Microscale neodymium distribution in sedimentary planktonic foraminiferal tests and associated mineral phases

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Abstract

Neodymium isotopic ratios recorded in calcareous foraminiferal tests (shells) and associated authigenic minerals were used to trace past water masses, although the origin of preserved Nd signals is still a matter of debate. We determined, for the first time, the microscale Nd distribution in two planktonic foraminifera species (Globigerinoides ruber and Neogloboquadrina dutertrei) and coexisting authigenic minerals from two selected time slices (15.6 and 129 kyr) of a marine sediment core in the Panama Basin. Elemental mapping of Nd, Ca, Fe, Mn, and Si was performed using NanoSIMS ion probe and electron probe microanalysis (EPMA) on uncleaned tests together with scanning electron microscopy (SEM) imagery. EPMA and SEM images revealed the presence of Fe-rich framboidal minerals inside test pores and inner chambers, particularly in the old samples. The young sample presented Fe- and Mn-rich patches on the inner test wall. The Nd intensity in Fe–Mn-rich patches and in some framboids was much higher than in foraminiferal calcite, where the Nd distribution was randomly heterogeneous with no systematic features such as an ontogenic Nd-rich layer or species-specific differences. The relationship between Nd, Fe, and Mn confirmed a significant role of Fe–Mn oxides as a Nd carrier. The high Nd enrichment in some framboids could be explained by Nd adsorption onto oxidized surface of Fe sulfides particles rather than direct incorporation. Since the authigenic precipitates are major Nd carrier phases, the Nd isotopic signals in sedimentary foraminiferal tests likely reflect bottom/pore water values rather than surface water ones.

1. INTRODUCTION

The Nd isotopic ratios of seawater $^{143}\text{Nd}/^{144}\text{Nd}$, or $\varepsilon_{\text{Nd}} = \left(\frac{^{143}\text{Nd} / ^{144}\text{Nd}}{^{143}\text{Nd} / ^{144}\text{Nd}_{\text{CHUR}}} - 1\right) \times 10^4$, where CHUR stands for chondritic uniform reservoir which represents a reference $^{143}\text{Nd}/^{144}\text{Nd}$ value of present-day average Earth (Jacobsen and Wasserburg, 1980)—characterize water masses, reflecting the age and nature of continents surrounding oceans (Lacan et al., 2012 and references therein). Biological Nd isotopic fractionation is negligible in marine environments, and the residence time of dissolved Nd isotopes is shorter than the global mixing time of the ocean (300–1000 years; Tachikawa et al., 1999; Arrouse et al., 2009). Therefore seawater $\varepsilon_{\text{Nd}}$ values, if faithfully preserved in marine archives, can be used to trace past oceanic circulation on different timescales (Frank, 2002; Goldstein and Hemming, 2003; van de Flierdt and Frank, 2011 and references therein).

Seawater $\varepsilon_{\text{Nd}}$ values recorded in Fe–Mn oxide coatings of bulk sediments have been successfully used to study variability in bottom water circulation, such as Atlantic meridional overturning circulation, on glacial/interglacial and millennial timescales (Rutberg et al., 2000; Bayon et al.,...
and *u*ruber uncleaned planktonic foraminiferal tests (Vance et al., 2004). However, recent studies have shown that the reductive leaching of bulk sediments to extract bottom water $\varepsilon_{Nd}$ values recorded in Fe–Mn oxides might partially dissolve the terrigenous fraction, especially volcanogenic materials (Roberts et al., 2010; Elmore et al., 2011). Since this dissolution could bias Nd isotopic signals in leachates, the use of calcareous foraminiferal tests (shells) was proposed (Roberts et al., 2010; Elmore et al., 2011). Sedimentary foraminiferal tests involve different Nd contaminating phases that should be removed prior to measurement of isotopic ratios. Multi-step cleaning has been used for this purpose, including mechanical cleaning by ultrasonication to remove clay minerals, an oxidative step with hot $\text{H}_{2}\text{O}_{2}$ in NaOH to remove organic matter, and reductive cleaning with hot hydrous hydrazine in $\text{NH}_{4}\text{OH}$ and citric acid at high pH to remove Fe–Mn oxide coatings (Boyle and Keigwin, 1985/1986; Boyle and Rosenthal, 1996). Nonetheless, it is still a matter of debate whether the $\varepsilon_{Nd}$ values derived from planktonic foraminiferal tests reflect seawater Nd isotopic signals at the calcification depths of the organisms (Vance et al., 2004) or bottom water signals that are acquired by post-mortem processes within the sediment (Roberts et al., 2010; Elmore et al., 2011).

The puzzling features of Nd extracted in sedimentary planktonic foraminiferal tests can be summarized by three points: (1) $\varepsilon_{Nd}$ values from uncleaned (only mechanically cleaned) and fully cleaned tests are similar, even though the Nd/Ca ratios decrease with the cleaning steps (Palmer and Elderfield, 1986; Vance et al., 2004; Roberts et al., 2010); (2) cleaned and uncleaned foraminiferal tests from core-tops show $\varepsilon_{Nd}$ values close to surface water values at some sites, and bottom water values at other sites (Palmer and Elderfield, 1986; Vance et al., 2004; Roberts et al., 2010); and (3) the Nd partition coefficient between foraminiferal calcite and seawater (Kd) is much higher compared to other minor and trace elements in carbonates (Shaw and Wasserburg, 1985; Vance et al., 2004). To explain the higher Kd (point 3), it was proposed that Nd is incorporated in intratrace organic matter during calcification, not in the calcite lattice (Haley et al., 2005; Martinez-Boti et al., 2009). Nonetheless, this hypothesis is out of line with the bottom water $\varepsilon_{Nd}$ values acquired via full-cleaned planktonic foraminifera (Roberts et al., 2010) (point 2). The redorsorption of Nd from Fe–Mn oxide coatings in foraminiferal tests during reductive cleaning under high pH conditions (Sholkovitz, 1989; Haley et al., 2005) could partly account for the bottom water $\varepsilon_{Nd}$ Values. However, the same cleaning technique yields surface water $\varepsilon_{Nd}$ values at some sites (Vance et al., 2004).

Here we present the microscale Nd distribution of two uncleaned planktonic foraminiferal tests (*Globigerinoides ruber* and *Neogloboquadrina dutertrei*) and coexisting authigenic minerals obtained using a NanoSIMS ion probe together with the Ca, Fe, Mn and Si distribution. Scanning electron microscopy (SEM) images and electron probe microanalysis (EPMA) were used for sample selections and to identify minerals present in the tests. The studied core had been retrieved in the Panama Basin, in the eastern equatorial Pacific, and has already been well characterized (Leduc et al., 2007, 2010). In contrast to previous studies focused on core-top materials, we carried out downcore sedimentary foraminiferal tests in order to clarify how Nd carrier phases have evolved with diageneric processes. Our results revealed a very low Nd concentration in calcite tests, whereas an extremely high Nd intensity was obtained for Fe–Mn oxides and Fe sulfides that were transformed into Fe oxyhydroxides/oxides by oxidation. We discuss the paleoceanographic implications of these results.

### 2. MATERIALS AND METHODS

*G. ruber* (white variety, 250–355 μm) and *N. dutertrei* (355–425 μm) specimens were picked from core MD02-2529 (08°12.339N, 84°07.329W, 1619 m water depth) that was collected during an IMAGES 2002 cruise in the eastern equatorial Pacific. The core location was below the present-day oxygen minimum zone. Due to the existence of epibenthic foraminiferal species (*Cibicidoides wuellerstorfi*) and the bioturbated sediment structure, the bottom water was estimated to have been oxic for the last 140 kyr (Leduc et al., 2007, 2010). The two time slices (15.6 and 129 kyr) were selected on the basis of Mn/Ca and Fe/Ca values obtained in *N. dutertrei* tests involving conventional reductive–oxidative cleaning (Boyle and Keigwin, 1985/1986; Boyle and Rosenthal, 1996) followed by ICP-OES (Jobin–Yvon Ulinma C) measurements at CEREGE (Table 1, Supplementary Information S1I and Fig. S1b). The cleaned tests from the first interval were free of clay minerals and Fe–Mn oxides (Fe/Ca below detection of several tens μmol/mol, with Mn/Ca at 58 μmol/mol). The tests from the second interval showed higher Fe/Ca (0.809 mmol/mol), with an exceptionally high Mn/Ca (353 μmol/mol). This Mn/Ca value was likely related to the occurrence of Mn carbonate overgrowth, a specific feature in the Panama Basin, because of the high biological productivity and Mn supply from hydrothermal activity (Pedersen and Price, 1982; Pena et al., 2005). These contrasted samples provide complementary information on the test chemistry and the influence of diagenetic precipitates.

Uncleaned *G. ruber* and *N. dutertrei* tests were sent to JAMSTEC (Japan) for EPMA mapping and SEM imagery. Prior to analysis, the specimens were embedded in epoxy resin to fill the chamber cavities and polished with diamond pastes to expose test cross-sections. Then the surface was coated with a 20-nm thick carbon film by vacuum evaporation. SEM images were obtained prior to elemental measurement by EPMA (JEOL JXA-8900RL, JAMSTEC). Calcium, Si, Mn and Fe mapping were performed at an accelerating voltage of 15 kV, a beam current of 300 nA with a dwell time of 50 ms. These results were used to select zones to be analyzed by NanoSIMS and to gain insight into the mineralogy of the co-existing phases. Raman spectral analysis was carried out only for some selected spots in the specimens using a Raman microprobe (Photon Design, JAMSTEC) to identify minerals present in the foraminif-
eral tests (see also Supplementary Information SI2). The samples were excited with a 532 nm line of a 100 mW diode-pumped solid-state (DPSS) laser probe (<1 μm diameter). The collected Raman spectra were compared with references from the RRUFF website (http://rruff.info/).

After analysis at JAMSTEC, the samples were mounted in a 10 mm Cu cylinder (4 mm high) with epoxy resin at CEREGE (France) and polished. Images were acquired using a NanoSIMS 50 ion probe (CAMECA) after Au coating at the University of Rennes I (France). Primary negative oxygen ions were used with an accelerating voltage of 16 kV. The current and lateral resolution of the secondary ion beam varied according to the applied diaphragm. Five diaphragms were available. We used D1-1, providing an O⁻ beam current of around 180 pA and a beam size ranging from approximately 800 nm to 1 μm. Areas of interest were presputtered for around 15 min prior to image acquisition in order to enhance the generation of secondary ions and surface decontamination. The secondary ions ²⁸Si⁺, ⁴⁴Ca⁺, ⁵⁵Mn⁺, ⁵⁴Fe⁺, ⁵⁶Fe⁺ and ¹⁴²Nd⁺ were recorded on masses 28, 44, 55, 54, 56 and 142, respectively (see Supplementary Information SI3 for detail). The exact position of ¹⁴²Nd was checked with a neodymium phosphate standard (NdP₂O₄ with 27.6% of Nd, SPI) and found to be located at 141.681 amu. During the measurement session, it ranged from 141.687 to 142.146 due to variability in the magnetic field. The instrument was tuned to reach a mass resolution power of 2500–3000. By monitoring ¹⁴⁰Ce⁺ peaks (abundance ¹⁴⁰Ce is 88.45%) that has never attained to ¹⁴²Nd⁺ peaks, the isobaric ¹⁴²Ce⁺ interference on ¹⁴²Nd⁺ was likely minor (abundance ¹⁴²Ce is 11.11%).

According to the beam conditions and sample size, the analysis times ranged from 10 to 40 ms/pixel and the size of the analyzed area were 60 × 60, 40 × 40 and 35 × 35 μm, with an image resolution of 256 × 256 or 128 × 128 pixels (Supplementary Information SI3 and Table S1). Note that precise quantification of the Nd concentration using NanoSIMS is hampered by the fact that the intensity could vary with the matrix and speciation of the element of interest (adsorbed onto some phases or located in a crystal lattice) as well as the measurement conditions (raster size, image resolution and counting time, Supplementary Information SI3). For quantitative comparison of Nd, Mn and Fe intensities between different samples, we analyzed twice the same sample zone of 60 × 60 μm with an image resolution of 128 × 128 pixels, with 80 ms/pixel measurements for Nd and, 40 ms/pixel for Mn and Fe (Table S1 for detail). All elemental mapping and data management was performed using the MIMS plugin for ImageJ software (http://www.nrims.hms.harvard.edu/NRIMS_ImageJ.php).

3. RESULTS

3.1. SEM images and EPMA of G. ruber and N. dutertrei

The SEM images highlighted the presence of several types of phases within the foraminiferal tests (Fig. 1). Firstly, spherical particles of variable sizes (~30 μm down to a few microns) were observed within foraminiferal test pores and inner chambers of G. ruber (Fig. 1b) and N. dutertrei (Fig. 1d) specimens. Such particles are referred to as “framboidal structures” in the following. This phase was abundant in the 129 kyr samples, particularly in N. dutertrei (Fig. 1d) whose pores were filled with the frambooidal particles. The EPMA results indicated high Fe contents in the frambooidal aggregates, and these results were consistent with the NanoSIMS elemental mapping (see Section 3.2). We selected zones containing the Fe-rich frambooidal structure for NanoSIMS Nd analysis (zone 4 in Fig. 1b, and zones 5 and 6 in Fig. 1d).

Secondly, the SEM images revealed patches attached on the inner chamber walls that were clearly visible in the 15.6 kyr G. ruber specimen (zones 1 and 2 in Fig. 1a). Manganese and Fe contents were high in this phase according to EPMA.

Finally, the inner chambers of both G. ruber (Fig. 1b) and N. dutertrei (Fig. 1d) specimens from 129 kyr samples were filled with large aggregates with high Si contents, which were assumed to be clay minerals. Clay fractions were also observed on the outer test walls, filling foraminiferal pores, as shown in the 15.6 kyr G. ruber specimen (Fig. 2a and Section 3.2).

A Raman spectral analysis was focused on the 15.6 kyr N. dutertrei specimen in order to obtain mineralogical information on phases within the foraminiferal test (Fig. 1c). Based on SEM image and EPMA elemental mapping, we measured frambooidal aggregates in the pores and the foraminiferal test (white squares in Fig. 1c and Supplementary Information SI2). Raman shift peaks indicated that the foraminiferal test was obviously formed with calcite (CaCO₃) with no specific contaminating minerals (Supplementary Information SI2). The frambooidal particles revealed pyrite (FeS₂) spectra in the first analysis. Several months later, the same frambooidal particles were analyzed again and, interestingly, hematite (Fe₂O₃) was identified instead of pyrite (Supplementary Information SI2, Fig. S2).

Table 1

<table>
<thead>
<tr>
<th>Depth in sediment (cm)</th>
<th>Age (kyr BP)</th>
<th>Species</th>
<th>Mn/Ca (μmol/mol)</th>
<th>Fe/Ca (μmol/mol)</th>
<th>CaCO₃ in bulk (%)b</th>
<th>Cope in bulk (%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>453</td>
<td>15.6</td>
<td>N. dutertrei</td>
<td>58</td>
<td>Below detection</td>
<td>14.2</td>
<td>3.1</td>
</tr>
<tr>
<td>1727</td>
<td>129</td>
<td>N. dutertrei</td>
<td>353</td>
<td>0.809</td>
<td>12.1</td>
<td>2.5</td>
</tr>
</tbody>
</table>

a Conventional batch cleaning “Cd method” followed by ICP-OES analysis for N. dutertrei tests.

b Data from Leduc et al. (2010).
3.2. Elemental distribution in foraminiferal tests and coexisting phases obtained by NanoSIMS

Both elemental mapping and transect plots were applied (Figs. 2-5) for the different phases (foraminifera, clays, patches and framoidal aggregates) to localize Nd carriers. Even though the Ca, Si, Mn and Fe distributions have already been obtained using EPMA, these elements were further analyzed using NanoSIMS to maintain the consistency of the mapping with Nd, which was only measured with NanoSIMS. The EPMA and NanoSIMS results were in excellent agreement with respect to the Ca, Si, Mn and Fe distributions. Note that there could be some slight differences between NanoSIMS and SEM images concerning the sample surface state because the NanoSIMS images were obtained after the second surface polishing.

The Ca distribution of the 15.6 kyr G. ruber specimen (zone 1 in Fig. 1a) indicated a clear correspondence with the SEM image (Fig. 2a). Clay minerals identified by a high Si content filled foraminiferal pores (Fig. 2a) and were inserted between the test and the Mn- and Fe-rich patches (Fig. 2b). One of the most remarkable features of the Nd distribution in this zone was its enrichment in the Fe- and Mn-rich patches (Fig. 2a). The Nd intensity (around 40 counts per second, cps) in the patches was much higher than in clay minerals (Fig. 2a and b) and in the foraminiferal test, where the intensity of this element was only 1–3 cps (“Nd zoom” in Fig. 2b). A high Nd content in Fe- and Mn-rich patches (Fig. 6b) was observed in the second zone of the same specimen (zone 2 in Figs. 1a and 6b).

Another striking feature of the Nd distribution was the extremely high intensity of Fe-rich framoidal particles formed in pores (Fig. 3), as noted in the 129 kyr N. dutertrei specimen (zone 5 in Fig. 1d). The strong link between Nd and Fe was confirmed by the transect plot, which showed a very similar pattern for both elements (Fig. 3b). Again, the Nd intensity in the clay minerals was much lower than in the framoidal particles (Fig. 3b). Even though the Nd content in the foraminiferal test seemed low, this element was certainly incorporated in test parts since the intensity in the tests was significantly higher than in resin (“Nd zoom” in Figs. 2b, 3b, 4b and 5b). Nd enrichment in framoidal particles (Fig. 4a and b) was also observed in the 129 kyr G. ruber specimen (zone 4 in Fig. 1b), thus this is not a species-dependent feature. In contrast, some framoidal particles did not have a high Nd content, as shown for the 129 kyr N. dutertrei specimen (zone 6 in Fig. 1d). For this sample, the presence of Fe-rich framoidal particles inside the pores was clearly revealed by the SEM image and Fe distribution, although the corresponding Nd peak was absent (Fig. 5a and b). The phase of this sample with a moderately high Nd intensity was found outside of the test (Fig. 5a and b). Barium was tentatively measured since the Ba-rich phase (possibly barite, BaSO₄) was proposed as a potential Nd carrier (Haley and Klinkhammer, 2002). No significant Ba enrichment was detected in this phase. The reason for the slight Nd enrichment was unclear.

Finally, Mn was found to be heterogeneously distributed in the old samples in the foraminiferal tests (Figs. 3a, 4a and 5a). The 129 kyr N. dutertrei specimen (zones 5 and 6 in Fig. 1d) indicated Mn enrichment in the part corresponding to inner calcite (Fig. 3a and b). The 129 kyr G. ruber specimen (zone 4 in Fig. 1b) showed some Mn-rich layers (Fig. 4a). Such Mn heterogeneity was not noted in the 15.6 kyr N. dutertrei specimen (Fig. 1c, based only on the EPMA results) and the 15.6 kyr G. ruber specimen (Fig. 2a, zone 1 in Fig. 1a). There was no clear correspondence between the Mn heterogeneity and the Nd distribution (Figs. 3–5).

3.3. Comparison of Nd distributions between different samples

In order to quantitatively compare the Nd distribution between different samples, the same raster size, image resolution and counting time (60 × 60 μm, 156 × 156 pixels, 80 ms/pixel) were applied to all of the analyzed zones (Fig. 6).

Outside of the calcite tests, Nd enrichment was clearly identified in Fe- and Mn-rich patches (zones 1 and 2 in Fig. 6), and Fe-rich framoidal particles (zones 4 and 5 in Fig. 6), although the degree of enrichment differed according to the areas, even for the same specimens. For instance, the average Nd intensity in Fe- and Mn-rich patches of zone 1 (the area indicated by a yellow rectangle in Fig. 6) was 55 cps whereas the average intensity for zone 2 was only 6 cps (the area indicated by a yellow rectangle in Fig. 6). Some framoidal particles were characterized by an average Nd intensity as high as 65 and 84 cps (the areas indicated by yellow rectangles in zones 4 and 5 of Fig. 6, respectively). But a framoidal particle in zone 2 had an average Nd intensity of only 2 cps (the area indicated by a yellow rectangle in Fig. 6).

In the calcite tests, the Nd distribution was also heterogeneous, without any systematic trend with respect to the sediment age, species and ontogenetic test structure (Fig. 6): two selected zones in the 15.6 kyr G. ruber specimen (zones 1 and 2 in Fig. 1a) were characterized by quite different Nd intensities (zones 1 and 2 in Fig. 6), demonstrating high Nd heterogeneity within a single test. On the other hand, the Nd intensities of the two zones in the 129 kyr G. ruber specimen (zones 3 and 4 in Fig. 6) were quite close. It is known that N. dutertrei tests consist of inner primary calcite and an outer crust that are formed within different water masses, as demonstrated by the distinct Mg contents (Sadekov et al., 2005). The analyzed Nd distribution did not show such a difference between the inner and outer calcite of the N. dutertrei specimen (zones 5 and 6 in Fig. 6). Moreover, Nd-rich layers within the test wall, which could correspond to organic-rich intra-test lamellae (Vance et al., 2004; Haley et al., 2005), were not clearly detected in all of the analyzed samples (Fig. 6). Finally, the Nd content was not systematically high in test parts in contact with Fe- and Mn-rich patches and Fe-rich framoidal particles (zones 1, 2, 4 and 5 in Fig. 6).

4. DISCUSSION

The main features of the Nd distribution obtained using NanoSIMS can be summarized by the following five points.
The Nd intensity was high in Fe- and Mn-rich patches even though the degree of enrichment varied in the different zones. Fe-rich framboidal particles represented another phase with a high Nd content, although some particles had a very low Nd content. The Nd intensity in foraminiferal tests was generally very low and its distribution was heterogeneous, without any clear trend. The presence of Mn-rich calcite, possibly MnCO$_3$ overgrowth (Pedersen and Price, 1982; Pena et al., 2005) in the 129 kyr samples, seemed to have little impact on the Nd distribution. No clear Nd-rich layer was observed in the calcite tests, suggesting that Nd accumulation in organic-rich intra-test lamellae (Vance et al., 2004; Haley et al., 2005) was less likely in the samples analyzed in this study. These observations are consistent with the previous studies reporting that 80–90% of rare earth elements, including Nd, reside in the authigenic phases (Palmer, 1985; Roberts et al., 2012).

Based on the Fe and Mn distribution, SEM images and Raman spectra, it could be reasonably assumed that the Fe- and Mn-rich patches corresponded to Fe-Mn oxide coatings. If our findings represent a general feature of Fe-Mn oxide coating formed on foraminiferal tests, the phase was patchy rather than covering all of the outer foraminiferal calcite. It is known that framboidal structures correspond to aggregates of pyrite (FeS$_2$), greigite (Fe$_3$S$_4$), hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) (Wilkin and Barnes, 1997). Since these structures were more abundant in the old samples than in the young samples (Fig. 1), we deduced that Fe-rich framboidal minerals were principally Fe sulfides formed under reducing conditions.

In the following, we focus our discussion on the relationship between Nd, Mn and Fe to identify the most effective Nd carriers associated with foraminiferal calcite. Then the provenance of Nd isotopes extracted from sedimentary planktonic foraminiferal tests is evaluated. Finally, we discuss the paleoceanographic implications of our results.

4.1. Identification of major Nd carriers associated with foraminiferal test samples

The high affinity of Nd to Mn and Fe oxides and Fe oxyhydroxides has been reported based on the findings of experiments involving sorption onto synthetic minerals (Koeppenkastrop and De Carlo, 1992), and estimation of partition coefficients for Fe–Mn crusts (Bau et al., 1996). On the other hand, some authors have proposed that Mn oxides are not a principal Nd carrier for sedimentary foraminifera (Vance et al., 2004) because the Nd/Mn ratio of uncleaned foraminifera is too high to be explained by Nd associated with Fe–Mn oxides (Bau et al., 1996). In order to
gain further insight into the role of minerals containing Mn and Fe as Nd carriers, we examined relationships between Nd, Mn and Fe in the areas marked with yellow rectangles in Fig. 6.

We noted tight positive relationships between Nd and Mn for Fe–Mn oxide coatings (Fig. 7a) in the 15.6 kyr G. ruber specimen (zones 1 and 2 in Fig. 6), thus confirming a significant role of Mn oxide as a Nd carrier. However, the Nd intensity of the coating in zone 1 (Figs. 1a and 6) was almost 10-fold higher than in the coating in zone 2 (Figs. 1a, 6 and 7a). Furthermore, Fe sulfides (zones 4 and 5 in Fig. 6) had a Nd intensity as high as that of the oxide coating (zone 1 in Fig. 6) in spite of its low Mn content (Fig. 7a). These results suggested that Mn oxides were not the only Nd carriers.

Another efficient Nd carrier could be Fe minerals, as shown by the remarkable positive correlations between Nd and Fe for both oxide coatings and framboidal Fe sulfides (Fig. 7b). Similar linear relationships were obtained for framboids in the 129 kyr G. ruber specimen (zone 3) and in the 129 kyr N. dutertrei specimen (zone 5, Fig. 7b), indicating that Nd enrichment associated with Fe sulfides was not dependent on the foraminiferal species. The slopes for the Nd–Fe relationship concerning Fe sulfides were steeper than those for the oxide coatings (Fig. 7b). This suggests that Fe sulfides were related to more efficient Nd carriers than in the oxide coating, although direct Nd incorporation into Fe sulfides has never been reported. Besides, Mn and Fe in oxide coatings were positively correlated but the slopes varied with the coating zones (Fig. 7c). This finding indicates that the Fe–Mn proportion was not constant in the oxide coatings, and additional Nd carriers could have been present in zone 1 oxide coatings in relation to Fe minerals.

We propose that Nd was adsorbed by oxidized Fe sulfides not directly incorporated by the sulfide minerals. Pyr-
ite or greigite (precursor of pyrite) oxidation is an electrochemical process that occurs in nature when O$_2$ and H$_2$O are adsorbed onto sites with Fe species of reduced coordination (Chandra and Gerson, 2011). During this process, Fe-oxy species are formed, which may function as an active surface to adsorb trace elements, as already noted with respect to goethite (Koeppenkastrop and De Carlo, 1992). Therefore, the foraminiferal Nd/Mn ratio higher than expected from Fe–Mn crust could be explained by the contribution of Nd related to Fe minerals. However, if Fe sulfides are not oxidized, the minerals do not efficiently adsorb Nd, which explains the absence of Nd enrichment in some Fe-rich framboidal particles (Figs. 5a, b, 6 and 7b).

4.2. Diagenetic processes and origin of Nd isotopes recorded in sedimentary foraminifera

The Fe–Mn oxide coating observed in this study was attached on inner test wall, suggesting that this precipitate was formed by postmortem processes. Another Nd-rich phase, i.e. oxidized Fe sulfides, was also formed during diagenesis. Consequently, Nd adsorbed on these minerals seemed to originate from bottom and pore waters. Considering the marked difference in Nd intensity when comparing authigenic precipitates and planktonic foraminiferal tests (Fig. 6), if trace amounts of Nd associated with authigenic phases remain after the cleaning, Nd isotopic signatures derived from the sedimentary foraminiferal tests could be biased in favor of bottom and pore water signals. Redorption of Nd from Fe–Mn oxide coatings on foraminiferal tests during reductive (Sholkovitz, 1989; Haley et al., 2005) and oxidative cleanings (Roberts et al., 2012) has already been reported, which is consistent with potential bottom/pore water Nd contributions, even after cleaning. Below we discuss this possibility in terms of a “bottom/pore water hypothesis” in relation to diagenetic processes.

The bottom water at the core location MD02-2529 in the Panama Basin is estimated to have been oxic for the last 140 kyr (see Section 2). This condition allows the precipitation of Fe–Mn oxides and oxyhydroxides at the water/sed-

Fig. 3. Elemental distribution in zone 5 of the 129 kyr *N. dutertrei* specimen indicated in Fig. 1d. (a) Mapping of Nd, Ca, Si, Fe and Mn. The thin yellow line, color code and SEM image are the same as in Fig. 2. (b) Nd, Ca, Si, Fe and Mn distribution along the transect indicated with a thin yellow line. “Nd (zoom)” is as for Fig. 2. Light gray, dark gray and ochre bands indicate foraminiferal calcite, Fe-rich framboidal particles, and clay minerals, respectively. 60 × 60 μm image with 128 × 128 pixel resolution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Because of a relatively high organic carbon content in the studied core (2.4% in bulk sediment at the core-top, Fig. S1a), dissolved oxygen in pore water at the location is consumed within the upper few centimeters of the sediment, and the sediment becomes suboxic. Below the oxic/suboxic boundary, the Fe–Mn oxides and oxyhydroxides dissolve, releasing adsorbed Nd to the pore water. Then, the pore water Fe and Mn can be transported upward to the oxic layer by diffusion and/or bioturbation, which leads to re-precipitation of Fe–Mn oxides and oxyhydroxides. High Mn and Fe contents in bulk sediment of core MD02-2529 for the Holocene part are consistent with the processes (Fig. S1c). Dissolved Nd concentration in pore waters is generally higher than in the overlaying bottom waters, and this enrichment has been evaluated to be tightly associated with redox cycling of Mn and Fe (Elderfield and Sholkovitz, 1987). The importance of diagenetic Fe cycle as a factor controlling Nd concentration in pore waters was further confirmed (Haley et al., 2004). Therefore, the Fe–Mn oxides and oxyhydroxides originally record bottom water Nd isotopic ratios, but the contribution of Nd from pore waters could increase by enhanced reduction–oxidation cycles.

At depths deeper than oxic/suboxic boundary, other diagenic minerals such as MnCO₃ and the Fe sulfides precipitate. MnCO₃ is formed under suboxic/anoxic conditions with increased alkalinity (Pedersen and Price, 1982; Pena et al., 2005). NanoSIMS observation of N. dutertrei from the 129 kyr time slice (Fig. 3) indicates the occurrence of MnCO₃ that coincides with an increase in the cleaned foraminiferal Mn/Ca as well as Mn enrichment in the bulk sediment of core MD02-2529 (Figs. S1b and S1c). Recently, MnCO₃ formed in foraminiferal tests is proposed as one of the major Nd carrier phases, and the mobility of Nd in pore water is limited because the released Nd is incorporated in MnCO₃ formed in foraminiferal tests (Roberts et al., 2012). Although we did not observe clear correspondence between Nd distribution and MnCO₃ occurrence (Fig. 3), moderate Nd enrichment in MnCO₃ cannot be ruled out since the sensitivity of NanoSIMS measurements could be different for Nd adsorbed on Fe–Mn oxides and oxyhydroxides and for Nd incorporated in MnCO₃.
Under sulfate reducing conditions, Fe sulfide minerals are formed as micro-scale framboidal aggregates, as observed in this study (Figs. 1c, zones 3–5 and S2). If Fe-rich framboidal particles from anoxic sediments have contact with dissolved oxygen in pore waters of microenvironment and/or oxygen in air after sediment retrieval, their surface could be transformed into Fe oxyhydroxides and/or Fe oxides (Chandra and Gerson, 2011), providing active adsorption sites to Nd in pore waters. We speculate that oxidation of Fe sulfides in the 129 kyr samples essentially occurred after the sediment retrieval, considering its depth in core of about 17 m (Table 1). It is worth noting that the cleaned foraminiferal Fe/Ca values for 120–143 kyr time window of core MD02-2529 was generally low, except for some samples, which contrasts with the trend observed for the foraminiferal Mn/Ca (Fig. S1b). This result indicates that the mechanical cleaning allowed, at least partly, removing the framboidal particles. Indeed, the previous study reported that cleaned foraminiferal Nd/Ca was lower in anoxic intervals (e.g. sapropel layers), as compared to values from oxic layers (Vance et al., 2004). The framboidal particles do not seem to be chemically attached on foraminiferal tests.

Fig. 5. Elemental distribution in zone 6 of the 129 kyr N. dutertrei specimen indicated in Fig. 1d. (a) Mapping of Nd, Ca, Si, Fe and Mn. The thin yellow line, color code and SEM image are the same as in Fig. 2. (b) Nd, Ca, Si, Fe and Mn distribution along the transect indicated with a thin yellow line. “Nd (zoom),” light gray, dark gray and ochre bands are as for Fig. 2. 60 × 60 μm image with 128 × 128 pixel resolution for Nd and Mn, and 256 × 256 pixel resolution for Ca, Si and Fe. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Taken together, we propose that planktonic foraminiferal tests, even after cleaning, mainly record bottom/pore water Nd isotopic ratios rather than surface water values. According to redox cycles, the contribution of pore water Nd could vary. We evaluate that the oxidized Fe sulfides essentially record the pore water Nd isotopic signals. The next question is to which extent the contribution of Nd from pore waters smears bottom water Nd isotopic signals. To precisely discuss this point, a database of pore water Nd isotopic ratios is required, but such data are not available yet. If the main source to Nd in pore water is the bottom water Nd adsorbed on Fe–Mn oxides and oxyhydroxides, the pore water Nd isotopic signals within the upper few centimeters of the sediment would be close to the bottom water value. Temporal resolution of bottom water εNd reconstruction could be affected by oxidation–reduction cycles in the sediments.

Our bottom/pore water hypothesis could explain several contradictory features observed for Nd extracted from
foraminiferal tests: cleaned and uncleaned foraminifera have similar $\varepsilon_{\text{Nd}}$ values (Vance et al., 2004; Roberts et al., 2010) because bottom/pore water Nd isotopic signals are dominant in both cases; different planktonic foraminifera species that calcify at different water depths have similar $\varepsilon_{\text{Nd}}$ values (Vance et al., 2004); $K_d$ is too high compared to other biogenic carbonates and elements (Shaw and Wasesburg, 1985); the extracted $\varepsilon_{\text{Nd}}$ value is close to bottom water values in some cases (Roberts et al., 2010), whereas in other cases it seems to be close to surface water values (Vance et al., 2004).

4.3. Implication for paleoceanographic studies

The geochemical meaning of Nd isotopic signature recorded in sedimentary foraminiferal tests seems to be more complex than previously expected. We, however, believe that Nd isotopes are useful tracers for paleoceanography, especially when combined with other independent indicators such as $\delta^{18}O$, $\delta^{13}C$ and $\Delta^{14}C$ recorded in foraminiferal tests as well as $^{231}$Pa/$^{230}$Th in sediment (Vance and Burton, 1999; Scrivner et al., 2004; Osborne et al., 2008; Roberts et al., 2010). In fact, it is unlikely that all concomitant time-dependent variations in foraminiferal $\varepsilon_{\text{Nd}}$ values with other paleoproxies are fortuitous.

To examine the utility of Nd isotopic ratios recorded in sedimentary foraminiferal tests as a tracer of past water masses, we compare the $\varepsilon_{\text{Nd}}$ values of cleaned planktonic foraminiferal tests (Stoll et al., 2007) with seawater $\varepsilon_{\text{Nd}}$ values obtained along latitudinal transect in the Bay of Bengal (Amakawa et al., 2000; Singh et al., 2012). The foraminiferal tests have been extracted from the upper sediments (3–13 cm) that correspond to the late Holocene interval (Stoll et al., 2007). The cores are located below the present-day oxygen minimum zone (Garcia et al., 2010). Since seawater Nd isotopic signals in the Bay of Bengal are characterized by strong latitudinal and vertical gradients due to unradiogenic Nd contribution from Himalayan rivers (Singh et al., 2012), this is an ideal region to assess our hypothesis.

Both foraminiferal and seawater $\varepsilon_{\text{Nd}}$ values present a clear latitudinal gradient between $5^\circ$N and $20^\circ$N with lower...
The observed correspondence between foraminiferal Nd isotopic signatures with bottom water values is not limited to the Bay of Bengal. It has been demonstrated that the sedimentary foraminiferal $\varepsilon_{\text{Nd}}$ values from the late Holocene generally agree with the bottom water Nd isotopic signals in the North Atlantic (Roberts et al., 2010, 2012; Elmore et al., 2011). Extended comparison of $\varepsilon_{\text{Nd}}$ values between sedimentary foraminifera (Palmer and Elderfield, 1985; Roberts et al., 2010; Elmore et al., 2011) and seawaters (Lacan et al., 2012 and references therein; Stichel et al., 2012) throughout the Atlantic Basin is shown in Fig. S3. A broad agreement of geographical trend is found between the foraminiferal and the bottom water data (Fig. S3). We notice, however, two examples showing marked decoupling between the foraminiferal tests and the bottom water $\varepsilon_{\text{Nd}}$ values. The first example is Eirik Drift in the North Atlantic, the site influenced by lateral transport of Icelandic material (Elmore et al., 2011). The foraminiferal $\varepsilon_{\text{Nd}}$ value of $\varepsilon_{\text{Nd}} = 8.6$ is much higher than the bottom water value ($\varepsilon_{\text{Nd}} = 12.1$; Lacan and Jeandel, 2005). One of the most probable reasons for the offset is partial dissolution of Icelandic volcanogenic material that releases radiogenic Nd to the pore water, affecting the Nd isotopic ratio recorded by foraminiferal tests (Elmore et al., 2011). The second example is found in the east of Newfoundland where the Canadian Shield provides unradiogenic Nd to sediment (Elmore et al., 2011). The foraminiferal $\varepsilon_{\text{Nd}}$ value of $\varepsilon_{\text{Nd}} = 23.3$ (Elmore et al., 2011) is much lower than the bottom water $\varepsilon_{\text{Nd}}$ value of $\varepsilon_{\text{Nd}} = 13.4$ (Piepgras and Wasserburg, 1987). The difference could be explained by unradiogenic Nd contribution from glacial flour to the pore water (Elmore et al., 2011).

Overall, sedimentary planktonic foraminiferal tests indicate Nd isotopic ratios close to the bottom water $\varepsilon_{\text{Nd}}$ values when the bottom water is oxic and terrigenous Nd contribution to pore water seems to be minor. The reductive–oxidative cleaning of foraminiferal tests does not necessarily improve the agreement of the Nd isotopic ratios with the bottom water values (Elmore et al., 2011). It rather introduces a larger offset by artificial dissolution of volcanogenic matter in some cases (Roberts et al., 2010; Elmore et al., 2011). For further application of foraminiferal tests as recorders of bottom water Nd isotopic ratios in paleoceanographic studies, we recommend the following: (i) rigorous mechanical cleaning to remove oxidized Fe sulfides that are known to be one of the most prominent diagenetic Nd carriers; (ii) in addition to Mn/Ca, monitoring of Fe/Ca to trace the Nd contribution associated with Fe minerals; and (iii) combination of foraminiferal $\varepsilon_{\text{Nd}}$ values with independent proxies.

5. CONCLUSIONS

We identified major Nd carriers in foraminiferal tests and associated authigenic precipitates by combining Nd,
Ca, Si, Mn and Fe mapping of two planktonic foraminiferal species obtained using NanoSIMS and EPMA, as well as SEM images and Raman spectral analysis. Samples were collected from the Panama Basin in the eastern equatorial Pacific. Our principal findings are as follows.

Major Nd carriers were Fe–Mn oxides and oxidized Fe sulfides formed on inner foraminiferal chambers and inside pores by postmortem processes. These authigenic precipitates were more abundant in old (129 kyr) than in young samples (15.6 kyr).

The Nd content was much lower in foraminiferal tests than in authigenic precipitates, and close to the NanoSIMS detection limit. The Nd distribution in the tests was randomly heterogeneous without any systematic trend, such as an Nd-rich organic layer, species-specific variability or a difference between primary calcite and crust. Manganese carbonate overgrowth had little impact on the test Nd content. Neodymium diffusion from authigenic precipitates towards calcite tests seemed negligible.

In spite of the fact that the planktonic foraminiferal tests might preserve initial seawater Nd isotopic signals at calcification depths, $\varepsilon_{Nd}$ values extracted from sedimentary tests could be mainly controlled by contributions from bottom/pore waters because of readsoption of Nd from authigenic precipitates during cleaning. This bottom/pore water hypothesis could at least partly explain the puzzling features of foraminiferal Nd/Ca and Nd isotopic signals.

We recommend rigorous mechanical cleaning to remove oxidized Fe sulfides and monitoring of Fe/Ca values. Combining foraminiferal $\varepsilon_{Nd}$ values with independent paleopro-

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**APPENDIX A. SUPPLEMENTARY DATA**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2012.10.010.

**REFERENCES**


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