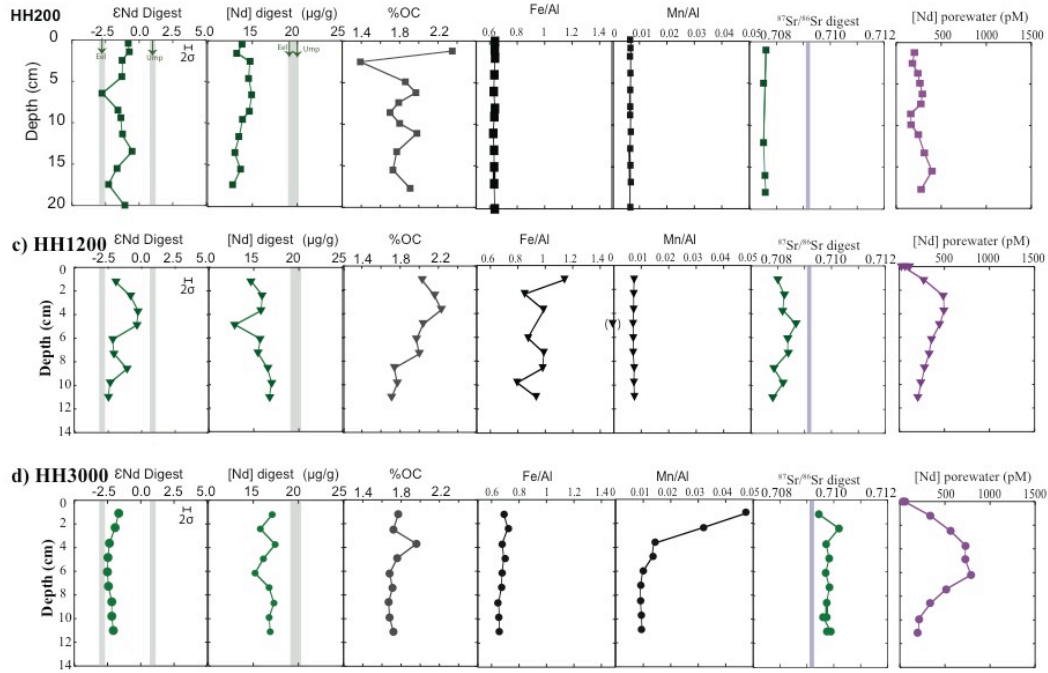
4.3 Fluid Phase Characteristics

Pore fluid profiles from **A)** HH200, **B)** HH1200, and **C)** HH3000 for dissolved iron, manganese, lithium, phosphorous, neodymium and ϵNd . 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 ϵNd profiles indicate bottom water ϵNd signatures.



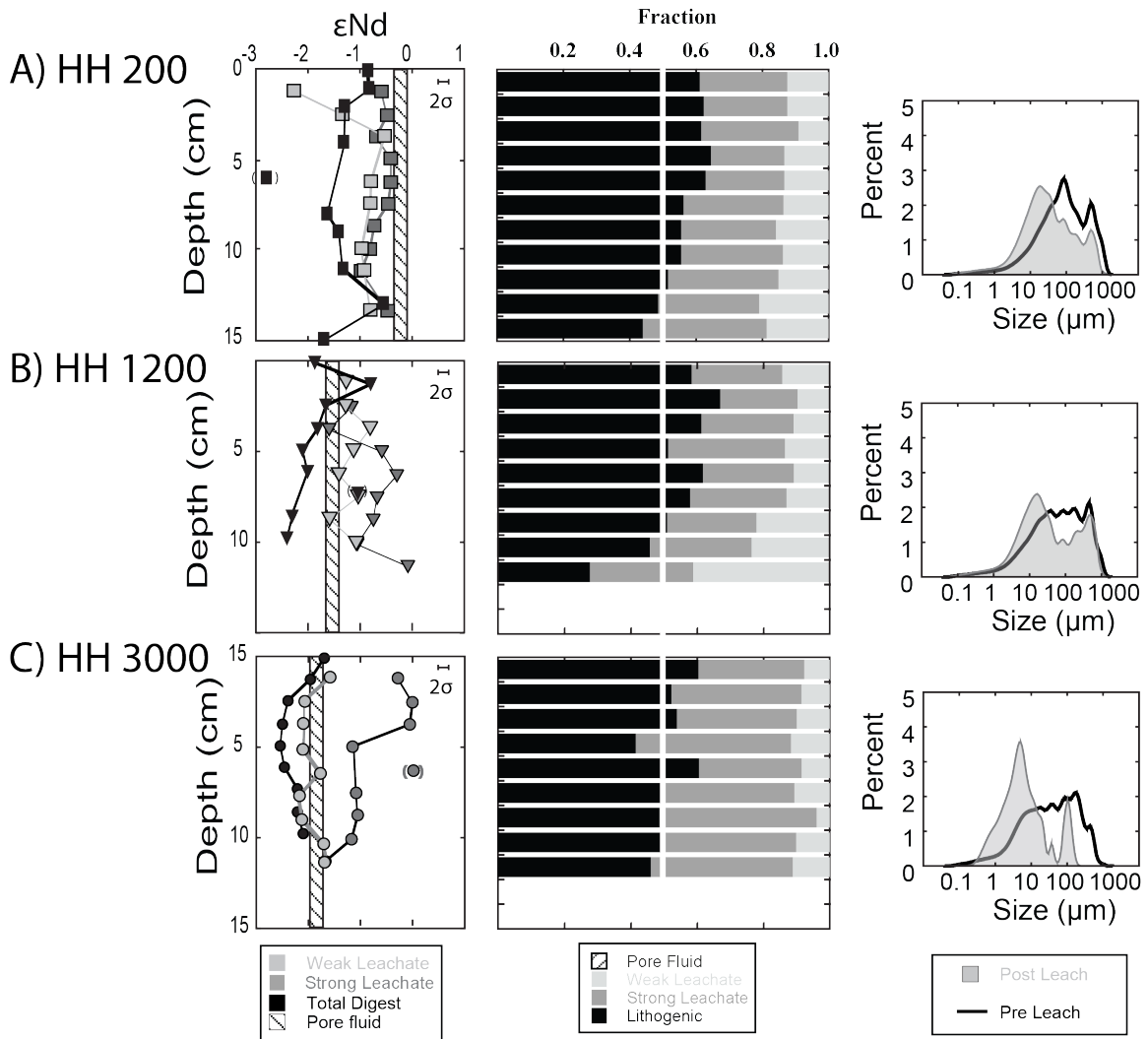
4.4 Solid Phase Characteristics

Total sediment digest profiles from **A)** HH200, **B)** HH1200, and **C)** HH3000 for ϵNd , Nd concentration, percent organic carbon (%OC), Fe/Al, Mn/Al, and $^{87}\text{Sr}/^{86}\text{Sr}$. The shaded bar for $^{87}\text{Sr}/^{86}\text{Sr}$ indicates the global seawater value.



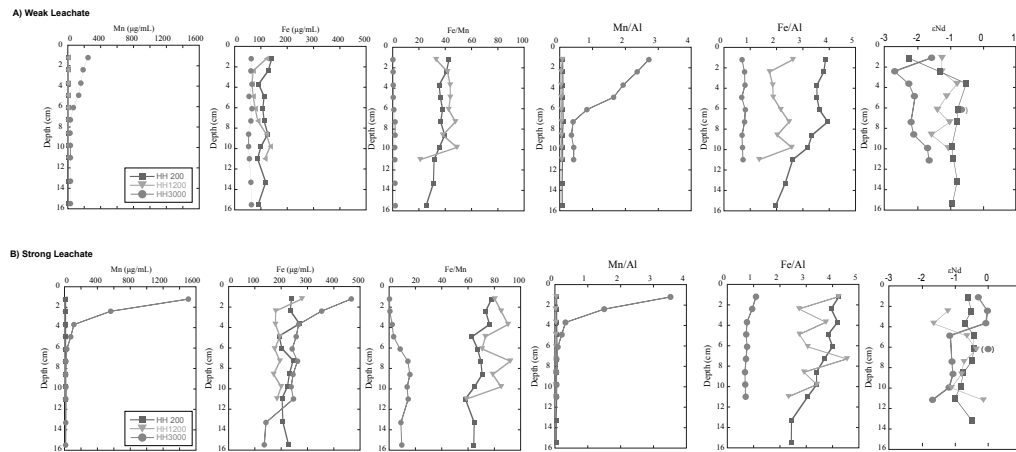
4.5 $^{87}\text{Sr}/^{86}\text{Sr}$

$^{87}\text{Sr}/^{86}\text{Sr}$ for acid leachable (triangle) and reducible leachates (diamonds), total sediment digest (solid squares), and pore fluids (striped squares). Pore fluid $^{87}\text{Sr}/^{86}\text{Sr}$ 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.



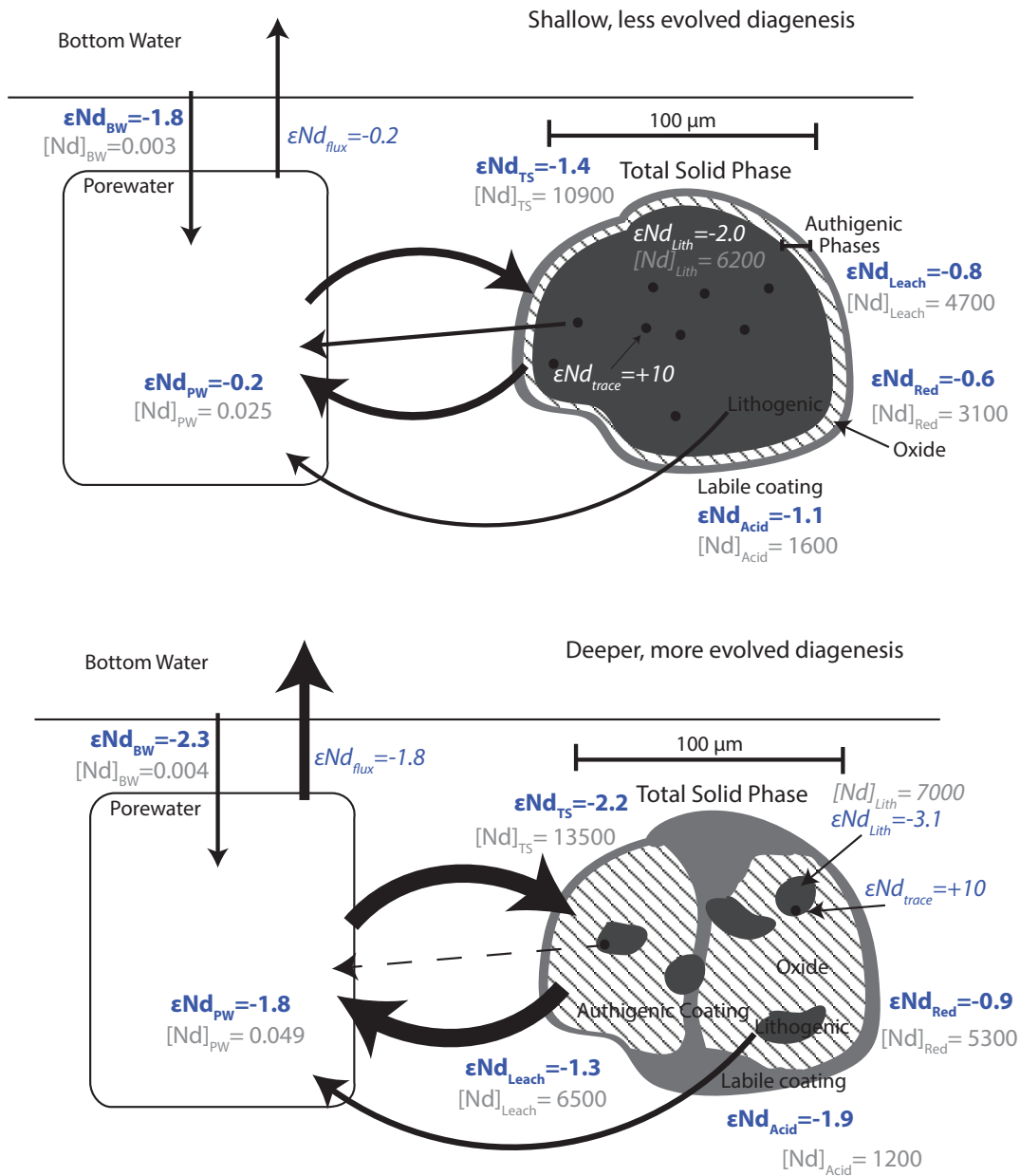
4.6 Mechanism Indicators

A) ϵ_{Nd} profiles for the weak leachate (light grey), the strong leachate (dark grey), the total digest (black), and the pore fluid (striped) for HH200, HH1200, and HH3000. **B)** Relative distribution of Nd among weak leachate (light grey), strong leachate (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.



4.7 Leachate Characteristics

Fe, Mn, Fe/Mn, Fe/Al, Mn/Al and ϵNd for **A)** weak acetic leachates and **B)** strong hydroxylamine leachates from HH200 (squares), HH1200 (triangles), and HH3000 (circles).



4.8 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 (grey), authigenic oxides (stripes) and a lithogenic (refractory; dark grey) component. The particle is drawn approximately to scale. Calculated ϵNd values are in *italics*, measured ϵNd values are in **bold**. All concentrations are in $ng\ cm^{-3}$.

	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	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

4.1 Reservoir εNd

Site average εNd and Nd concentrations for bottom water, pore fluid, total leachate, weak leachate, strong 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 weak and strong leachates. The total solid includes the lithogenic and total leachate reservoirs. * indicates unfiltered bottom water. Reservoirs for which εNd was calculated instead of measured directly are indicated by **.

4.A1 Supplemental Information

4.A1.1 Subsequent Experiments

Identical leaching procedures on sediment samples from the same core were performed on sediments from HH200 and HH1200 and two samples from HH3000. The concentration of Nd in the leachate was between 50 and 70% of the total sediment digest Nd concentration and varied between these subsequent leaching experiments. Generally, the Nd recovered in the weak leach was twice (average at HH200 2000 ng Nd g⁻¹ sed; HH1200 2770 ng Nd g⁻¹ sed; HH3000 3700 ng Nd g⁻¹ sed) that recovered in the second experiment as in the first (average at HH200 1020 ng Nd g⁻¹ sed; HH1200 1130 ng Nd g⁻¹ sed; HH3000 1570 ng Nd g⁻¹ sed; supplemental information table 6; supplemental figure 1). The Nd recovered in the strong leachate was on average 25% lower in the second experiment (average at HH200 3800 ng Nd g⁻¹ sed; HH1200 3040 ng Nd g⁻¹ sed; HH3000 6800 ng Nd g⁻¹ sed) than in the first experiment (average at HH200 4000 ng Nd g⁻¹ sed; HH1200 4500 ng Nd g⁻¹ sed; HH3000 4350 ng Nd g⁻¹ sed; supplemental information table 6).

The leachable fraction at over 50% of the total sediment is a large reservoir of reactive Nd. In our repeated leaching experiment, between 56 and 58% of the total sedimentary Nd came off in the leachates for sediments from HH200, between 48 and 64% for the sediments from HH1200, and between 61 and 76% for the sediments from HH3000 (supplemental information table 6). On average, 45% of the leachable Nd was in the weak leachate and 65% in the strong leachate, but the distribution between the strong and weak leachate varied widely between experiments (e.g. 22% to 71% in acetic at HH1200). However the ϵ Nd of each leachate was consistent between experiments suggesting the leach targeted the same phase in each experiment.

4.A1.2 Phase Comparisons

The direct comparison of Nd in each reservoir required concentrations in each reservoir to be normalized by volume. For this calculation, we assumed a porosity of 70% and a sediment density of 2.6 g cm⁻². Specifically, pore fluid Nd per cubic centimeter ([Nd]_{vP}) was calculated as:

$$[Nd]_{vPW} = \frac{pM}{1000} \times P \times \frac{M}{1000} \quad (\text{Eq. 1})$$

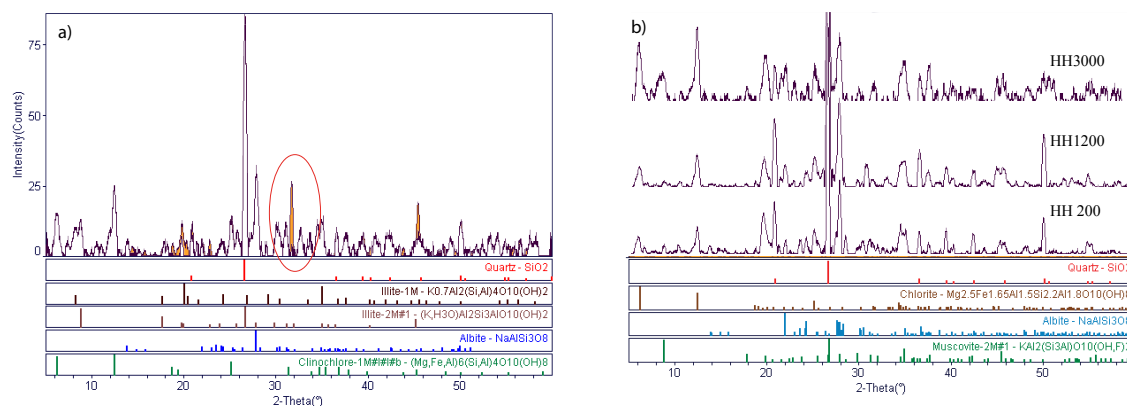
where in pM is the measured picomolar concentration of Nd in pore fluids, P is the porosity, and M is the atomic mass of Nd in grams mol⁻¹. Weak and strong leachate Nd per cubic centimeter ([Nd]_{vL}) were calculated as:

$$[Nd]_{vL} = [Nd]_L \times (1 - P) \times \rho \quad (\text{Eq. 2})$$

where in [Nd]_L is the measured ng Nd g⁻¹ dry leached sediment, P is the porosity, and ρ is the sediment density. The lithogenic Nd per cubic centimeter ([Nd]_{vLith}) was calculated as:

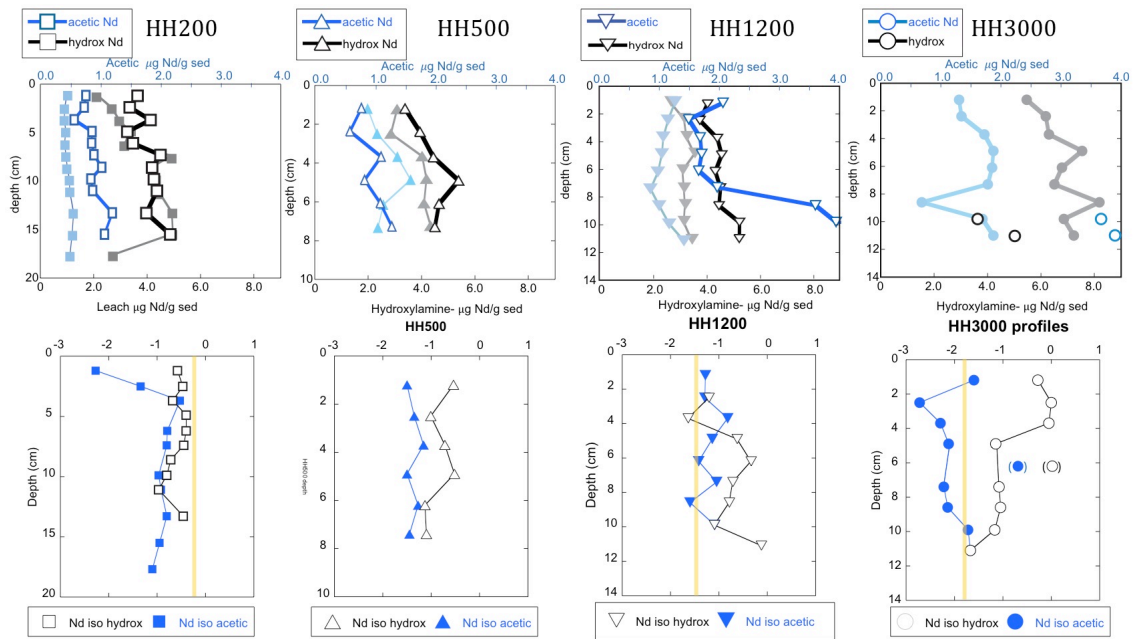
$$[Nd]_{vLith} = [[Nd]_{Lith} \times (1 - P) \times \rho] - \Sigma [Nd]_{vL} \quad (\text{Eq. 3})$$

where in $[\text{Nd}]_{\text{Lith}}$ is the calculated ng Nd g⁻¹ sediment remaining after the leach procedures, P is the porosity, ρ is the sediment density, and $\Sigma[\text{Nd}]_{\text{VL}}$ is the sum of the weak and strong leachate Nd per cubic centimeter. Even with the assumption that pore fluid occupies 70% of the volume of any given cubic centimeter, the Nd in the pore fluid reservoir remains <0.001% of the total Nd in that area for all sites (supplemental information table 7).



4.A1 XRD Mineralogy

a) Comparison of pre-leach (yellow) and post-leach mineralogy. The only significant difference is the loss of halite (red circle). **b)** Comparison of post-leach mineralogy from HH200, HH1200, and HH3000. All samples consist of quartz, albite, a white mica (e.g. illite or muscovite) and a chlorite mineral (e.g. clinocllore).



4.A2 Repeated Leaching Experiment

Nd profiles for both the strong (black) and weak leachate (blue) at HH200 (squares), HH1200 (triangles), and HH3000 (circles) for the first (solid) and second (open) leaching experiments. Only the bottom two intervals were re-leached from HH3000.

Supplemental Table Captions (*tables online only*)

4.A1 Grain Size Distributions

A) Summary of grain size data including the range and average peak grain size for the largest two peaks in each bimodal distribution for pre-leach and post-leach samples and the difference between the pre-leach and post-leach peak grain size. **B)** Grain size data for each bin for all samples from HH200, HH1200, and HH3000. Replicates are included where available. The average distribution for pre-leach and post-leach distributions are provided by site.

4.A2 Pore Fluid Characteristics

4.A3 Total Sediment Digests

Neodymium and strontium isotope compositions, REEs concentrations, and accessory data for total sediment digests from HH200, HH1200, and HH3000. The minimum detection limit (MDL) is provided in the case of a measurement below minimum detection limit (BMDL).

4.A4 Leachate Accessory Elements

Accessory data for leachate samples. All accessory elements measured on second leaching experiment unless otherwise noted by a * next to top depth. The minimum detection limit (MDL) is provided in the case of a measurement below minimum detection limit (BMDL).

4.A5 Leachate Isotopes

Neodymium isotopic composition and strontium isotopic composition of leachates collected during acetic (weak) and hydroxylamine (strong) leaching procedures for HH200, HH1200, and HH3000. The depths provided are the top of the interval in the sediment core.

4.A6 Leachate REEs

Concentration of REEs in each leachate normalized to pre-leach dry sediment weight (ng REE/g sed). Leach type and sediment depth provided for each sample. Number after leach type indicates leach experiment. Not all samples were leached during both experiments, all results are provided.

4.A7 Reservoir Comparison

Amount (in ng) of Nd in the weak leachate, strong leachate, pore fluid, and lithogenic reservoirs normalized to a volume of one cubic centimeter. For these calculations, we assume a porosity of 70% and a sediment density of 2.6 g cm^{-2} .

Chapter 5: Conclusions

5.1 Summary

Pore fluid rare earth element concentrations were measured at eight sites representing shelf-to-slope settings in the northeast Pacific Ocean. These locations lie above, within, and below the oxygen minimum zone of the North Pacific along the California and Oregon margins. Our data add to a limited existing pore fluid dataset. Based on the concentration gradient observed in the neodymium profile at HH3000, we calculate that the benthic flux can account for upwards of 95% of the neodymium entering the ocean. These data show that the benthic flux of rare earth elements to the ocean via the pore fluids is the major source to the ocean. The benthic flux can account for the “missing” source that has been identified in coupled ocean-atmospheric models. The magnitude of the benthic flux makes this source greater than the input from riverine dissolved load, atmospheric deposition, and hydrothermal vents combined. Therefore, we hypothesize these sources have relatively small, localized influences. This hypothesis contrasts with models that assume the dominant source of REEs to the ocean is from dissolved riverine input. Additionally, the magnitude of the flux is greatest at our deepest site (HH3000) and smaller near shore (HH200). The increase in flux with water depth is consistent with sediment diagenesis and, more specifically, it is consistent with the alteration of sedimentary phases as an important driver of the benthic flux. In short, the cycling of REEs in the upper sediment column determines broad-scale REE distribution in the ocean.

The ϵ_{Nd} of pore fluids was measured at three of these eight sites. Our pore fluid ϵ_{Nd} profiles are the first of their kind and show a generally consistent ϵ_{Nd} profile down core at each site. The ϵ_{Nd} of the flux is equivalent to pore fluid ϵ_{Nd} , meaning we could

examine the flux's influence on bottom water ϵNd by measuring pore fluid ϵNd . Based on these measurements, the ϵNd of the flux determines the ϵNd of bottom water. The degree of alteration to the bottom water ϵNd depends on the difference between the ϵNd of the initial bottom water and the ϵNd of the flux, the magnitude of the flux, and the exposure time. Modeling the sensitivity of the bottom water to a benthic flux over exposure times commensurate with modern day circulation patterns (exposure time < mixing time) demonstrates that the benthic flux can result in the ϵNd distribution observed in the modern ocean. Additionally, the benthic flux provides a mechanism for the radiogenic ϵNd end member water mass signatures observed in the North Pacific in the absence of deep-water formation.

The benthic flux of Nd is driven by sediment diagenesis. Bottom water does not govern the Nd concentration or the ϵNd of the pore fluids because of the insignificant amount of Nd present in bottom water. Pore fluids contain 1 to 2 orders of magnitude more Nd per area than bottom water, and the solid phases contain 5 to 6 orders of magnitude more Nd per area than the pore fluids. Given this distribution of Nd, the solid phase must control the ϵNd composition of the fluid phases. Specifically, our model indicates the pore fluids receive Nd from the lithogenic and authigenic components of the total sediment. The amount of coatings increase from less diagenetically evolved nearshore sites (e.g. HH200) to more evolved sites further off shore (e.g. HH3000). The coatings can be measured by the change in grain size distributions between pre-leach (untreated) and post-leach sediment samples as the pre-leach distribution is an artifact of a conglomerate of lithogenic particles held together by the reactive coatings.

In the open ocean the amount of reactive authigenic coatings determine the capacitance of sediment to drive the benthic flux, but this becomes more complicated in marginal areas. In marginal regions, the very different ϵNd signatures of reactive trace mineral phases may disproportionally influence the ϵNd signature of the flux. While these trace mineral phases are likely only associated with less diagenetically evolved sediments and therefore a small benthic flux, the difference between the ϵNd signature of the flux and the bottom water ϵNd is potentially large meaning that the resulting change in bottom water ϵNd as a result of the flux may be observable. In other words, even a small flux with an ϵNd that is very different from bottom water ϵNd would be noticeable on short time scales. The occurrence of these trace mineral phases in less diagenetically evolved sediments limits the influence of their influence largely to marginal areas, possibly explaining boundary exchange has largely only been observed in near shore regions.

5.2 Future Work

The results presented here call for a revised oceanic Nd budget and reconsideration of ϵNd records. Future work to test the spatial extent and ϵNd signature of the benthic flux in the abyssal Pacific and other major ocean basins should be considered. Our data suggest that the comparison of pre- and post-leach grain size or the difference between measured bottom water ϵNd and bottom water ϵNd predicted by temperature and salinity water mass identification may provide a first order estimate of regions where the benthic flux is most significant. The identification of the factor or factors that determine the depth of the Nd source in the pore fluid profile requires further

investigation. While we propose a pH shift occurring above the redox boundary as one of these factors, concurrent REE and pH profiles are necessary to test this hypothesis. The benthic flux of Nd and the mechanisms driving this flux may be applicable to other trace metals that are either redox sensitive (e.g. Fe) or typically associated with redox sensitive metals (e.g. As).

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