Neodymium isotopes as a new tool for quantifying exchange fluxes at the continent–ocean interface

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Abstract

Continental margins are, via river sediment discharges, the major source of a number of elements to the ocean. They are also, for several reactive elements, sites of preferential removal from the water column, due to enhanced scavenging [1] [M.P. Bacon, Tracers of chemical scavenging in the ocean: Boundary effects and large-scale chemical fractionation, Philos. Trans. R. Soc. Lond., A 325 (1988) 147–160]. They can therefore be understood as sources of elements for the ocean, sinks or both. Although exchanges of matter are suspected to occur at the continent/ocean interface [2] [P.H. Santschi, L. Guo, I.D. Walsh, M.S. Quigley, M. Baskaran, Boundary exchange and scavenging of radionuclides in continental margin waters of the Middle Atlantic Bight: implications for organic carbon fluxes, Cont. Shelf Res. 19 (1999) 609–636.] and despite their probable importance for the ocean chemistry, closed budgets have still yet to be determined. Here, based on neodymium isotopic composition data obtained during the past 6 yr, we document and quantify significant neodymium exchange at ocean boundaries, in areas covering a large spectra of hydrographical, biological and geochemical characteristics : Eastern Indian Ocean, Western Equatorial Pacific, Western Tropical Pacific and Northwestern Atlantic, with neodymium removal fluxes accounting for 74±23%, 100±38%, 62±54% and 84±45% of the neodymium input fluxes, respectively. Recognition of boundary exchange and its potential globalization have important implications for (1) our understanding of margin/ocean interactions and their influence on the oceanic isotopic chemistry, and (2) geochemical cycling of reactive elements (including pollutants) at ocean margins.

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1. Introduction

Continental margins occupy less than 20% of the surface area of the world ocean. However, they are regions of enhanced biological production and thus were estimated to be as important as the open ocean in
the carbon and nitrogen cycles [3]. Whereas upwelling waters seem to provide 90% of the nitrate required to sustain primary production above the margins, river inputs are the main sources of silica and phosphate into the ocean [3–5]. In addition, the strong diffusive and advective fluxes characterizing these areas yield water mass exchanges between the shelf/slope and open ocean [6,7] as well as resuspension of sediments on continental shelves and export of resuspended sediments to deeper waters [8,9]. These processes may have two inverse effects: (1) river inputs being the source of most of the elements in the ocean (essentially the lithogenic and anthropogenic ones), water mass mixing and lateral transport of resuspended sediments may enhance the continent to ocean transfer of these elements, (2) on the opposite, the continent/ocean interface is often understood as a sink for a number of elements. Particle fluxes being much greater in ocean margins than in the open ocean, they yield more efficient removal of the reactive elements from the water column in these areas. Depending on their residence time (i.e. their sensitivity to scavenging), some reactive elements remain under the dissolved form sufficiently long to be transported by lateral mixing from the center of a gyre to areas as continental margins, where strong particle fluxes will remove them actively towards the sediment. The combination of lateral mixing of ocean waters and lateral gradients in particle fluxes leading to enhanced deposition together with fractionation of particle-reactive substances is called boundary scavenging [1,8,10,11]).

Therefore, continental margins can be understood either as a source of elements for the ocean or as a sink, or both. Santschi et al. [2] showed that strong scavenging affects the whole water column of the Middle Atlantic Bight continental slope leading to the inshore transport of dissolved species, followed by their removal and the offshore transport of particulate species, including carbon. Simultaneously, their $^{228}$Ra/$^{226}$Ra data suggest that exchanges affect the benthic boundary layer water mass composition.

Although exchanges of water, chemical species and matter are suspected to occur at the continent/ocean interface, and despite the importance of these processes for the biogeochemical cycles, closed budgets have still yet to be determined and quantifications of these processes are scarce. Estimation of long term particle and dissolved export rates on large scales by direct observations is difficult because of the episodic nature of the processes, the different nature/behavior of the already studied margins and the need of long time series of data [12]. Indirect approaches are possible by the use of tracers that allow following long term fate of particles and their bound substances. Such an approach was developed by Bacon et al. [12] using $^{210}$Pb.

The neodymium isotopic composition (Nd IC) is expressed as $\varepsilon_{\text{Nd}}$, defined by:

$$
\varepsilon_{\text{Nd}} = \left( \frac{\frac{^{144}\text{Nd}}{^{142}\text{Nd}} \text{Sample}}{\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \text{CHUR}} - 1 \right) \times 10^4 \quad (1)
$$

Where CHUR stands for Chondritic Uniform Reservoir and represents a present day average earth value; $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}}=0.512638$ [13]. The Nd IC of the continents is heterogeneous, varying from $-45$ in old granitic cratons to $+12$ in recent mid oceanic ridge basalts [14]. Nd ICs of marine lithogenic particles are therefore used to follow their pathways [15,16]. In the ocean, Nd is a trace element (concentrations of the order of $10^{-12}$ g g$^{-1}$), predominantly found in the dissolved form (90–95% [17]). Its residence time is around 500 to 1000 yr [14]. The oceanic Nd IC distribution is heterogeneous, as shown on the compilation of 544 $\varepsilon_{\text{Nd}}$ data (Fig. 1), varying from $-25$ in the extreme North West Atlantic to 0 in the North Pacific. On first order, this variation reflects the dominant imprint of the surrounding continent of each oceanic basin [18]. In the absence of lithogenic input, $\varepsilon_{\text{Nd}}$ behaves conservatively in the ocean and since variations have been observed between the different water masses of the same water column, it is used as a water mass tracer [18–21]. On the other hand, in the presence of lithogenic inputs (aeolian, riverine or derived from the sediments), this tracer is no more conservative. The processes by which water masses acquire their Nd signatures remain unclear. Previous studies underlined the role of sediment/water mass interactions in this acquisition ([22–24] and references therein). Remobilization of Rare Earth Elements (REE) during early diagenesis has already been suggested as a potential source to the overlying seawater [25–29], but precise quantifications are still lacking. This work exploits a compilation of Nd IC data obtained at continent/ocean boundaries allowing (1) evidencing that significant dissolved/partic-
ulate exchange occurs at the ocean boundaries and (2) quantifying this exchange. Two set of the data discussed here have been published in works using $\varepsilon_{\text{Nd}}$ as a tracer of water mass origin and mixing, both restricted to intermediate waters along equatorial basaltic margins [20,21]. Data from a third work focused on water mass pathways in the North West Pacific are also used in the present article,
since they were never discussed in term of exchange at the margin [30]. Finally, a new set of data describing Nd IC modifications affecting the North West Atlantic Bottom Water along South Greenland is also presented and discussed. Comparison of these different data sets shows for the first time that exchange is occurring along granitic as well as basaltic margins, under different latitudes, depths, hydrodynamical forcings, erosion regimes and productivity conditions. These results have further reaching implications about (1) our understanding of margin/ocean interactions and their influence on the oceanic isotopic chemistry, and (2) geochemical cycling of reactive elements at ocean margins.

2. Analytical procedures

The analytical procedures corresponding to the published data used in this work can be found in [20,21,31–33]. Concerning the new data set, briefly, for Nd IC measurements: (1) 10 L seawater samples were preconcentrated on a C18 cartridge loaded with a REE complexant (HDEHP/H2MEHP); (2) REE were separated from the remaining seawater matrix by a cationic exchange chromatography; (3) Nd was separated from the other REE by anionic exchange chromatography. Samples were then measured by thermal ionization mass spectrometry (Thermo Finnigan MAT 261, at the Observatoire Midi Pyrénées, Toulouse, France; in static mode, Nd was analyzed as Nd+). The national Rennes Nd standard gave 143Nd/144Nd=0.511962 (2σ, 160 runs), which corresponds to a La Jolla value of 0.511849 [33]. No corrections were applied to measured isotopic ratios. External reproducibility measured on seawater samples was ±0.4 εNd unit. Blank values were ≤700 pg (3.5% of the most depleted sample and 2% on average, which allows neglecting them). Concerning the Nd concentration measurements, REE were extracted from 500 mL seawater samples by iron oxide co-precipitation. The iron was then removed by anionic exchange chromatography. Nd concentrations were determined by isotopic dilution on ICPMS (Perkin Elmer Elan 6000, in the same laboratory). Reproducibility of the Nd concentration measurements was better than 5%. Blanks values were lower than 3%. Internal precision (2σ) lower than 0.2 ppt (part per trillion, i.e. 10⁻¹² g g⁻¹).

3. Results

Fig. 2 and Table 1 display Nd ICs and concentrations for 4 different water masses, upstream and downstream of a continental contact area. As discussed below these sites cover a significant range of hydrographical and biogeochemical properties.

3.1. Data compilation

The sampling sites are displayed in Fig. 2. The data reported in Table 1, in the “Initial, before mixing corrections” and “Final” columns, were compiled as follows: Concerning the North Indian Intermediate Water (NIIW), the upstream and downstream values correspond to one measurement and the average of four measurements, respectively. These samples were taken along the same isopycnal and display very close hydrographical properties (S=34.7, θ=8 °C at depths ranging from 500 to 800 m along the Java margin, and by S=34.8, θ=8 °C at depths ranging from 600 to 800 m in the South Somali Basin) [20,31]. Concerning the Antarctic Intermediate Water (AAIW) in the Pacific Ocean, the upstream and downstream values correspond to one measurement and the average of two measurements, respectively. The samples, collected along the same isopycnal, display similar hydrographical properties (S=34.54, θ=5.3 °C at 835 m depth). Concerning the North Pacific Tropical Water (NPTW) the upstream and downstream values correspond to one measurement and the average of two measurements, respectively. The samples, collected along the same isopycnal, display similar hydrographical properties (S=34.54, θ=5.3 °C at 835 m depth). Concerning the North Pacific Tropical Water (NPTW) the upstream and downstream values correspond to the average of three and two measurements, respectively [19,30,32]. The NPTW is characterized by a vertical salinity maximum (S>34.8) around 250 m depth within the Kuroshio (downstream samples). Since this water mass is believed to be formed by subduction of surface water in the Western Subtropical North Pacific, the upstream samples were taken at the surface and subsurface in the source water region [30]. Hydrographical features of NIIW, AAIW and NPTW are discussed in more details in [20,21,30], respectively. Finally, concerning the North West Atlantic Bottom Water...
(NWABW), the upstream and downstream values correspond to one measurement and the average of two measurements, respectively. These samples were collected at the bottom of the water columns, characterized by local vertical salinity minima and dissolved oxygen maxima ([18] and the Signature/GINS cruise, R/V Marion Dufresne, Institut Paul Emile Victor, August 1999). Since NWABW data are published for the first time here, further details on this hydrography are given below.
Table 1
Neodymium property variations associated with margin/water mass interactions, and related fluxes

<table>
<thead>
<tr>
<th>Water mass</th>
<th>Flow depth (m)</th>
<th>Initial, before mixing corrections</th>
<th>Significance of mixing</th>
<th>Initial Nd conc.</th>
<th>Final Nd conc.</th>
<th>Flow magnitude (10^6 m^3/s)</th>
<th>F_{Nd} Addition (ton (Nd)/yr)</th>
<th>F_{Nd} Removal (ton (Nd)/yr)</th>
<th>F_{Nd} Addition/Removal (%)</th>
<th>Nd sediment discharge (ton (Nd)/yr)</th>
<th>Contact area</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIIW</td>
<td>700</td>
<td>-6.7a 1.7a nil</td>
<td>nil</td>
<td>-6.7a 1.7a</td>
<td>-2.6b 2.2b</td>
<td>1^a</td>
<td>366±233</td>
<td>272±246</td>
<td>74±23</td>
<td>1635</td>
<td>Java Slope (Indonesia)</td>
</tr>
<tr>
<td>AAIW</td>
<td>800</td>
<td>-8.0b 1.4c nil</td>
<td>nil</td>
<td>-8.0b 1.4c</td>
<td>-2.8c 1.4c</td>
<td>7c</td>
<td>70±21</td>
<td>70±39</td>
<td>100±38</td>
<td>7740</td>
<td>Vitiaz Strait (Papua New Guinea)</td>
</tr>
<tr>
<td>NPTW</td>
<td>250</td>
<td>-4.1d 0.6d nil</td>
<td>nil</td>
<td>-4.1d 0.6d</td>
<td>-8.0d 0.9d</td>
<td>-11c</td>
<td>295±240</td>
<td>181±289</td>
<td>62±54</td>
<td>57,354</td>
<td>East China Sea Shelf</td>
</tr>
<tr>
<td>NWABW</td>
<td>2600</td>
<td>-10.5g 2.8g cf. text</td>
<td>nil</td>
<td>-11.6g 2.7g</td>
<td>-13.6b 2.8b</td>
<td>-22l</td>
<td>122±57</td>
<td>103±84</td>
<td>84±45</td>
<td>–</td>
<td>West Greenland and Labrador Slopes</td>
</tr>
</tbody>
</table>

Isotopic compositions (IC) and concentrations for several water masses (NIIW: North Indian Intermediate Water, AAIW: Antarctic Intermediate Water, NPTW: North Pacific Tropical Water and NWABW: North West Atlantic Bottom Water), upstream and downstream of a continental margin contact area (specified). 1 ppt (part per trillion)=10^{-12} g g^{-1}. When hydrographical properties showed the occurrence of water mass mixing (significant only in the case of the NWABW), the latter was taken into account, so that the Nd property variations displayed in the “Initial” and “Final” columns reflect interactions with external sources only (The “Initial before mixing corrections” column display the measured values upstream of the margin; see the Result section). The Nd IC of the input matter is given. F_{Nd} Addition and F_{Nd} Removal are defined in the text; their relative magnitude is given. The water mass and margin Nd IC and concentration uncertainties were determined as follows: (i) when a single data is available, the uncertainty is the standard deviation of the measurement; (ii) when several data are averaged, the uncertainty is the average deviation from the mean. However, to simplify the calculations and increase the result robustness, these uncertainties were set to their maximum values calculated in the four different cases; those are: 0.5 and 2 e_{Nd} units, and 0.2×10^{-12} g/g for the water mass and margin Nd IC and concentration, respectively. Uncertainties for the other parameters were calculated propagating those values.

3.2. Need of external inputs to account for the Nd IC variations

The four water masses display large Nd IC variations (cf. Table 1). Concerning the first 3 water masses (NIIW, AAIW and NPTW), combined hydrodynamical and geochemical studies suggest that the proportion of the Nd property variations which can be attributed to water mass mixing is insignificant [20,21,30]. This results either (1) from the fact that the hydrographical properties within the same water mass remain almost constant and therefore suggest almost no water mass mixing [21], or (2) from the fact that, even when significant mixing could occur, the Nd IC of the surrounding water masses (potentially involved in the mixing) cannot induce the observed variations. Either these Nd IC are similar to that of the studied water mass and are therefore unable to significantly modify it, or they are significantly different, but their isotopic values would lead to a reverse variation than the observed one, which rule out the hypothesis of any mixing effect [20,30].

In the following, we will illustrate this reasoning in the case of the NWABW.

The NWABW (which constitutes the precursor of the lower layer of the North Atlantic Deep Water), flows within the deep western boundary current along the Labrador Sea continental margin (see Fig. 2d). At the southern tip of Greenland, its characteristics are: $\theta=1.29 \, ^\circ C$, $S=34.838$, $[O_2]=9.82 \, \text{mg/L}$, $\varepsilon_{Nd}=-10.5$ and $[Nd]=2.8 \, \text{ppt}$ (R/V Marion Dufresne, cruise FL3519992, station 2, 2800 m, July 1999). Downstream of this current, in the North of the Labrador Sea, its characteristics are: $\theta=1.85$, $S=34.87$, $[O_2]=9.445 \, \text{mg/L}$, $\varepsilon_{Nd}=-14.9$ and [Nd] is unknown (same cruise, station 3, 2430 m, indicated by a cross in Fig. 2d). The hydrographical property variations suggest a significant mixing with the overlying water mass, the North East Atlantic Deep Water (NEADW), characterized by $\theta=2.10 \, ^\circ C$, $S=34.885$, $[O_2]=9.26 \, \text{mg/L}$, $\varepsilon_{Nd}=-12.1$ and [Nd]=2.6 ppt (same cruise, station 2, core of the NEADW, 2550 m, July 1999). Salinity, potential temperature and dissolved oxygen concentration imply mixing proportions of $68\%$, $69\%$ and $66\%$ of NEADW, respectively. The similarity of these results definitely confirms the hypothesis of a water mass mixing. However, considering these mixing proportions and the Nd characteristics of the two end members, the resulting water mass (the one sampled at station 3) should have an $\varepsilon_{Nd}$ of $-11.6$ and a concentration of $2.7 \, \text{ppt}$ (value reported in Table 1 as the initial value). This value is $3.3 \varepsilon_{Nd}$ units larger than the one measured ($-14.9$). Therefore, even though water mass mixing cannot be neglected in this case, this calculation shows that a large $\varepsilon_{Nd}$ decrease can not be explained by water mass mixing and is therefore the result of external inputs.

3.3. Need of exchange fluxes to reconcile the Nd IC and concentration balances

For the four water masses, large Nd IC variations imply the occurrence of external inputs. These variations occur with little or no concentration changes (cf. Table 1). Exchange fluxes (i.e., fluxes from the water mass to the margin in addition to fluxes from the margin to the water mass) are therefore required to explain the data. The goal of the following calculation is only to quantify the fluxes required to balance the data. In particular it does not intent to resolve the processes involved in these exchanges (those could include sediment resuspension, remineralization, dissolution, desorption, scavenging, precipitation, etc.). Therefore we estimated the fluxes using the box model schematized in Fig. 3. Steady state and mass conservation imply the following equations (quantities defined in Fig. 3).

\[
F_W \times [Nd]_{\text{Final}} = F_W \times [Nd]_{\text{Initial}} + F_{\text{Addition}}^{Nd} - F_{\text{Removal}}^{Nd}
\]  \hspace{2cm} (2)

\[
F_W \times [Nd]_{\text{Final}} \times \varepsilon_{Nd}^{\text{Final}} = F_W \times [Nd]_{\text{Initial}} \times \varepsilon_{Nd}^{\text{Initial}} + F_{\text{Addition}}^{Nd} \times \varepsilon_{Nd}^{\text{Addition}} - F_{\text{Removal}}^{Nd} \times \varepsilon_{Nd}^{\text{Final}}
\]  \hspace{2cm} (3)

From which we draw:

\[
F_{\text{Addition}}^{Nd} = F_W \times [Nd]_{\text{Initial}} \times \frac{\varepsilon_{Nd}^{\text{Final}}}{\varepsilon_{Nd}^{\text{Initial}}} - \frac{\varepsilon_{Nd}^{\text{Initial}}}{\varepsilon_{Nd}^{\text{Addition}}} - \frac{\varepsilon_{Nd}^{\text{Addition}}}{\varepsilon_{Nd}^{\text{Final}}}
\]  \hspace{2cm} (4)

\[
F_{\text{Removal}}^{Nd} = F_W \times \frac{[Nd]_{\text{Final}} \times (\varepsilon_{Nd}^{\text{Final}} - \varepsilon_{Nd}^{\text{Addition}}) - [Nd]_{\text{Initial}} \times (\varepsilon_{Nd}^{\text{Initial}} - \varepsilon_{Nd}^{\text{Addition}})}{\varepsilon_{Nd}^{\text{Addition}} - \varepsilon_{Nd}^{\text{Final}}}
\]  \hspace{2cm} (5)

The lack of time series prevents us to assess the reliability of the steady-state hypothesis. Due to the
variability that could affect the hydrography and surface productivity along these boundaries, the studied systems could not be at steady state, implying different fluxes than those calculated below (which could be either greater or smaller). However, the few data available in other areas submitted to hydrographical variability, e.g. the Denmark Strait and the Faroe Shetland Channel, show remarkably constant values in the course of time, arguing in favor of the steady state hypothesis (for samples taken in 1981 and 1999, respectively: Denmark Strait Overflow Water: $\epsilon_{\text{Nd}}=-8.4$ and $-8.6$ and $[\text{Nd}]=3.2$ and $3.0$ ppt; Iceland Scotland Overflow Water: $\epsilon_{\text{Nd}}=-8.2$ and $-7.7$ and $[\text{Nd}]=3.1$ and $3.1$ ppt [18,23,24]).

The fluxes, calculated for the 4 studied water masses, according to the above equations, are reported in Table 1. $F_{\text{Nd}}^{\text{Removal}}$ represents $62\pm54\%$ of $F_{\text{Nd}}^{\text{Additional}}$ for the NPTW flowing along the East China Sea shelf; in other words, for 100 g of Nd supplied by the margin to the water mass, 62 $\pm$ 54 g are scavenged from the water mass to the margin (cf. Table 1 legend for uncertainty calculations). Concerning the NWABW, flowing along the Labrador Sea continental margin, our data yielded a ratio $(F_{\text{Nd}}^{\text{Removal}}/F_{\text{Nd}}^{\text{Additional}})$ of $84\pm45\%$. Finally, we estimated this ratio to be $74\pm23\%$ and $100\pm38\%$ for the NI IW and the AAIW, respectively, definitely confirming our former hypothesis that exchange processes could occur along the Java and Papua New Guinea margins [20,21].

4. Discussion

Although the above uncertainties remain significant, the present data set seems to constitute a robust evidence of the occurrence of processes that yield exchange fluxes between margins and water masses. In the following, we will name this process “boundary exchange”. The nature, time and space scales of the processes involved are not precisely known and will need further investigations.

The four sites presented here are characterized by contrasting geographical, lithological, and dynamical properties. They range from 250 to 2500 m depth. They are located in contrasting climatic areas, which implies notably different (i) sedimentary sources and fluxes, including various erosion products (river borne and aeolian particles, from different lithologies), and (ii) types of organic matter with different export rates. The water masses overlying these margins also display different dissolved oxygen content. Thus, the reactions within these sediments, which are highly dependent on the organic carbon accumulation rates and the dissolved oxygen contents of the overlying water masses, are likely different among these four margins. Therefore, the following discussion does not intent to draw a unique picture of the boundary exchange, but to summarize the potential processes that could yield such exchange and which relative importance may greatly vary from a site to another. Note also that all types of margins are not represented in our study, in...
particular significant upwelling and oxygen minimum zones are not documented.

4.1. Sources of the external inputs

For all of the water masses reported in Table 1, we suggest that the most likely Nd source is the remobilization—which includes dissolution as well as particle resuspension—of the margin deposited sediments (shelf or slope or both). The following arguments are put forward. (1) Aeolian particles settling within the water column have been shown to enrich surface water REE content without significant influence on deeper layers [25,34]. On the other hand, although REE aeolian inputs can rapidly reach deep waters [17,35], no significant influence on deep water dissolved REE budgets have been evidenced so far [19,36]. Similarly, dissolved riverine and groundwater inputs (having low densities) would also preferentially enrich surface waters. Since all the water masses considered here flow deeper than 250 m and since the corresponding surface waters do not display such enrichment, another source has to be invoked. These water masses flowing along continental margins, sediment/water mass interactions is a good candidate. (2) Above all, sediment remobilization is the only source that is large enough to provide the calculated fluxes, the other sources being orders of magnitudes too low. For instance, dissolved riverine input from the northeastern coast of Papua New Guinea could not account for more than 5% of the AAIW Nd property variations [21], whereas 1% remobilization of the fluvial sediment discharge in that area would be sufficient (cf. Table 1 for sediment discharge data). Similarly, aeolian fluxes along the west Greenland coast of the Labrador Sea could account for only 1% of the flux required to explain the NWABW Nd property variations [25].

4.2. Processes involved

Precise mechanisms yielding sediment/water Nd fluxes at the margins are still poorly documented. Studies in the early eighties already suggested that bottom water REE enrichments in the North East Atlantic could be due to diffusion from pores waters of REE released during early diagenesis and that the magnitude of these fluxes should be considerable [25]. REE concentration measurements have been conducted in pore waters of margin sediments under various diageneric conditions (oxic, suboxic and anoxic) [26–29] and references therein. All these works show that these sediments are significant sources of REE to the pore waters, under both oxic and anoxic conditions, leading to pore water REE concentrations up to 50 times typical seawater values. Some of these works also show the occurrence of significant dissolved REE fluxes from the pore waters to the overlying seawater, under contrasting diageneric conditions, notably with oxic surface layers ranging from 1 mm to 6 cm [25,29]. However, quantifications of such fluxes are still scarce. For instance, Elderfield et al. [26] estimated them to be of similar importance as the dissolved REE input rates from local rivers, in a case study of reducing nearshore sediments.

Although all these works involve diagenesis, the precise processes remain unclear. Most of the studies suggest that REE sources mainly include reduction of iron oxyhydroxides and degradation of organic matter (as well as Ce-oxide reduction in the case of Ce). However, whereas reduction of manganese oxides was traditionally though to be a potential REE source, Haley et al. [29] recently suggested that these are not significant REE carriers. Pore water REE sinks are also uncertain. Whereas REE uptake by phosphate minerals does occur in an oxic deep sea environment [38], we still do not know if it is the case within pore waters. Iron precipitation is well known to effectively scavenge REE. Finally barite formation has also been suggested as a REE sink in pore waters [29].

Despite the complexity of the REE cycling within the sediment/pore water environments, it appears that larger pore water REE concentrations are found in anoxic conditions associated with iron oxyhydroxides reduction (with pore water Nd concentration as high as 170 ppt), whereas much smaller concentrations are found in oxic/suboxic conditions. Moreover, Sholkovitz et al. [27] observed an excellent correlation between the seasonal cycles of REE and Fe in the bottom water of Chesapeake Bay (North West Atlantic), with release of REE into bottom waters during the transition from oxic/suboxic to anoxic conditions. Therefore, one could expect larger REE fluxes from anoxic margins than from oxic/suboxic ones. The reducing character of a margin is notably
enhanced by (i) significant fluxes of organic matter towards the sediments, which itself is favored by large export productions and shallow water columns, and (ii) old water masses having low dissolved oxygen concentration. Moreover, diagenetic reactions are enhanced by high temperature. Therefore, REE fluxes from the sediments to the overlying waters are expected, and have been showed [27], to be subject to large seasonal cycles.

According to Jahnke [39], the four presented margins display benthic oxygen fluxes (which reflect organic matter remineralization), ranging from ca. 0.1 (Papua New Guinea) to ca. 0.3 mol m$^{-2}$ yr$^{-1}$ (South Greenland). However, this range is relatively small compared to values of the order of 0.8 mol m$^{-2}$ yr$^{-1}$ above the most reducing margins (notably in the Eastern Pacific and North Indian oceans). These latter sites need therefore to be documented, since the above discussion suggests that they could yield significantly larger Nd fluxes than those estimated here.

Within the water column, REE scavenging by settling particles and their subsequent burial within the sediments has been widely documented and is likely to play a major role in the Nd removal at the margin ocean interface [17,25,31,35,40]. However most of these studies were conducted in the open ocean and little is known about the specific behavior of REE relative to scavenging near the sediment/seawater interface. Nevertheless, the large particulate fluxes occurring in margin environments (due to large biological and terrigeneous particulate fluxes) and the remobilization of the sediments deposited on the margin by dynamic flows are likely to enhance scavenging processes along this interface. Assuming that scavenging is the main process responsible for the Nd subtraction fluxes evidenced above, we can speculate that this sink is more diffuse than the input fluxes associated with sediment remobilization, since scavenging can occur: (1) throughout the entire water mass thickness (in contrast with sediment remobilization restricted to the interface), (2) not only above the margins, but also upstream and downstream of them (i.e. in the open ocean).

4.3. Role of the hydrodynamical forcing

Boundary exchange could be enhanced by high hydrodynamic conditions. All the margin/water mass interactions reported in Table 1 are located within western boundary currents or straits. Although this does not imply that such processes could not take place elsewhere, we suspect that the high dynamic conditions (strong vertical mixing, internal waves, intensified contour and boundary currents and turbulences etc.) found in such areas could enhance the remobilization of sediment and its dissolution. Moreover, it seems that a high contact area/water mass volume ratio enhances those fluxes. The horizontal dimension being roughly three orders of magnitude larger than the vertical one in the ocean, contact areas involving horizontal parts such as straits or shelves should constitute preferential sites for sediment/water mass interaction.

4.4. Remark about the lithology

Sediment/water mass interactions could also depend on sediment lithology. In this study, we present the first evidences of exchange fluxes along granitic margins. Fig. 1 shows the progressive Nd IC increase, associated with the global thermohaline circulation, from $\approx -13$ in the North Atlantic Ocean, to $\approx -4$ in the North Pacific Ocean. In the present work, we suggest that this evolution takes place mainly along continental margins. However, there is a wide predominance of unradiogenic river sources surrounding the oceans (Amazon $\varepsilon_{\text{Nd}}=-9.2$; Ganges $\varepsilon_{\text{Nd}}=-15.4$; Yellow River $\varepsilon_{\text{Nd}}=-12.6$; etc. [41]). In particular, the fraction of the Pacific Ocean drainage basins composed of acid volcanic rocks and basalts (that are radiogenic enough to yield the North Pacific mean Nd IC) is only $\approx 13\%$ [42]. Therefore, we suspect that sediments derived from those type of rocks are more efficient in modifying water mass Nd IC than other types of sediment. This hypothesis is supported by the fact that acid volcanic rocks and basalts are more rapidly weathered than granites and gneisses [42].

4.5. Globalization

The dataset presented here is still too small to directly extrapolate our conclusions to the global scale. However, the new evidences presented here, along the East China Sea shelf and Labrador Sea margin, in addition to the previous results from the
Indonesian volcanic arc (Java and Papua New Guinea), show that boundary exchange occurs in widely diverse area, characterized by very different lithologies (granitic versus basaltic), latitudes and therefore climates and weathering regimes (equatorial, sub-tropical, subpolar), nature and intensity of primary productivities, water dynamics and depths. This allows expecting that boundary exchange could occur in other areas.

Modeling studies are required to explore the global significance of boundary exchange. The global Nd IC and concentration distributions have been studied with a ten-box ocean model [14]. The authors estimate that aeolian and riverine inputs are insufficient to account for the Nd IC and concentration variations observed among the different oceanic basins. They suggest that continental margins could supply the missing Nd to the ocean. Our data and the necessary reconciliation between Nd IC and concentration variations within a given water mass are a strong evidence that supports their hypothesis.

In order to explore the significance of boundary exchange in the control of the global oceanic cycle of the Nd IC relative to the other fluxes, a parameterization of the Nd boundary exchange has been implemented in an oceanic global circulation model (OPA-ORCA, LSCE France). This ongoing work will be published elsewhere. However preliminary results suggest that boundary exchange could have a similar or even greater importance than net terrigeneous inputs on the global scale.

5. Conclusion

In summary, we showed that particulate/dissolved exchange processes along continental margins are necessary to explain the Nd IC of several water masses in the three oceans and along geologically different margins. It is stipulated for the first time that such processes occur along granitic as well as basaltic margins and in subpolar and subtropical as well as equatorial regions. The diversity of the studied sites suggests that boundary exchange could occur in other areas, opening the way to further investigations. We also showed that Nd IC allows quantifying these processes. Modeling approaches suggest that Nd exchange fluxes could be of the same order of magnitude or larger than net terrigeneous inputs on a global scale. Therefore, instead of considering margins as scavenging boundaries, they could be considered as exchange boundaries for several elements (in other words, both sources and sinks) and we suggest naming this process boundary exchange. It could play a significant role in the oceanic chemistry of many reactive elements and could be an important factor in interpreting sedimentary records. However, we know very little about its spatial and temporal variability, and still need to investigate the precise processes involved. Early diagenesis and scavenging processes are likely key factors controlling Nd sources and sinks, respectively, at the margin/seawater interface. However, we also suggest that the lithology of the material eroded towards the margin and the dynamic of the flow could play an important role. In situ (including sediment, pore water and seawater samples) multi-tracer approaches (Nd, Th, Ra, Pb and Fe isotopes, and Mn content) and modeling studies should help better understanding the precise processes involved and the global significance, respectively, of boundary exchange.

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