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Author(s):
Du, Jianghui; Haley, Brian A.; Haley, Brian A.; Abbott, April N.; McManus, James; Vance, Derek

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Reactive-transport modeling of neodymium and its radiogenic isotope in deep-sea sediments: The roles of authigenesis, marine silicate weathering and reverse weathering

Jianghui Du a,*, Brian A. Haley b, Alan C. Mix b, April N. Abbott c, James McManus d, Derek Vance a

a Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zürich, Clausiusstrasse 25, 8092, Zürich, Switzerland
b College of Earth Ocean and Atmospheric Sciences, Oregon State University, 104 CEGAS Admin. Bldg., Corvallis, OR 97331, USA
c Department of Marine Science, Coastal Carolina University, 100 Chanticleer Drive E, Conway, SC 29526, USA
d Bigelow Laboratory for Ocean Sciences, 60 Bigelow Drive, East Boothbay, ME 04544, USA

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A B S T R A C T
Dissolved Rare Earth Elements (REE) and radiogenic neodymium (Nd) isotope composition (εNd) of seawater are widely used geochemical tools in studying marine processes, but their modern ocean budgets are poorly understood. Recent discoveries of large benthic fluxes of REE with unique εNd signatures from marine sediments, particularly in the deep-sea, have led to a “bottom-up” hypothesis, which suggests that early diagenesis below the sediment-water interface (SWI) controls the ocean’s REE and εNd budgets. To investigate such sedimentary processes, we created a reactive-transport model for the biogeochemical cycling of Nd and εNd in marine sediments. Here, we attempt to quantify the roles of authigenesis, marine silicate weathering and reverse weathering in the diagenetic cycling of Nd and εNd at a deep-sea (3000 m) site on the Oregon margin.

Our model predicts that, at this site, Nδ carried by Fe/Mn oxides into sediments eventually transforms to authigenic Nδ-phosphate, during which ∼9% of the incoming solid Nδ flux is released as a dissolved benthic flux back to the overlying bottom water. We also find that the classic reversible scavenging formulation applied to Nδ co-cycling with Fe/Mn oxides is inconsistent with the data. Rather, a co-precipitation formulation, assuming Nδ is structurally incorporated into Fe/Mn oxides, successfully simulates the data. The model also shows that authigenesis alone cannot explain the pore water and authigenic εNd, which are both more radiogenic than bottom water at this site. However, the weathering of volcanic silicates sourced from the local subduction zone can successfully explain εNd. We suggest that, because reverse weathering by authigenic clay formation maintains the under-saturation of primary silicates in pore water, marine silicate weathering can proceed. The processes we model likely affect the sedimentary cycling of many other trace elements and isotopes, with much broader implications for the understanding of ocean biogeochemistry.

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1. Introduction
The seawater Rare Earth Elements (REE) are widely used geochemical tools for tracing ocean processes, such as circulation and the particulate-dissolved interaction known as Boundary Exchange (Elderfield and Greaves, 1982; Lacan and Jeandel, 2005; Piepgras et al., 1979). Among the 14 REE, neodymium (Nd) has received the most attention because its radiogenic isotope composition, expressed as εNd = [(143Nd/144Nd)sample/(143Nd/144Nd)CHUR − 1] × 104 where CHUR is the Chondritic Uniform Reservoir, gives additional constraints on the oceanic cycles of the REE (Goldstein and Hemming, 2003).

The applications of marine REE proxies have been hampered by our limited understanding of their modern oceanic budgets. Studies of marine Nd cycle have long identified a “missing source” problem: the known riverine and atmospheric inputs are too small to balance the global budgets, and some ∼90% of the required sources needed to maintain the ocean inventory appears to be “missing” (Arsouze et al., 2009; Bertram and Elderfield, 1993; Tachikawa et al., 2003; Goldstein and Jacobsen, 1988).

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Recently, the discovery of large benthic fluxes from marine sediment, with \( \varepsilon_{\text{Nd}} \) values that also satisfy the isotope budget, provides a promising candidate for this "missing source", leading to the "bottom-up" hypothesis of the marine REE cycles (Abbott et al., 2015a; Du et al., 2020; Haley et al., 2017). In this hypothesis, the sedimentary flux is the dominant source of ocean REE, and seawater \( \varepsilon_{\text{Nd}} \) signatures are acquired at the sediment-water interface (SWI) rather than at the river/atmosphere-ocean interface. Anomalous behavior of \( \varepsilon_{\text{Nd}} \) at the SWI has been documented (Grenier et al., 2013; Lacan and Jeandel, 2005; Lambelet et al., 2018), suggesting that processes involved in Boundary Exchange are indeed critical to trace element and isotopic budgets. It is thus important to understand the mechanisms of early diagenesis within sediments that derive these benthic fluxes, and how these processes contribute to the broader concepts of Boundary Exchange (Jeandel, 2016).

If correct, the "bottom-up" hypothesis would significantly change our interpretations of marine REE proxies; for example, the use of \( \varepsilon_{\text{Nd}} \) to trace paleo-circulation (Abbott et al., 2022; Du et al., 2020, 2018). However, studies of pore water REE concentrations and \( \varepsilon_{\text{Nd}} \) are scarce and mostly observational, with the mechanisms regulating the flux obscured by the complexity of sedimentary processes.

Here we report a reactive-transport model of the early diagenesis of Nd and \( \varepsilon_{\text{Nd}} \) in marine sediments with the intent of establishing the "bottom-up" hypothesis in mechanistic and quantitative terms. We focus on deep-sea sediments where the benthic flux is the largest yet measured, potentially dominating the global budget (Abbott et al., 2015b; Du et al., 2020). We also present a test application of the model to a deep-sea site on the Oregon Margin, to date the only region for which a comprehensive pore water dataset exists (Abbott et al., 2019, 2016, 2015b, 2015a). We test three processes hypothesized to be critical in the diagenetic Nd cycle: (1) authigenesis of Fe-Mn oxides and phosphates (Schijf and Byrne, 2021; Takahashi et al., 2015; Bi et al., 2021; Abbott et al., 2016); (2) weathering of lithogenic sediments, for example silicate minerals (Abbott et al., 2022; Blaser et al., 2019; Du et al., 2020; Jeandel and Oelkers, 2015; Lacan and Jeandel, 2005), and (3) reverse weathering through conversion of biogenic silica to authigenic clay (Aller, 2014; Mackin and Aller, 1984). These processes are likely important for the sedimentary cycle of many trace elements and isotopes (TEIs), and our general modeling approach as well as the specific results for this site thus have implications for the global budgets of these TEIs. Our model also helps illuminate how authigenic phases acquire \( \varepsilon_{\text{Nd}} \) diagnostically, thus providing key insights for the use of authigenic \( \varepsilon_{\text{Nd}} \) in paleoceanography.

2. Study region

Paired REE and \( \varepsilon_{\text{Nd}} \) measurements in pore water and sediment, as well as ancillary data needed by the model, have only been made by Abbott et al. (2019, 2016, 2015b, 2015a) at three sites on the Oregon margin, Northeast Pacific (Fig. 1). We choose to model site HH3000 at 3000 m water depth, because it has one of the highest benthic Nd fluxes yet measured (~30 pmol/cm²/yr). The water column here has a uniform \( \varepsilon_{\text{Nd}} \) of ~2.4 \( \varepsilon \), but pore water \( \varepsilon_{\text{Nd}} \) (~1.8 \( \varepsilon \)) is more radiogenic, the first evidence that diagenetic processes can decouple bottom and pore water \( \varepsilon_{\text{Nd}} \).

The site underlies oxic bottom water (~100 \( \mu M \)) and has a low organic carbon rain rate (200 \( \mu g/cm²/yr \)) (Lyle et al., 1992). These conditions lead to a weakly reducing shallow sediment package, with dissolved Mn (~50 \( \mu M \)) higher than Fe (<10 \( \mu M \)) in pore water (Abbott et al., 2016). Sediments are composed mainly of terrigenous materials (~90 wt%) with moderate organic carbon (OC) (~1.8 wt%), significant biogenic opal (~6 wt%), but negligible carbonate (~0.05 wt%). The accumulation rate is ~13 cm/kyr (Abbott et al., 2016; Lyle et al., 1992). Terrigenous sediments are delivered by small coastal rivers that drain across the Oregon Coastal Range and Cascade Arc. The mineral assemblage consists of quartz, plagioclase, chlorite and muscovite/illite, with minor clinopyroxene, amphibole and volcanic glass (Abbott et al., 2019), reflecting their sources in the igneous and low-grade metamorphic rocks of the continental arc (VanLaningham et al., 2008).

3. Diagenetic modeling

Ours is a classic 1D reactive-transport model describing the distributions of dissolved species in pore water and solid species in sediments (Boudreau, 1997). Physical transport includes molecular diffusion, burial and bio-irrigation for dissolved species, and bioturbation and burial for solid species. The model includes the classic sequence of organic matter decomposition, and uses the continuum formulation of the reactivity of organic matter. The model also includes secondary redox reactions, dissolution of biogenic opal, CaCO₃ and precipitation of Fe₂O₃. We also model pH for speciation calculations. Complete model details are given in the Supplementary Methods; here we only present those that relate to Nd and \( \varepsilon_{\text{Nd}} \).

We model \(^{144}\text{Nd}\) and radiogenic \(^{143}\text{Nd}\) as two separate tracers. The convention for reporting radiogenic \( \varepsilon_{\text{Nd}} \) is to remove the natural and instrumental stable isotope fractionation by normalizing the \(^{142}\text{Nd}/^{144}\text{Nd}\) ratio to a fixed \(^{146}\text{Nd}/^{144}\text{Nd}\) ratio of 0.7219. A model of \( \varepsilon_{\text{Nd}} \) thus has no need to consider stable isotope fractionation. Modeled Nd concentration is the sum of these two isotopes divided by the summed natural abundance (0.35971). Nd speciation for both isotopes is computed following Schijf and Byrne (2021), considering complexation with dissolved ligands CO₃²⁻, HCO₃⁻, Cl⁻, SO₄²⁻ and H₂SiO₄⁻. We do not consider organic ligands since they have not been characterized in sediment pore water.

3.1. Authigenic Fe/Mn oxides

To date, interaction of Nd with solid phases in ocean models has been formulated as equilibrium reversible scavenging (Siddall et al., 2008). Using MnO₂ as an example (same for FeOOH):
\[ ^1\text{Nd}_{\text{MnO}} = ^1\text{Nd}_d \times K_{\text{ads-MnO}_2} \times \text{MnO}_2, \]  

where \(^1\text{Nd}_d\) is the total dissolved Nd concentration \((i = 143 \text{ or } 144)\); \(^1\text{Nd}_{\text{MnO}}\) is the adsorbed Nd concentrations; \(K_{\text{ads-MnO}_2}\) is the adsorption constant specific to \(\text{MnO}_2\).

We also consider an alternative kinetic co-precipitation formulation:

\[ R^1\text{Nd}_{\text{Mn-pre}} = R_{\text{Mn-ads}} \times D_{\text{Nd/Mn}} \times ^1\text{Nd}_d/\text{Mn}_d, \]  

\[ R^1\text{Nd}_{\text{Mn-dis}} = R_{\text{MnO}_2} \times ^1\text{Nd}_{\text{MnO}_2}/\text{MnO}_2, \]  

where \(R^1\text{Nd}_{\text{Mn-pre}}\) is the co-precipitation rate of Nd when dissolved Mn \((\text{Mn}_d)\) is oxidized at a rate of \(R_{\text{Mn-ads}}\); \(D_{\text{Nd/Mn}}\) is the partition coefficient controlling the enrichment of Nd relative to Mn in \(\text{MnO}_2\); \(R^1\text{Nd}_{\text{Mn-dis}}\) is the release rate of solid Nd \((^1\text{Nd}_{\text{MnO}_2})\) in \(\text{MnO}_2\) during dissolution \((R_{\text{MnO}_2})\).

In this formulation, newly formed oxides have the same \(\varepsilon_{\text{Nd}}\) as the pore water precipitating them, and during dissolution the release of dissolved Nd isotopes is proportional to the release of dissolved Mn according to the solid concentration ratio of Nd isotopes to Mn in \(\text{MnO}_2\) (i.e., dissolution is congruent).

### 3.2. Authigenic phosphate

We consider the precipitation-dissolution of rhabdophane \((\text{NdPO}_4)\) using the classic linear Transient State Theory (TST) \((\text{Steefel et al., 2014})\):

\[ R^1\text{Nd}_{\text{PO}_4} = k_{\text{NdPO}_4} \times a_{\text{NdPO}_4} \times \left( [^1\text{Nd}^{3+}] \times [\text{PO}_4^{3-}] / K_{\text{NdPO}_4}/a_{\text{NdPO}_4} - 1 \right), \]  

where \(k_{\text{NdPO}_4}\) is the precipitation rate constant; \(a_{\text{NdPO}_4}\) is the activity of the isotopic \(\text{NdPO}_4\) species \((i = 143, 144)\), which we assume to form an ideal solid-solution so that the activity is equal to the mole fraction; \([^1\text{Nd}^{3+}]\) is the free Nd concentration of an isotope; \([\text{PO}_4^{3-}]\) is the concentration of \(\text{PO}_4\) ion; \(K_{\text{NdPO}_4}\) is the apparent solubility.

Positive \(R^1\text{Nd}_{\text{PO}_4}\) favors precipitation while negative values imply dissolution. This formulation ensures that newly formed \(\text{NdPO}_4\) has the same \(\varepsilon_{\text{Nd}}\) as the pore water.

### 3.3. Marine silicate weathering

We model the dissolution of four silicate phases: basalt glass, clinopyroxene, plagioclase and chloride. The general TST law of silicate dissolution is \((\text{Heřmanšká et al., 2022})\):

\[ R_{\text{silicate}} = k_{\text{silicate}} \times S_{\text{silicate}} \times M_{\text{silicate}} \times \text{silicate} \times (1 - \Omega_{\text{silicate}}). \]  

Which is used for clinopyroxene and chloride, but modified for basalt and plagioclase to include the Al-inhibition term \((\text{Heřmanšká et al., 2022})\):

\[ R_{\text{basalt}} = k_{\text{basalt}} \times S_{\text{basalt}} \times M_{\text{basalt}} \times \text{basalt} \times (a_{H^+}/a_{Al})^{1/3} \times (1 - \Omega_{\text{basalt}}), \]  

\[ R_{\text{plag}} = k_{\text{plag}} \times S_{\text{plag}} \times M_{\text{plag}} \times \text{plag} \times (a_{H^+}/a_{Al})^{0.35} \times (1 - \Omega_{\text{plag}}), \]  

where \(k\) is the surface area normalized Si release rate at \textit{in situ} temperature and the pH range of 7–8; \(S\) is the specific surface area; \(M\) is the mineral molecular weight; \(\text{Silicate}/\text{Basalt}/\text{Plag}\) is the mineral concentration in solid sediment; \(\Omega\) is the saturation state in pore water, and dissolution is allowed only when \(\Omega < 1\); \(a\) refers to aqueous activity.

The release of Nd isotopes is assumed congruent to Si:

\[ R^{143}\text{Nd}_{\text{silicate}} = R_{\text{silicate}} \times R_{\text{Nd/Si}} \times 0.35971 \times 143\text{Nd}/144\text{Nd}_{\text{silicate}} / (143\text{Nd}/144\text{Nd}_{\text{silicate}} + 1), \]  

\[ R^{144}\text{Nd}_{\text{silicate}} = R_{\text{silicate}} \times R_{\text{Nd/Si}} \times 0.35971 / (143\text{Nd}/144\text{Nd}_{\text{silicate}} + 1), \]  

where \(R_{\text{Nd/Si}}\) is the molar Nd/Si ratio in silicates; \(143\text{Nd}/144\text{Nd}_{\text{silicate}}\) is the Nd isotopic ratio of silicates.

### 3.4. Reverse weathering

In the model, reverse weathering includes two reactions: (1) opal dissolution, releasing dissolved Si to pore water, and; (2) authigenic illite formation, previously identified in marine sediments \((\text{Mackin and Aller, 1986})\), that consumes cations and alkalinity from pore water while releasing CO\(_2\). The net reaction is:

\[ 3.15\text{SiO}_2 + 2.85\text{Al(OH)}_3 + 0.85\text{K}^+ + 0.85\text{HCO}_3^- \rightarrow K_{0.85}\text{Al}_2\text{.85Si}_3\text{.15O}_1\text{.10(OH)}_2 + 0.85\text{CO}_2 + 3.7\text{H}_2\text{O}, \]  

Opal dissolution also releases Al according to a molar Al/Si ratio of 0.0025 in diatom frustules \((\text{Van Cappellen et al., 2002})\), and marine silicate weathering provides additional Al sources.

The dissolution rate of opal is \((\text{Van Cappellen et al., 2002})\):

\[ R_{\text{opal}} = k_{\text{opal}} \times \text{opal} \times (1 - \Omega_{\text{opal}}), \]  

where \(k_{\text{opal}}\) is the opal dissolution rate constant and, \(\Omega_{\text{opal}}\) is the opal saturation state.

The rate of authigenic illite precipitation is computed using the TST rate law Eq. (5) when \(\Omega_{\text{illite}} > 1\).

### 3.5. Model simulations

We perform two types of simulations: baseline simulations and simulations that further add silicate weathering and reverse weathering. The baseline simulations include the sediment biogeochemical reactions and the authigenic Fe/Mn oxides and phosphate phases, and we test both the reversible scavenging and co-precipitation formulations. In the silicate weathering and reverse weathering simulations, silicate phases are added to the sediments to study their behavior. We test the model sensitivity to the dissolution rates of silicates, and the precipitation rates of authigenic clay during reverse weathering.

The model domain is the top 50 cm of the sediment, representing ~3500 years of sedimentation. This depth domain is discretized into 200 intervals, with finer grid spacing close to SWI to capture the large biogeochemical gradients there, resulting in 6600 coupled and stiff differential equations in the baseline simulations. Boundary conditions and the model solution are described in the Supplementary Methods.
Fig. 2. Modeled sediment biogeochemistry. (a) POC oxidation rates. (b) Mn and Fe cycling rates. (c–h) Solid and dissolved species (lines) compared with measured values (colored dots with red borders). (i) Pore water pH (free proton scale). The prefix “T” in names indicates total concentrations summed over all species (e.g., TH3PO4 = H3PO4 + H2PO4⁻ + HPO4²⁻ + PO4³⁻).

4. Results

4.1. Sediment biogeochemistry

The model reproduces the classic redox sequence at site HH3000 (Fig. 2). The depth-integrated OC remineralization rate is 0.5 mmol/m²/d, typical of this margin at similar water depth (McManus et al., 2012). The remineralization pathway is dominated by aerobic respiration (37.6%) and sulfate reduction (52.6%) (Fig. 2a). Despite its importance, sulfate reduction is still far from complete, with only ∼0.5 mM of SO4 consumed in the top 50 cm (Fig. 2f) and little formation of Fe sulfides (∼0.12 wt%, Fig. 2c). Denitrification (8.0%) and MnO2 reduction (1.6%) also contribute to carbon remineralization, but there is little FeOOH reduction (0.25%) and methanogenesis is negligible (Fig. 2a). Organic carbon respiration slightly decreases pH from ∼7.7 in the bottom water to ∼7.3 in the deep pore water (Fig. 2d). Pore water total silica concentration is relatively high (∼620 μM, Fig. 2g) because of high opal content.

In the model, the surface benthic layer is ∼6 cm thick. To fit the OC profile (Fig. 2d), the initial age of OC in the continuum reactivity model is 60 yr, higher than that of fresh phytoplankton but within the range observed in deep-sea studies (Arndt et al., 2013). To fit the dissolved phosphate profile (Fig. 2h), the required P/C ratio is 1/170, lower than the classic Redfield ratio (1/106). Together, the lower reactivity and P/C imply the presence of refractory terrestrial OC at this site (Hastings et al., 2012).

Assuming sediments below 6 cm represent the lithogenic background, the excesses of MnO2, presumably authigenic, are ∼0.45 wt% near the surface (Fig. 2d) (Abbott et al., 2016). Modeled surface sediment MnO2 (∼0.05 wt%) has to be lower than this value to fit the pore water Mn profile (Fig. 2c), suggesting that the surface enrichment might be a transient feature, or that other interfaces or microbial processes are involved but not modeled. Estimated authigenic (0.5 wt%) and modeled (0.2 wt%) FeOOH are similar (Fig. 2d). The authigenic enrichment of Fe is thus much lower than Mn, given the higher lithogenic background for Fe (∼5 wt%) versus Mn (∼0.07 wt%). Model results are consistent with elemental mapping using energy dispersive X-ray spectroscopy (EDS), which shows that Fe is located mainly in silicates, while Mn is enriched in amorphous nanoparticles that are likely authigenic (Abbott et al., 2019). Modeled Mn cycling is more intense than Fe cycling, at rates one order of magnitude higher for Mn than Fe (Fig. 2d). The modeled benthic Mn flux is 0.14 μmol/m²/d, in the range of measurements at similar depths at this margin (McManus et al., 2012). The modeled benthic Fe flux is ∼0.005 μmol/m²/d, also consistent with measurements (McManus et al., 1997).
5. Discussion

5.1. Authigenesis

Authigenesis has typically been considered the main process affecting the early diagenesis of REE (Haley et al., 2004; German and Elderfield, 1989), which in turn has justified the assumption that pore water and authigenic Nd are simply derived from bottom water Nd at the SWI (Goldstein and Hemming, 2003). Here we investigate to what degree authigenesis alone can explain the observations of the diagenetic Nd cycle.

5.1.1. Authigenic Fe/Mn oxides and co-precipitation

Our co-precipitation formulation is controlled by the partition coefficients (D). We use the results of the GEOTRACES Pacific GP16 cruise (Haley et al., 2021; Lam et al., 2018) to derive these parameter values. \( D_{\text{Nd/Fe}} \) is calculated as \( (N_{\text{auth}}/M_{\text{MnO}_2})/(Nd_{p}/M_{\text{Fe}}) \). \( N_{\text{auth}} \) is the measured particulate Nd corrected for lithogenic background, using a lithogenic Nd/Al mass ratio of 3.375 x 10^-4 and measured particulate Al. Data for authigenic MnO2, FeOOH, dissolved Nd and Mn are from the cited studies (Haley et al., 2021; Lam et al., 2018). We find \( D_{\text{Nd/Fe}} = 0.025 \) and \( D_{\text{Nd/Fs}} = 0.005 \) in the deep-sea (>2500 m). Using these values, the fluxes of Nd carried by MnO2 and FeOOH into sediments at the study site are 612 and 40 pmol/cm^2/yr, respectively, based on the MnO2 and FeOOH fluxes in the model (Supplementary Information).

For co-precipitation, the modeled pore water and authigenic Nd agree well with measurements (Fig. 3). MnO2 reduction (by POC, Fe^{2+} and \( H_2S \)) is predicted to be the major source of pore water Nd (Fig. 3d), while Mn oxidation (by \( O_2 \)) is a small sink. The depth-integrated MnO2 reduction source (647 pmol Nd/cm^2/yr) far outweighs the Mn oxidation sink (35 pmol Nd/cm^2/yr). In comparison, FeOOH reduction (by POC and \( H_2S \)) is a much smaller source of pore water Nd (Fig. 3d), while Fe oxidation (by O2 and MnO2) is a relatively larger sink. The depth-integrated FeOOH reduction source (120 pmol Nd/cm^2/yr) slightly exceeds the Fe oxidation sink (80 pmol Nd/cm^2/yr).

5.1.2. Authigenic Fe/Mn oxides and reversible scavenging

The reversible scavenging formulation is controlled by the adsorption constants (\( K_{\text{ads}} \)). We use values of \( K_{\text{ads-MnO}_2} = 5 \times 10^7 \) (M^-1) and \( K_{\text{ads-FeOOH}} = 0.8 \times 10^7 \) (M^-1), to deliver the same amount of Nd to the sediment via Fe/Mn oxides as in the co-precipitation simulation (Supplementary Methods).
These model results cannot explain the pore water Nd profile (Fig. 4). Modeled peak Nd concentration is far deeper than measured (Fig. 4c). Model sensitivity tests show that by varying $k_{\text{ads}}$, the magnitude of the peak Nd concentration would change, but it would not affect the depth of the peak (Supplementary Fig. 1). This is because, in the presence of MnO$_2$ and FeOOH, Nd remains in the adsorbed form, and is converted to dissolved Nd only when the concentrations of oxides greatly decrease (Fig. 4b). In contrast, in the co-precipitation formulation Nd is released to pore water as soon as oxide reduction begins (Fig. 3d). The failure of reversible scavenging is perhaps not surprising given that reversible adsorption is a first step toward irreversible structural incorporation (co-precipitation), and laboratory experiments have identified the gradual structural incorporation of adsorbed trace metals into Mn oxides (Atkins et al., 2016).

Most existing ocean models rely on reversible scavenging to explain increasing seawater REE (and other TEs) concentrations with increasing water depth in the open ocean (Arsouze et al., 2009; Siddall et al., 2008), on the premise that the concentrations of particular scavengers decrease with depth. However, no ocean REE model has included Fe/Mn oxides, despite the fact that they are amongst the most important scavengers, especially in the deep ocean (Schijf et al., 2015). If Fe/Mn oxide concentrations in seawater increase with depth, as recent GEOTRACES results have shown (Lam et al., 2018), reversible scavenging onto Fe/Mn oxides would predict a decrease, rather than an increase, of seawater REE concentrations with depth. Our results do not necessarily indicate that adsorption is unimportant, but rather that the reversible scavenging formulation in present ocean models may be unsuitable to describe this process, or that kinetic rather than equilibrium process may better describe particulate-dissolved interaction in seawater. We suggest that future studies need to include Fe/Mn oxides to robustly evaluate the appropriateness of reversible scavenging.

5.1.3. Authigenic phosphate

Solid REE concentrations in Pacific sediments are most strongly correlated to phosphate, more so than Fe/Mn oxides and other elements (Bi et al., 2021). Also, bioapatite becomes strongly enriched in REE post-deposition (Toyoda and Tokanami, 1990). Diagenetic Nd formed on foraminiferal tests is associated with oxides, but also phosphorous (Robert et al., 2012). Transformation of labile Fe/Mn oxide-associated REE to stable phosphate phases has been identified in pelagic sediments, suggesting phosphate is likely the ultimate sink of REE (Takahashi et al., 2015). Whether REE form their own phosphate minerals, are incorporated into authigenic Ca-phosphates, or are taken up by biogenic phosphate, is unclear. In the model, we choose rhabdophane, a common REE mineral forming in low-temperature environment (Gausse et al., 2016; Liu and Byrne, 1997; Pearce et al., 2013), as the authigenic phosphate (NdPO$_4$), largely because relevant thermodynamic data exist.

Literature values of log($K_0^{(\text{NdPO}_4)}$) at standard state and zero ionic strength are in the range of $-26 \sim -24$ (Gausse et al., 2016). The corresponding apparent log($K_0^{(\text{NdPO}_4)}$) in seawater medium at in situ temperature (2°C) and atmospheric pressure is estimated to be $-20 \sim -18$ using the activity coefficients of Pierrot and Millero (2017), but we lack the thermodynamic data to compute the constant at in situ pressure. Model sensitivity tests show that the higher end of solubility estimates fits the pore water Nd profile better (Supplementary Fig. 2), which could be because either greater pressure leads to higher solubility than reported values at the standard state, or because NdPO$_4$ formed in sediments is less crystalline than the versions used in some solubility experiments (Gausse et al., 2016). The saturation concentration of total Nd with respect to NdPO$_4$ is

$$Nd_{\text{saturation}} = K_0^{(\text{NdPO}_4)} \times f_{\text{Nd}^{3+}}.$$

where $f_{\text{Nd}^{3+}}$ is the fraction of the free Nd$^{3+}$ ion.

Given $K_0^{(\text{NdPO}_4)} = 100$ pmol/cm$^3$/yr, the modeled pore water Nd fits observations very well (Fig. 3g). Pore water becomes oversaturated below $\sim$1 cm. Close to the SWL solid NdPO$_4$ that is formed in the over-saturation zone beneath is brought up to the undersaturation zone by bioturbation, and its dissolution is a greater source of pore water Nd than MnO$_2$ reduction (Fig. 3d, e). Overall, phosphate precipitation is the dominant sink of pore water Nd, far surpassing that of MnO$_2$ oxidation (Fig. 3d–e). As modeled oxides disappear below 30 cm, the model predicts pore water Nd concentration that are nearly at equilibrium with NdPO$_4$ (Fig. 3g). The modeled total (MnO$_2$, FeOOH and phosphate related) authigenic Nd concentration ($\sim$9 ppm) also matches estimates based on an operationally defined acid-reductive leaching (Abbott et al., 2016). Though leaching studies of authigenic Nd have traditionally focused on the role of Fe/Mn oxides, it is well-known that the acetic acid used in these studies can also extract authigenic and biogenic phosphates (Ruttenberg, 1992).

5.1.4. Authigenesis and benthic flux

The benthic Nd flux in the model is affected by molecular diffusion and bio-irrigation (i.e., convective exchange between pore water and bottom water due to the activity of benthic organisms) (Supplementary Methods). Using the co-precipitation formulation and including authigenic phosphate, the modeled diffusive flux is 39 pmol/cm$^2$/yr, agreeing well with the estimate (24–41 pmol/cm$^2$/yr) based on the measured pore water profile (Abbott et al., 2015b). The model uses the bio-irrigation parameterization of Melle and Van Cappellen (2003), derived from the globally measured O$_2$ flux. The resulting bio-irrigation Nd flux is 20 pmol/cm$^2$/yr. This value is an upper limit because the impact of bio-irrigation on other dissolved species is likely weaker than on
O$_2$ (Meile et al., 2005). Taken together the total benthic flux is 59 pmol/cm$^2$/yr.

The authigenic minerals influence the benthic Nd flux in different ways. Both MnO$_2$ and NdPO$_4$ are sources of pore water Nd at the SWI, and thus support the benthic flux. However, when integrated over the sediment column, MnO$_2$ is a net source of pore water Nd while NdPO$_4$ is a net sink (Fig. 3d–f). In contrast, FeOOH is a sink of pore water Nd at the SWI and thus decreases the benthic flux (Fig. 3d–f), despite the fact that FeOOH is a net source of pore water Nd integrated over the sediment column.

In summary, in the baseline simulation including only authigenesis, the early diagenetic Nd cycle at the study site can be described as near total (~91%) conversion of Nd carried by incoming MnO$_2$, and to a lesser degree FeOOH, to authigenic NdPO$_4$, with a small fraction (~9%) returning to bottom water via diffusion and irrigation. Since, in this model, all Nd sources ultimately come from incoming water column-derived Fe/Mn oxides, modeled pore water and authigenic $\varepsilon_{Nd}$ are the same as bottom water (Fig. 3i).

5.2. Silicate weathering

The observed relatively small $\varepsilon_{Nd}$ difference (+0.6 $\varepsilon$) between pore water and bottom water is an indication that bottom water $\varepsilon_{Nd}$ is strongly influenced by pore water $\varepsilon_{Nd}$ because of a large benthic flux (Abbott et al., 2016). To explain this difference additional processes must be invoked. Much larger differences between pore water/authigenic and bottom water $\varepsilon_{Nd}$ exist elsewhere, linked to smaller benthic flux or reactive lithogenic sediments (Abbott et al., 2016; Blaser et al., 2019; Du et al., 2016; Wilson et al., 2013). Moreover, variations in authigenic $\varepsilon_{Nd}$ on glacial-interglacial timescales are on the order of 1–2 $\varepsilon$, sometimes correlated to changes of lithogenic sediment $\varepsilon_{Nd}$ (Du et al., 2020 and references therein). It is thus important to understand $\varepsilon_{Nd}$ differences on this order of magnitude for robust circulation reconstruction.

5.2.1. The reactive spectrum of silicate minerals

Our next model iteration investigates the impact of marine silicate weathering on the diagenetic cycle of $\varepsilon_{Nd}$, focusing on mineral reactivity. We model four phases: basaltic glass, clinopyroxene, chlorite and plagioclase (albite): all present in the study region (Abbott et al., 2019; VanLaningham et al., 2008). Volcanic glass, often derived from ash deposition that reaches far into the ocean interior, is ubiquitous in Pacific sediments (Du et al., 2020; Straub and Schmincke, 1998). Clinopyroxene is a mafic mineral that is commonly found in sediments near volcanic arcs. Chlorite often exists as a clay mineral, as the metamorphic alteration production of igneous minerals (Griffin et al., 1968). Plagioclase is not necessarily volcanic but is the most abundant primary silicate mineral, after quartz, in marine sediments (Li and Schoonmaker, 2014). Collectively they represent a large range of silicate reactivity in terms of abundance, dissolution rate and solubility.

We add these phases separately to the baseline model, with deposition fluxes that are proportional to the total incoming sediment: 2 wt% of basalt glass and clinopyroxene, 10 wt% of chlorite and 20 wt% of plagioclase respectively, based on published abundance data in the study region (Abbott et al., 2019; VanLaningham et al., 2008; Zemmel and Cook, 1973). Interrogation of the GEOROC database (Supplementary Methods), either using data from the Cascade Arc or other convergent margins, suggests that the average Nd/Si molar ratios of basalt glass, clinopyroxene and plagioclase are 1.9 $\times$ 10$^{-5}$, 1.8 $\times$ 10$^{-5}$ and 1.9 $\times$ 10$^{-6}$ respectively (Supplementary Fig. 3), consistent with the partition coefficients of Nd in silicates (Taylor and McLennan, 1988). For chlorite, we use the average Nd/Si ratio (1.6 $\times$ 10$^{-5}$) of clay minerals from rivers draining volcanic terrains, as compiled by Bayon et al. (2015). In comparison, the average Nd/Si ratio of volcanic rocks from the Cascade Arc is 1.7 $\times$ 10$^{-5}$, similar to that of basalt glass, clinopyroxene and clay, but 1-order of magnitude higher than plagioclase. The average $\varepsilon_{Nd}$ of Cascade volcanic rocks is +6.2 $\varepsilon$ which we use for all four silicates. Dissolution parameters for these phases are reported in Supplementary Table 6.

We further assume that during silicate weathering the Nd/Si dissolution rate ratio is the same as the Nd/Si ratio in silicates (i.e., congruent dissolution). In the laboratory dissolution experiment of Pearce et al. (2013), the ratio of gross Nd/Si release, estimated using $\varepsilon_{Nd}$, from three basalt samples at the end of 121 days is ~2.5 $\times$ 10$^{-5}$. This value is similar to the Nd/Si ratio in their basin samples (~2.1 $\times$ 10$^{-5}$), supporting our assumption. No other experimental studies of Nd and $\varepsilon_{Nd}$ during silicate dissolution exist to our knowledge, thus whether this assumption is true for other silicates is presently not tested.

Field-derived weathering rates are often lower than laboratory-derived values, a conundrum that has been attributed to inadequate dissolution rate laws, the loss of reactive surface sites due to occlusion, fluid transport limitation and the influence of secondary phases on saturation state (e.g., Maher et al., 2006). For example, Maher et al. (2006) suggested that the plagioclase dissolution rate in deep-sea sediments is 10$^5$ times lower than in the laboratory for the linear TST rate law at their study site. To investigate our model sensitivity, we vary the silicate dissolution rates by 6 orders of magnitude, from the laboratory-derived rates to values 1 to 5 orders of magnitude lower.

At higher dissolution rates, silicates are quickly consumed, while at lower rates greater amounts of minerals are preserved (Fig. 5). The modeled pore water Nd concentration, however, do not respond linearly to changes of dissolution rate (Fig. 5–6). In the upper sediment (<10 cm), dissolved Nd still largely agrees with the observed concentrations (Fig. 6), as silicate Nd release at even the highest dissolution rates are slower than Nd release from MnO$_2$/NdPO$_4$ (Fig. 3). In the deeper sediment, modeled dissolved Nd exceeds the measured values at intermediate dissolution rates, but neither with the highest nor lowest rates: the former because the silicates are spent and the latter because dissolution is slow at all depths. Modeled dissolved Si is subject to a similar influence (Fig. 5).

Model sensitivity also depends on mineral abundance, Nd/Si ratio and solubility (Fig. 5–6). Modeled Nd, Si concentrations and $\varepsilon_{Nd}$ are not sensitive to dissolution of basaltic glass nor clinopyroxene because their Nd and Si reservoirs are small due to low abundance at the study site (Fig. 5a–h, 6a–h). In contrast, modeled Si concentration is very sensitive to plagioclase dissolution (Fig. 5i–l) because it is more abundant and thus has greater potential to affect pore water chemistry, such as pH. This in turn drives large changes of Nd speciation and dissolved Nd concentration (Fig. 6i). The influence on $\varepsilon_{Nd}$ is however limited too because low Nd/Si in plagioclase leads to a small Nd reservoir. In comparison, despite a relatively high abundance and large Nd reservoir, modeled $\varepsilon_{Nd}$ is not much more sensitive to plagioclase dissolution rates because of its relatively low solubility (Fig. 5m–p, 6m–p).

5.2.2. Best-fit silicate weathering models

Considering the fit to observed pore water $\varepsilon_{Nd}$, Nd and Si concentrations, the best-fit models include the weathering of volcanic phases such as basaltic glass and clinopyroxene, at dissolution rates within 2 orders of magnitude of laboratory-derived rates (Fig. 5a–h, 6a–h), and with their presence at <2 wt%. This relatively high reactivity may be explained by their “freshness,” because of direct volcanic ash deposition, or fast physical erosion of volcanic rocks in the Costal Range and Cascade Arc, coupled to short transport times in coastal rivers and efficient dispersal
of fluvial sediments on the Oregon margin (Wheatcroft and Sommerfield, 2005). In contrast, to explain pore water $\varepsilon_{\text{Nd}}$ requires that nearly all plagioclase dissolves, inconsistent with its observed abundance at $\sim$20 wt%. The model using chlorite cannot fit Nd concentration and $\varepsilon_{\text{Nd}}$ simultaneously, and its abundance at $\sim$10 wt% also suggests it is likely not reactive. The inferred low reactivity of plagioclase and chlorite implies that at site HH3000 these minerals are probably not of volcanic origin (i.e., sedimentary or metamorphic), and have experienced loss of reactivity before reaching the seafloor.

Adding silicate weathering increases diffusive benthic Nd fluxes from 39 pmol/cm²/yr in the baseline model to 41–42 pmol/cm²/yr in the best-fit models (the range is given for basalt weathering using dissolution rates that are $10^{-1}$ to $10^{0}$ times of laboratory-derived rate). Thus, the impact of silicate weathering on the elemental Nd benthic flux is likely non-measurable at site HH3000. In contrast, the $\varepsilon_{\text{Nd}}$ of the flux increases from $-2.4 \varepsilon$ to $-1.7 \sim -1.3 \varepsilon$, a significant difference given the analytical uncertainty ($2\sigma = 0.27 \varepsilon$). Modeled pore water $\varepsilon_{\text{Nd}}$ is more radiogenic than bottom water ($-2.4 \varepsilon$), and importantly, the trend of pore water

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**Fig. 5.** Model sensitivity to silicate dissolution rate. (a) Nd release rate by basalt dissolution. (b) Basalt concentration. (c) Dissolved silica. Red dots indicate measurements. (d) Basalt saturation index. Red dashed line indicates saturation. The color legend in (a) indicates the orders of magnitude of dissolution rate reduction in the sensitivity tests. “1e0” means dissolution rate is the same as the laboratory-derived value. “1e1” means a dissolution rate that is 1-order of magnitude lower etc. (e–h) are the same as (a–d) but for clinopyroxene. (i–l) are for plagioclase, and (m–p) are for chlorite.
Fig. 6. Sensitivity of the Nd cycle to silicate weathering. (a–d) Pore water Nd, authigenic Nd, pore water $\varepsilon_{\text{Nd}}$, and authigenic $\varepsilon_{\text{Nd}}$ respectively in the basalt weathering sensitivity tests. The color legend in (a) indicates the orders of magnitude of dissolution rate reduction in the sensitivity tests as in Fig. 5. Red dots indicate direct measurements, except that authigenic Nd and $\varepsilon_{\text{Nd}}$ are estimated using an operationally defined acid-reductive leach. In (c–d) the $2\sigma$ analytical errors of $\varepsilon_{\text{Nd}}$ are shown. (e–h), (i–l) and (m–p) are the results of model tests with weathering of clinopyroxene, plagioclase and chlorite respectively.

$\varepsilon_{\text{Nd}}$ deviating toward bottom water $\varepsilon_{\text{Nd}}$ at $\sim$5 cm is reproduced (Fig. 6c, 6g). This depth is where MnO$_2$ reduction rate is at a maximum, and thus is the peak release for seawater derived Nd (Fig. 3d). Modeled authigenic $\varepsilon_{\text{Nd}}$ is similar to pore water, but has a smoother profile (Fig. 6d, 6h), as authigenic phases integrate over longer timescales and are subject to bioturbation. However, modeled authigenic $\varepsilon_{\text{Nd}}$ is still not as radiogenic as the operationally defined leachate $\varepsilon_{\text{Nd}}$ (Abbott et al., 2016), suggesting that the leach likely extracts some non-authigenic components that are refractory under in situ sediment conditions but reactive in laboratory leaching (Abbott et al., 2022, 2016; Du et al., 2016). If the lower pH and wash off of major cations during leaching increases the dissolution rates and under-saturation of silicate minerals like plagioclase and chlorite, enough silicate Nd could be released, just as our model demonstrates (Fig. 6p). At site HH3000, a combination of $\sim$8.5 ppm truly authigenic Nd ($\sim$1.8 $\varepsilon$) with $\sim$0.5 ppm Nd extracted from silicates ($\sim$6.2 $\varepsilon$), can explain the leachate Nd ($\sim$9 ppm and $\sim$−1.2 $\varepsilon$).
5.3. Reverse weathering

Authigenic clay formation during reverse weathering can affect the satiation state of primary silicates by influencing pore water Al concentration (Maher et al., 2006), thus indirectly controlling the diagenetic Nd cycle. In the “best-fit” silicate weathering models discussed above, we included reverse weathering using an authigenic illite precipitation rate of $10^{-15}$ mol/m$^2$/s, as suggested by a previous study (Maher et al., 2006), but ~6 orders of magnitude lower than laboratory-derived rates (Marty et al., 2015).

We ran further sensitivity tests of the influence of reverse weathering by varying the authigenic illite precipitation rate (Fig. 7): $10^{-13}$ mol/m$^2$/s in the “normal clay” model; $10^{-16}$ in the “fast clay”; $10^{-22}$ in the “slow clay”, and 0 in the “no clay” (no reverse weathering) models. At the study site illite is also a detrital mineral through riverine input (VanLaningham et al., 2008). Therefore, in the model, we add a detrital illite flux that represents 2 wt% of the total sediment. We model the total illite concentration, with the authigenic fraction as the excess above the detrital input. In these tests we include basalt weathering as discussed previously, at a dissolution rate $10^{-1}$ times the laboratory-derived value.

Close to the SWI (~0.2 cm), modeled Al and Si concentrations are positively correlated because of co-release by basalt and opal dissolution, but they become anti-correlated at depth because of authigenic illite formation, except in the “no clay” model wherein the positive correlation persists (Fig. 7e–f, 8). At depth, the Al concentration converges to equilibrium values with respect to illite solubility in the “fast clay” model, but reaches an asymptote to values that are congruent to Si with respect toopal in the “no clay” model. Pore water total dissolved Al in the upper sediment increases from ~1 nM in the “fast clay” model to ~1000 nM in the “no clay” model (Fig. 7e), reducing basalt under-saturation, until over-saturation (Fig. 7g). Authigenic illite concentration is <1.2 wt% in all models.

Pore water Al was not measured at HH3000. We compare the modeled Al-Si relationship with published seawater and pore water data to evaluate if model results are reasonable (Fig. 8). Al-Si trends in the “fast clay” and “normal clay” models follow that of deep ocean water (GEOTRACES Intermediate Data Product Group, 2021) and East China Sea pore water (Mackin and Aller, 1984). Al-Si trends in the “normal clay” and “slow clay” models bracket pore water data from the North Atlantic, Southern Ocean and Amazon shelf (Mackin and Aller, 1986, 1986; Stoffyn-Egli, 1982; Van Beusekom et al., 1997). The Al speciation in the model considers only hydrolysis, but if other ligands are present, which is likely in reality, then the same free Al$^{3+}$ concentration in the model would lead to greater total Al concentrations. Thus the modeled
total Al concentration is likely a lower limit. Overall, we consider the “normal clay” model the best option given its consistency with literature data and the uncertainty in Al speciation. As long as the precipitation rate is higher than in the “slow clay” model, reverse weathering will drive basalt weathering, and modeled pore water $\varepsilon_{Nd}$ will agree with observations (Fig. 7i).

Finally, whether Nd is directly incorporated into authigenic clay is unknown. If it is, and assuming the same Nd/Si ratio as primary silicates, the authigenic ilite sink for Nd ($<3$ pmol/cm$^2$/yr) (Fig. 7a) would be much smaller than the phosphate sink ($\sim 200$ pmol/cm$^2$/yr) (Fig. 3d), and thus negligible.

6. Implications and perspectives

The modeled diagenetic Nd cycle at the study site is summarized in Fig. 9. Our aim was to investigate the roles of commonly suggested sedimentary processes, rather than comprehensively consider all potential processes. That the model successfully simulated observations indicates co-cycling with Fe/Mn, authigenic phosphate formation, silicate weathering and reverse weathering are indeed among the most important at the study site. Future studies should aim to examine other potential processes, such as the role of organic ligands and colloids in pore water.

Our study paves the way for modeling diagenetic Nd cycling at other sites and regions where the relative contributions of the studied processes may differ. For instance, site HH200 on the Oregon shelf (200 m) has a much larger pore water to bottom water $\varepsilon_{Nd}$ difference (+1.6 $\varepsilon$) than the study site HH3000 (+0.6 $\varepsilon$), corresponding to a greater abundance of volcanic phases like glass and clinopyroxene in sediments (Abbott et al., 2019). One would thus expect silicate weathering to be more important than at the deep-sea site HH3000.

Our study also has global implications. With authigenesis alone, a benthic flux only produces regenerated Nd (Fig. 9), with significant impact on the oceanic budget of Nd concentration but not $\varepsilon_{Nd}$. In contrast, silicate weathering produces a new external source of Nd (Fig. 9), which may have a small impact on the Nd concentration but a significant one on $\varepsilon_{Nd}$, particularly when the $\varepsilon_{Nd}$ difference between seawater and reactive silicate phases is large. This contrast in elemental versus isotopic sensitivity mirrors seawater observations and implies that diagenetic transformation at the SWI is likely a key component of Boundary Exchange (Jandel, 2016). The apparent conservative behavior of seawater $\varepsilon_{Nd}$ in the presence of non-conservative Nd concentration due to benthic flux can be preserved in the first case but not in the second. The reality is likely somewhere in-between (Du et al., 2020). We suggest the differing response of Nd concentration versus $\varepsilon_{Nd}$ to the benthic flux is key to resolving the “Nd paradox” (Goldstein and Hemming, 2003).

Our results may also explain why, globally, benthic Nd fluxes do not correlate to redox parameters such as bottom water oxygen and OC rain rate (Du et al., 2018). For example, strong redox cycling on the continental shelf does not convert to high benthic Nd flux (Abbott et al., 2015b; Deng et al., 2022) as it does for Fe and Mn (McManus et al., 2012, 1997). We suggest that the non-redox-sensitive Nd sink (phosphate) may play a more important role than the redox-sensitive source (Fe/Mn oxides). If phosphate precipitation/dissolution is fast enough, pore water Nd concentrations will be largely controlled by phosphate solubility, and only weakly dependent on redox cycling.

Our model illustrates the indispensable role of pore water TEI data in constraining diagenetic processes and fluxes across the SWI. In our best-fit models, with 2 wt% basalt clinopyroxene supply to sediments, only $<0.4$ wt% remains at the surface, and none
below 10 cm. Such small fractions are virtually undetectable by solid phase analysis methods, let alone when the solid phases have disappeared completely and leave only an imprint on pore water. Thus, it is not possible to study such processes using solid phase analysis alone: pore water TEs may be our only source of evidence.

The processes investigated here also affect the diagenesis of other TEs (Little et al., 2020; Jeandel, 2016). Presently, the application of diagenetic modeling to TEs is limited by the scarcity of comprehensive pore water data and measurements of the fluxes of all solid components into sediments. As fluxes at the SWI are increasingly seen to be a key part of the global ocean budgets of TEs (Homokey et al., 2016), it is important for further pore water and sediment trap TEs studies, as extensions of the GEOTRACES water column surveys.

7. Conclusions

We created the first reactive-transfer model for Nd and \( \varepsilon_{\text{Nd}} \) in marine sediments, and quantified the roles of authigenesis, silicate weathering and reverse weathering in the early diagenetic Nd cycle at the deep-sea site HH3000 on the Oregon margin.

The model correctly captured the biogeochemical processes at the site and successfully simulated the observed pore water Nd profile using the co-precipitation formulation of Nd co-cycling with Fe/Mn and authigenic phosphate formation. In the simulation, we found that MnO₂ reduction is the main source of Nd in pore water, phosphate formation is the main sink, and Fe cycling plays a minor role. Benthic Nd flux is mainly driven by MnO₂ reduction and phosphate dissolution close to the SWI. In contrast, the model cannot reproduce the pore water Nd profile via the reversible scavenging formulation of Nd co-cycling with Fe/Mn.

We further included silicate weathering and reverse weathering to simulate pore water Nd. We studied the model’s sensitivity to the dissolution of basaltic glass, clinopyroxene, plagioclase and chlorite, representing a wide range of mineral reactivity, abundance and solubility. The model correctly simulated pore water Nd (and other data) if it includes the weathering of basaltic glass or clinopyroxene with relatively high dissolution rates, supporting the hypothesis that weathering of volcanic sediments is responsible for the relatively more radiogenic Nd of pore water and authigenic phases in the Pacific. Furthermore, we show that reverse weathering is necessary to maintain relatively low pore water Nd concentrations, thus enabling the undersaturation of primary silicates and indirectly contributing to the diagenetic Nd cycle.

Data availability

Model output from this study can be found at: https://doi.org/10.5281/zenodo.6998239.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.epsl.2022.117792.

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