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Dominance of benthic flux of REEs on continental shelves: implications for oceanic budgets

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Abstract

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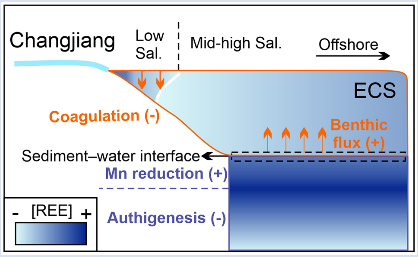

Rare earth elements (REEs) are powerful tools to track oceanic biogeochemical processes. However, our understanding of REE sources is incomplete, leading to controversial interpretations regarding their oceanic cycling. Continental margin sediments are often assumed to be a major source, but the sediment pore water data required to understand the processes controlling that potential source are scarce. Here, we measure and compile pore water and estuarine REE data from the Changjiang (Yangtze) estuary–East China Sea shelf. We show that release of REEs, from shallow pore water to overlying seawater, is coupled to Mn reduction. In contrast, REEs are removed in deep pore water, perhaps via formation of an authigenic REE-bearing phase. This sedimentary source can potentially explain REE addition in the estuary at mid-high salinity. Our calculations suggest that the benthic flux is the largest Nd source (~40 %) on the East China Sea shelf. Globally, however, despite a higher benthic Nd flux on the advection-dominated shelf, the much more extensive deep ocean still dominates the total area-integrated benthic flux. Our results call for a more extensive investigation of the magnitude of the benthic flux of REEs to the oceans.

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Introduction

The rare earth elements (REEs), as a series of particle-reactive elements, show non-conservative behaviour during transport from continental source to oceanic sink (Elderfield and Greaves, 1982; Rousseau *et al.*, 2015). As such, REE patterns are widely used in oceanographic studies, to track boundary exchange and internal cycling (Elderfield and Greaves, 1982; Jeandel and Oelkers, 2015). Nevertheless, source-to-sink processes for oceanic REEs remain poorly understood. Two hypotheses have been proposed to explain oceanic REE distributions: the top-down (Siddall *et al.*, 2008) *versus* the bottom-up control (Abbott *et al.*, 2015; Du *et al.*, 2020). The former emphasises reversible scavenging, while the latter focuses on the dominance of benthic processes. The resolution of this debate would provide valuable insights on the long-standing "Nd (Neodymium) paradox": while Nd isotopes appear to behave conservatively during water mass mixing, dissolved Nd concentrations ([Nd]$_{\text{diss}}$) reflect the behaviour of a reactive element (Arsouze *et al.*, 2009; Haley *et al.*, 2017). Such inconsistency impedes the application of Nd isotopes as a tracer for paleo-circulation (Du *et al.*, 2020; Patton *et al.*, 2021).

The ambiguities in the oceanic REE cycling and budget are partially caused by incomplete understanding of REE sources. The mass balance of oceanic REEs requires sources other than riverine input and atmospheric deposition (Elderfield and Greaves, 1982), such as a benthic dissolved flux across the sediment–water interface via porewater (Abbott *et al.*, 2015; Du *et al.*, 2016) and/or submarine groundwater discharge (Johannesson *et al.*, 2011). In particular, recent modelling efforts suggest that continental margin sediments can be a major source of oceanic REEs (Arsouze *et al.*, 2009; Rempfer *et al.*, 2011). On continental margins, isolating the contribution of a sedimentary REE flux to seawater is particularly difficult because of the complex interaction between riverine input, oceanic currents, and benthic processes. Dissolved REEs have been measured in many estuarine transects and an additional sedimentary source is often proposed to explain their spatial distribution (Wang and Liu, 2008; Rousseau *et al.*, 2015). However, the corresponding sediment porewater REE data, which provide the direct evidence for a benthic flux, are still scarce.

Here, we focus on one of the largest land–ocean interfaces in Asia, the Changjiang (Yangtze) River–East China Sea system. The Changjiang River delivers a huge amount of fresh water (~890 km^3/yr) and sediment (~450 Mt/yr) to the continental margin (Chen *et al.*, 2001), accounting for 2–3 % of global discharge. The East China Sea is characterised by one of the widest continental shelves (shelf area: ~5×10^5 km^2) and highest sedimentation rate (inner shelf: ~1–6 cm/yr) worldwide (Liu *et al.*, 2006). The high dissolved–particulate riverine fluxes make this region ideal for studying the effect of boundary exchange on REE cycling. This paper presents REE data for shelf sediment porewater profiles, as well as for estuarine water from this study and the literature. The main aim is to investigate REE cycling on the East China Sea shelf, with an emphasis on benthic processes,

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and to provide new insights on the role of the continental shelf in the global benthic REE flux.

REE Cycling on the Shelf

Along the salinity transect in the Changjiang estuary, estuarine $[\mathrm{REE}]_{\mathrm{diss}}$ decreases dramatically at salinity <1–2 psu, driven by scavenging, and gradually increases at mid-high salinity (Fig. S-3), hinting at a potential marine sedimentary source (Wang and Liu, 2008). We measured porewater $[\mathrm{REE}]_{\mathrm{diss}}$ for four multi-core stations at water depths of 6–46 m (Figs. 1, 2; locations in Fig. S-1). $[\mathrm{REE}]_{\mathrm{diss}}$ of shallow porewater is generally higher than that for bottom water, consistent with observations from other continental margins and with release of porewater REEs to the overlying seawater (Haley *et al.*, 2004; Abbott *et al.*, 2015).

At the shallowest site, C6-1 at 6 m, the REE patterns are relatively invariant (Fig. 1). However, porewater $[\mathrm{REE}]_{\mathrm{diss}}$ increases with core depth, implying a diagenetic source below the studied depth range and upward diffusion. The similarity between the porewater $[\mathrm{Mn}]_{\mathrm{diss}}$ and $[\mathrm{REE}]_{\mathrm{diss}}$ profiles (Fig. 2) at C6-1 suggests a source of both at depths at, or beneath, ~20 cm, most likely the reductive dissolution of Mn oxides. Porewaters at C10 (depth: 12 m) are characterised by a maximum in $[\mathrm{REE}]_{\mathrm{diss}}$ at shallow core depth (<7 cm), coincident with a maximum in $[\mathrm{Mn}]_{\mathrm{diss}}$ (Fig. 2). These observations are again consistent with a source of REE linked to Mn reduction. Indeed, REEs are commonly enriched in Mn oxides and they can be released together in a reductive environment (Blaser *et al.*, 2016). The change in porewater REE patterns also supports the control of Mn reduction. The correlation ($R^2 = 0.58$; <7 cm at C10; Fig. S-4) between porewater $[\mathrm{Mn}]_{\mathrm{diss}}$ and Ce anomaly ($\mathrm{Ce/Ce}^*$) values (Eq. S-1) is consistent with the well-known association of Ce with Mn oxyhydroxide (Schijf *et al.*, 2015). Besides, the Mn-Fe leachate from the Changjiang sediment with low ratios of heavy REEs to light REEs (HREE/LREE, Eq. S-2; <1 when normalised to the post-Archean Australian Shale or PAAS) (Wang and Liu, 2008) would release more dissolved LREEs (relative to bottom water) as observed (Fig. 1). In comparison, $[\mathrm{Fe}]_{\mathrm{diss}}$ is generally low (mostly <1 μM) throughout core C6-1 and at shallow depth in C10, and the highest $[\mathrm{Fe}]_{\mathrm{diss}}$ of all cores (at 16 cm of C10) corresponds to the lowest $[\mathrm{Nd}]_{\mathrm{diss}}$ in this core. Hence, either Fe cycling is not the major controlling factor of REEs in either core, or its effect is obscured by other factors.

At depths exceeding ~7 cm in C10, $[\mathrm{LREE}]_{\mathrm{diss}}$ decreases dramatically, accompanied by an HREE-enriched pattern (Fig. 1). This evolution with depth hints at the operation of a second early diagenetic process. Here, lower $[\mathrm{REE}]_{\mathrm{diss}}$ and preferential scavenging of LREEs suggest removal to an authigenic phase. High porewater $[\mathrm{P}]_{\mathrm{diss}}$ at depth (13–24 μM), in contrast to ~1 μM at <4 cm (Fig. 2), could facilitate the precipitation of minor phosphate (Byrne and Kim, 1993). This is consistent with in-situ formation of authigenic P at great sediment depth in this region (Liu *et al.*, 2020), and with the fact that phosphate precipitation would result in an HREE-enriched pattern in solution (Byrne and Kim, 1993).

More LREEs release at shallow core depth and preferential removal at great core depth can also be observed at greater water depth (33 m at C13 and 46 m at B14) (Fig. 1). Specifically, peaks in $[\mathrm{Mn}]_{\mathrm{diss}}$ and $[\mathrm{Nd}]_{\mathrm{diss}}$ are co-located at shallow core depth (≤6 cm; Fig. 2). $[\mathrm{Fe}]_{\mathrm{diss}}$ also peaks at ≤6 cm and thus its effect on $[\mathrm{Nd}]_{\mathrm{diss}}$ is difficult to isolate. For both stations, $[\mathrm{Nd}]_{\mathrm{diss}}$ becomes much lower at great depths (>7 cm) while $[\mathrm{P}]_{\mathrm{diss}}$ remains high (>10 μM). Note that the clear association of high porewater REE abundance and release of more LREEs (relative to bottom water) with Mn reduction could be obscured sometimes: REE concentrations and patterns reflect the competition between diverse sources and sinks, and the contribution of each component likely varies among basins (Haley *et al.*, 2004; Abbott *et al.*, 2015).

To further illustrate REE cycling through the Changjiang Estuary–East China Sea transect, we present the relationship between $\mathrm{Ce/Ce}^*$ and HREE/LREE (Fig. 3). Estuarine scavenging leads to a decrease in $\mathrm{Ce/Ce}^*$ and an increase in HREE/LREE

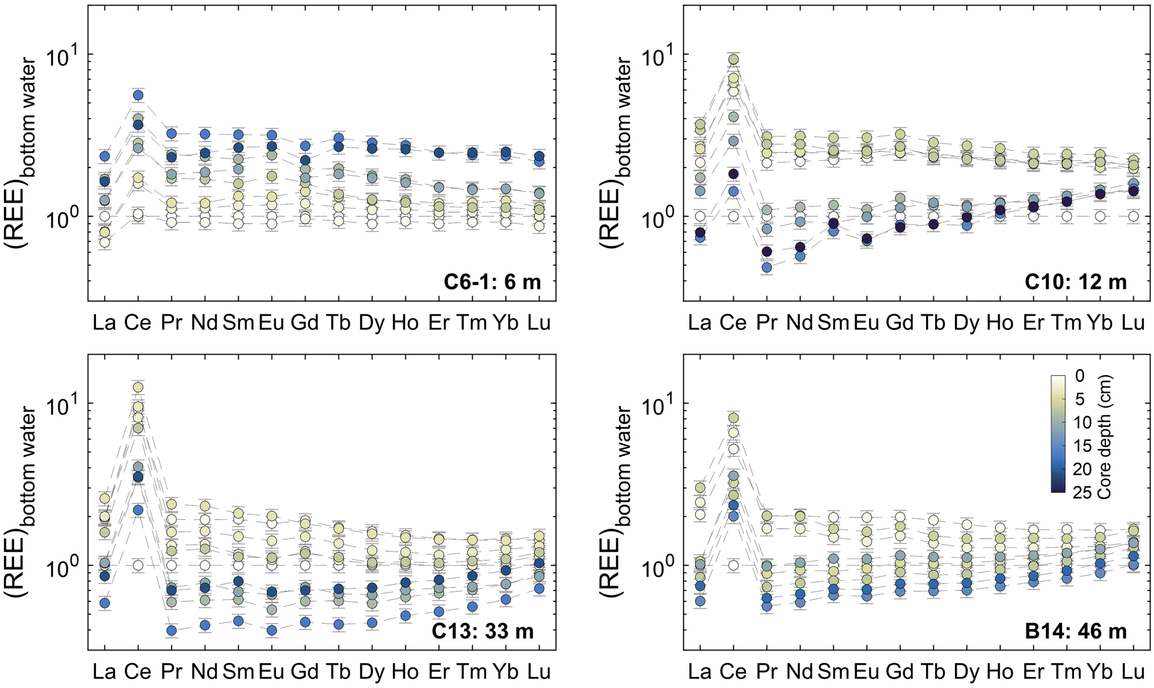

Figure 1 Sediment porewater REE pattern normalised to the bottom seawater (depth of 0 cm) at each station. Analytical uncertainties (see Supplementary Information) are shown here and in later figures.

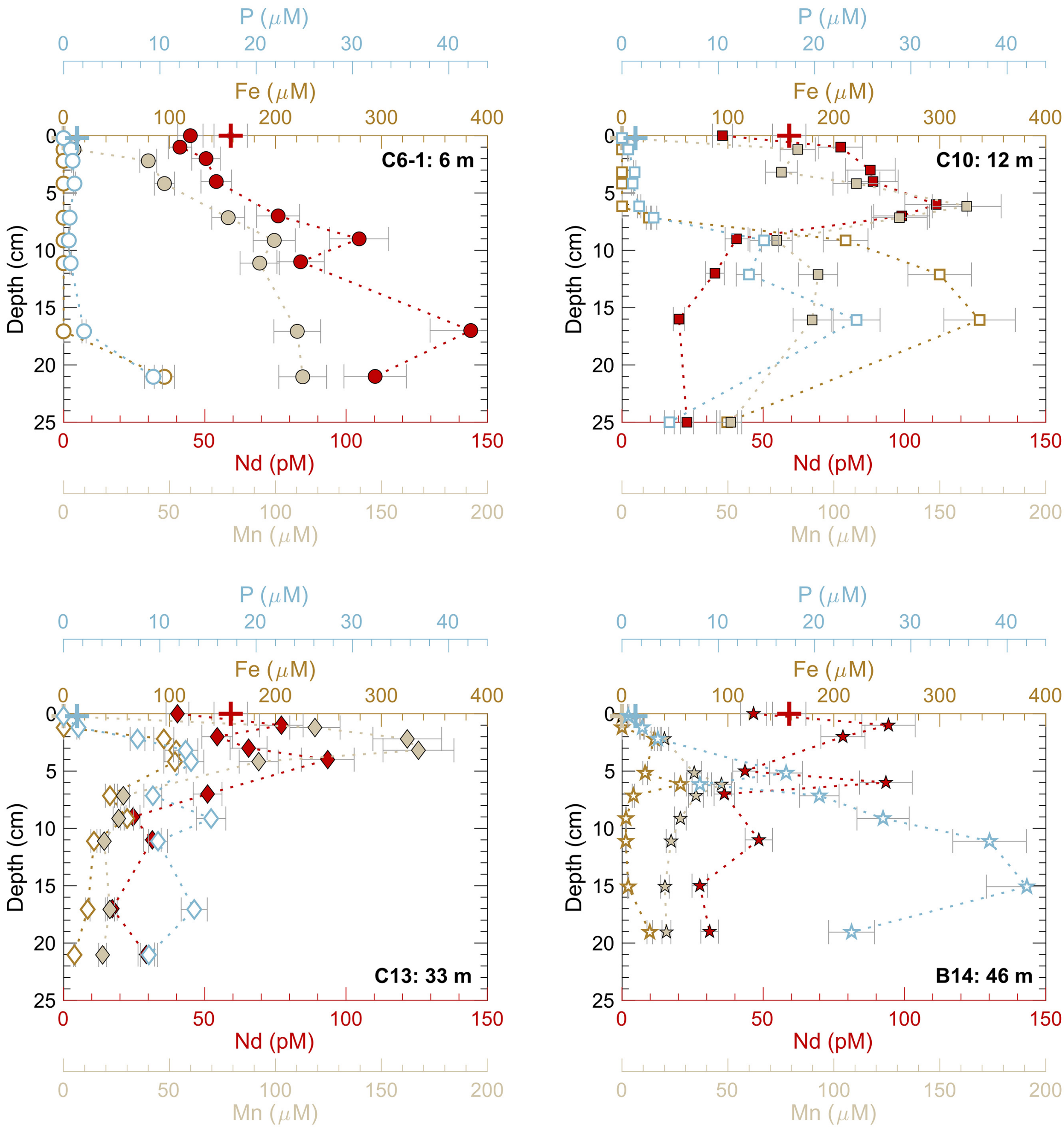

Figure 2 Porewater and bottom seawater (depth of 0 cm) Nd, Mn (filled symbols), Fe and P (open symbols) concentrations. "+" symbols refer to the water sample data at station C1 at 1 m.

(towards seawater end members), while the reductive release of REEs in shallow porewater shows a reverse trend, with lower HREE/LREE and higher Ce/Ce* (towards Mn-Fe leachate). At greater core depth, the REE patterns deviate from those controlled by these two processes and are characterised by a sharp rise in HREE/LREE and only a slight decrease in Ce/Ce*, suggesting the operation of a different process (authigenesis).

Implications for Nd Budget in the Marginal Sea and Global Oceans

Our data are clearly consistent with the interaction between REE scavenging in the estuary and reductive REE release from shallow sediments. We calculate the diffusive Nd flux from sediments based on porewater $[\mathrm{Nd}]_{\mathrm{diss}}$ gradient (Eq. S-5). The diffusive Nd flux is lowest (0.9 pmol/cm^2/yr) at 6 m and increases to a stable level at 6.0 ± 0.8 pmol/cm^2/yr (12–46 m). Figure 4 compares these diffusive fluxes with compiled literature porewater data. Our dataset falls within the global trend (Du *et al.*, 2018, 2020), which shows higher fluxes in the deeper ocean ($R^2 = 0.30$). Furthermore, there is no clear control of bottom dissolved oxygen (DO) on diffusive Nd flux (Abbott *et al.*, 2015), with no correlation between the two (Fig. 4; $p = 0.26$). The spatial trend of diffusive Nd flux is probably affected by multiple depth-related processes. At shallow water depths the exchange between porewater and overlying seawater is fast (Shi *et al.*, 2019; Patton *et al.*, 2021), resulting in a small Nd gradient at sediment–water interface. In comparison, in some deep ocean sediments high reactive authigenic [Nd] might contribute to a high benthic flux (Abbott *et al.*, 2016; Haley *et al.*, 2017).

To estimate the contribution of benthic processes to the Nd budget in the East China Sea shelf, Nd fluxes of all major sources need to be known (Table S-5), including the Changjiang River, atmospheric deposition, the Taiwan Strait Current, the Kuroshio Current intrusion (Liu *et al.*, 2021) and shelf benthic flux. The Changjiang-derived Nd flux (after

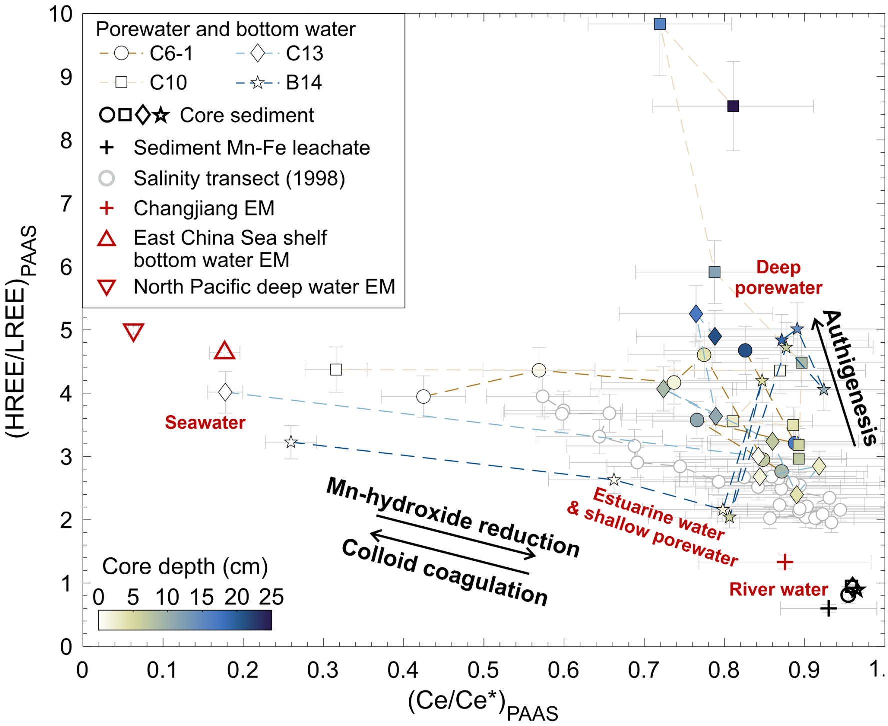

Figure 3 Shelf REE cycling shown by a Ce/Ce*-HREE/LREE plot. REE data for the salinity transect (1998) and Mn-Fe leachate are from Wang and Liu (2008). The data source for water mass end members (EMs) is provided in Figure S-3.

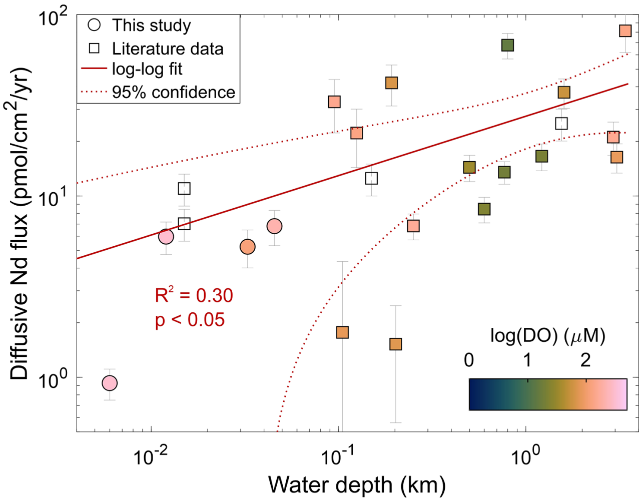

Figure 4 Diffusive sedimentary Nd flux variation with depth. The coloured symbols indicate bottom water DO and open symbols are those with no DO data available. Axes and colour bar are on log scale. Compiled dataset and references are provided in Table S-4.

estuarine scavenging) and the atmospheric input are $2.7 \pm 0.4 \times 10^4$ mol/yr and $1.7 \pm 0.4 \times 10^4$ mol/yr, respectively. In comparison, Nd fluxes from the Taiwan Strait Current and the intrusion of the Kuroshio Current are much higher at $21.6 \pm 3.8 \times 10^4$ mol/yr and $25.2 \pm 4.4 \times 10^4$ mol/yr, respectively (Table S-5). Given the similar porewater REE behaviours (Fig. 1) and small flux variability (Table S-4) at depth of ≥12 m, we use the average diffusion-based flux estimate (6.0 pmol/cm^2/yr) at this depth range for area extrapolation. The diffusive Nd flux in the whole East China Sea shelf is $3.0 \pm 0.4 \times 10^4$ mol/yr, higher than the riverine input. Furthermore, on the continental shelf, with dynamic hydraulic environments, advection via *e.g.*, bio-irrigation, rather than diffusion, may play the dominant role in benthic flux of trace metals (Shi *et al.*, 2019), implying a higher benthic flux. The benthic Nd flux accounting for advection processes can be estimated using Equations S-7 and S-8 (Shi *et al.*, 2019). The area-extrapolated advective Nd flux ($30.8 \pm 4.0 \times 10^4$ mol/yr; Table S-5) is ~10-fold higher than the diffusion-based estimate and becomes the largest source on the East China Sea shelf (38 % of the total input).

Our observations and calculations emphasise the role of benthic processes in the Nd cycling of marginal seas, and can provide valuable insights on the global sedimentary Nd flux. The best estimate so far (Abbott *et al.*, 2015; Du *et al.*, 2020) suggests a global benthic Nd flux of 115×10^6 mol/yr, assuming the dominance of diffusion process. However, advection may play a key role in the benthic Nd flux from the continental shelf (0–200 m). Hence, we can revise the shelf estimate by replacing it (~32 pmol/cm^2/yr) with our advection-based estimate (~62 pmol/cm^2/yr), considering that the average depth of our studied shelf (72 m) is close to the global average shelf depth (~60 m) and most global observations (73 %; World Ocean Database 2018, Boyer *et al.*, 2018) on shelves show a bottom water DO within our studied range (Table S-1). Despite the implied increase in the shelf-derived flux, the continental shelf only accounts for 14 % of the global area-integrated benthic Nd flux. This contrasts with previous thoughts that the sedimentary source is mainly from shallow water depths (*e.g.*, continental shelves); in fact, much more extensive deep oceans may dominate the benthic Nd source (Haley *et al.*, 2017; Du *et al.*, 2020). We thus suggest that future ocean models should reconsider the spatial pattern of this sedimentary source. Our results highlight the need for precise constraints on the benthic source if REE/Nd isotopes are to be robustly used as process/source tracer in both marginal seas and on global scales.

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2223.

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