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Nd/Ca ratios in plankton-towed and core top foraminifera: Confirmation of the water column acquisition of Nd

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[1] Planktic foraminifera have been used as recorders of the neodymium (Nd) isotopic composition of seawater, although there is still controversy over the precise provenance of the Nd signal. We present an extensive, multispecific plankton tow Nd/Ca data set from several geographic locations (SE Atlantic, NE Atlantic, Norwegian Sea, and western Mediterranean), together with core top samples from the Mediterranean region. The range of Nd/Ca ratios in plankton-towed foraminifera, cleaned only of organic material, from all regions (0.01–0.7 μmol/mol), is similar to previously published analyses of sedimentary foraminifera cleaned using both oxidative and reductive steps, with distribution coefficients (K_d) ranging between 4 and 302. For the Mediterranean, where core top and plankton tow data are both available, the range for plankton tows (0.05–0.7 μmol/mol) is essentially identical to that for the core tops (0.1–0.5 μmol/mol). Readsorption of Nd during cleaning is ruled out by the fact that the plankton tow samples underwent only an oxidative cleaning process. We find a relationship between manganese (Mn) and Nd in plankton tow samples that is mirrored by a similar correlation in core top samples. This relationship suggests that Fe-Mn coatings are of negligible importance to the Nd budgets of foraminifera as the Nd/Mn ratio it implies is over an order of magnitude greater than that seen in other Fe-Mn oxide phases. Rather, since both plankton tows and core tops present a similar behavior, the Nd/Mn relationship must originate in the upper water column. The data are consistent with the acquisition of Nd and Mn from the water column by binding to organic material and the fact that intratest organic material is shielded from both aggressive cleaning and diagenetic processes. Collectively, the results help to explain two abiding puzzles about Nd in sedimentary planktic foraminifera: their high REE contents and the fact that they record a surface water Nd isotopic signal, regardless of the cleaning procedure used.

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1. Introduction

[2] The use of planktic foraminifera as recorders of the surface ocean neodymium (Nd) isotopic signal and REE pattern has a relatively short history. After initial attempts to use these signal carriers in the mid-1980s [*Palmer and Elderfield*, 1985, 1986], it was not until the late nineties that the method was refined, and it was demonstrated that the Nd isotopic signal recorded by cleaned planktic foraminifera corresponded to that of the surface ocean [*Vance and Burton*, 1999]. Since then, the isotopic proxy has been successfully applied to a range of oceanic settings and time scales [e.g., *Burton and Vance*, 2000; *Scrivner et al.*, 2004; *Stoll et al.*, 2007; *Osborne et al.*, 2008], and it has recently been shown that benthic foraminifera may also represent a reliable archive of deep water Nd isotope composition [*Klevenz et al.*, 2008]. Furthermore, *Haley et al.* [2005] suggest that cleaned planktic foraminifera may record the REE pattern of the surface ocean.

[3] Nevertheless, the use of REE-based elemental and isotopic proxies in planktic foraminifera has always been surrounded by some controversy. This arises from the fact that Nd concentrations, and REE contents generally, in foraminiferal tests are high (and variable) compared to other marine carbonates and to other trace elements in foraminifera, which has cast doubt on the exact location of the isotopic signal in the test (see *Vance et al.* [2004] for a review of these and other aspects). Initially it was argued that rare earth elements (REE) contained in postmortem Fe-Mn oxide coatings are readsorbed onto the calcite during traditional reductive-oxidative cleaning methods, because of their higher reactivity compared to elements with a 2+ valence state [*Sholkovitz*, 1989; *Pomiès et al.*, 2002]. In this view, the use of cleaned planktic sedimentary foraminifera as a simple record of surface water Nd isotopes is potentially compromised by coating Nd added in sediment. Subsequently, however, it has been demonstrated that readsorption from mobilized Fe-Mn coatings cannot be the explanation for high Nd concentrations in sedimentary foraminifera. *Vance et al.* [2004] showed that the Nd/Mn ratios of uncleaned sedimentary foraminifera, where readsorption is not a concern, are up to two orders of magnitude higher than those obtained from independent analyses of Fe-Mn oxides. Their conclusion, that Fe-Mn oxide coatings are of negligible importance for the Nd inventory of foraminifers, was confirmed by *Haley et al.* [2005]. The latter authors used a time-resolved flow-through cleaning approach to demonstrate that REE and Mn/Fe are not coreleased from foraminifera. These findings run counter to the suggestion of *Pomiès et al.* [2002], that the Nd contents of water column foraminifera were consistent with contamination by Mn oxide coatings. This suggestion, however, was based on an assumed Nd/Mn ratio for Fe-Mn oxide phases that is about an order of magnitude higher than any value yet measured in, for example, Fe-Mn crusts [*Bau et al.*, 1996]. Thus, while it is clear from isotopic studies [*Vance et al.*, 2004] that sedimentary planktic foraminifera carry a surface ocean Nd isotopic signal, the carrier of that signal remains unresolved.

[4] In order to validate the proxy, limited water column foraminiferal samples (plankton tows and sediment traps) have been studied since they represent the "original" water column signal that is sought in paleoclimate studies, without the risks associated with postmortem alteration. However, the scarce plankton tow data available [*Vance and Burton*, 1999; *Pomiès et al.*, 2002; *Vance et al.*, 2004] are contradictory: while some studies have found Nd/Ca ratios ranging between 0.35 and 0.85 μmol/mol, others have presented ratios of around 0.02 μmol/mol. Though this range of Nd/Ca ratios is consistent with those found in sedimentary foraminifera, including the notably low values obtained from Mediterranean samples associated with organic carbon–rich sediments [*Vance et al.*, 2004], our lack of understanding of the large range is clearly unsatisfactory.

[5] The previous data sets for plankton tows are small. In this study, we present plankton tow data for 8 species from 4 different study areas (Figure 1): the SE Atlantic, the NE Atlantic, the Norwegian Sea and the W Mediterranean (with core tops also available in this latter region). We aim to dramatically extend the currently available water column

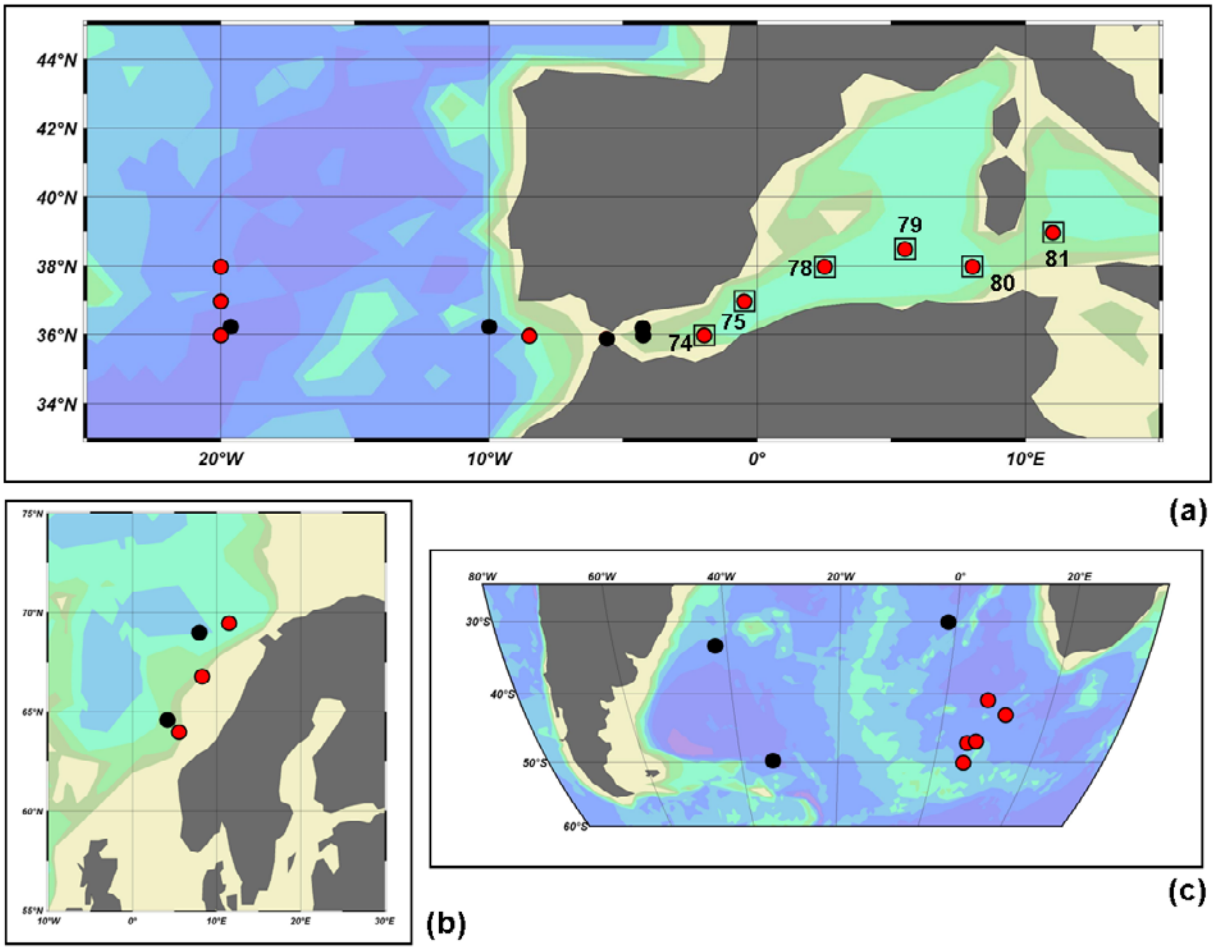

Figure 1. Position of sample stations (red circles) for this study: (a) NE Atlantic and western Mediterranean (squares denote stations from where core top sediment samples are also available), (b) Norwegian Sea, and (c) SE Atlantic. Black circles denote the position of the closest stations where water column Nd concentration data are available: *Tachikawa et al.* [2004], stations 5, B, and C, and *Piepgras and Wasserburg* [1987], stations 79 and 95 (Figure 1a); *Lacan and Jeandel* [2004], stations 25 and 26 (Figure 1b); and *Jeandel* [1993], stations SAVE 217, 271, and 302 (Figure 1c). Produced using Ocean Data View (R. Schlitzer, Ocean Data View, 2007, available at http://odv.awi.de).

data set, as well as to clarify some aspects of the systematics of Nd in planktic foraminiferal tests.

2. Materials and Methods

[6] Plankton tow samples from the SE Atlantic were collected during January–March 1996 on board R/V *Thomas Thompson* by means of a Multiple Opening-Closing Net and Environmental Sensing System (MOCNESS) [*Wiebe et al.*, 1976, 1985] at or near piston coring stations that later became coring stations for ODP leg 177 (41–50°S, 6–12°E) (Figure 1). The vertically stratified plankton tow samples were collected with 150 μm mesh nets within 333 μm nets used for structural support. The individual nets were sequentially opened and closed over discrete depth intervals between 0 and 800 m; the nine sample intervals and their vertical spacing varied from station to station (see *Mortyn and Charles* [2003] for additional information). MOCNESS samples were stored in 100% ethanol and wet-picked.

[7] Plankton samples from the Norwegian Sea (63–70°N, 4.5–12.5°E) were collected during July–September 2005 on board R/V *Polarstern*, pumping seawater from about 5–8 m depth and filtered through a 100 μm mesh net. Planktic foraminifera were rinsed with tap water in order to remove salt, and then frozen.

[8] Vertically towed samples from the NE Atlantic and western Mediterranean (36–39°N, 20°W–11°E)

were collected during March–April 2006 on board R/V *Poseidon*, by means of a multiple opening and closing net (MCN) with a 0.5 × 0.5 m mouth opening, equipped with five nets of 100 μm mesh size. Nets were sequentially opened and closed over discrete depth intervals between 0 and 300 m. Samples from the western Mediterranean represent a longitudinal transect from 2°W to 11°E along ~36/39°N (Figure 1). MCN samples were originally preserved with buffered formalin. Samples were rinsed back in the laboratory with buffered 12 MΩ water (70 ml of 25% NH_4OH in 1 l of water), and then frozen. Frozen samples were freeze-dried before picking, and then picked and separated into size classes 150–250 μm, 250–355 μm, 355–500 μm and >500 μm. Core top samples were collected from the western Mediterranean transect using a multicorer. For the core top study, only the top half centimeter was used. Samples were frozen immediately after collection, freeze-dried, wet-sieved to separate fines, dried at 40°C, and dry-sieved to separate into size classes 250–355 μm and 355–500 μm.

[9] The species analyzed in this study are the nongloborotaliids *Globigerina bulloides*, *Neogloboquadrina incompta*, *N. pachyderma*, *Orbulina universa* and *Turborotalia quinqueloba*, and the globorotaliids *Globorotalia inflata*, *G. hirsuta* and *G. truncatulinoides*. In the cases where it was not possible to work with monospecific or single-station samples, mixed samples were prepared. When possible, we aimed for sample masses of approximately 300 μg of calcite. This was possible in all core top samples, but was not achieved in most of the plankton tow samples, which in some cases were as small as 100 μg.

[10] Before analysis, plankton samples were cleaned using a modified version of the "Mg method" [*Rosenthal et al.*, 2004], with a high-peroxide oxidative step according to *von Langen et al.* [2005] and *Anand et al.* [2003]. Briefly, samples were cleaned to remove clays (water and methanol washes) and organic matter (50% H_2O_2 (30%) + 50% 0.1 M NaOH in a 75°C water bath for 30 min), followed by a weak acid leach (0.001M HNO_3). In this last step, each sample was treated individually, rather than as a batch, in order to prevent excess dissolution in small plankton tow samples (P. Anand, personal communication, 2006).

[11] Core top samples were cleaned with the "Cd method" [*Rosenthal et al.*, 2004], including a reductive step to remove possible Fe-Mn coatings that might influence Nd/Ca ratios. Furthermore, a cleaning test was performed in order to determine the difference in Nd/Ca ratios introduced by the inclusion of this reductive step. Splits of *G. inflata* 250–355 μm and 355–500 μm from the western Mediterranean transect were cleaned using the "Mg method" and the "Cd method." This also served as a "size fraction test," which enabled us to assess possible differences in Nd/Ca ratios due to foraminiferal test size. All the samples presented lower Mn/Ca ratios than the proposed "contamination threshold" of 100 μmol/mol [*Boyle*, 1983] for other trace element ratios in foraminiferal calcite.

[12] Nd/Ca ratios were measured in November 2007 at the University of Bristol by comparison of peak heights to a Bristol Spiked Gravimetric Standard (BSGS) using a Thermo Finnigan Element 2 Single-Collector Magnetic Sector Inductively Coupled Plasma Mass Spectrometer. Samples were introduced to the instrument via an ASX-100 microautosampler, a self-aspirating microconcentric nebulizer (with a flow rate of 100 μl/min), and a quartz glass cyclonic spray chamber. All samples were preliminarily analyzed and then diluted so that Ca content matched working standards in a second analysis. Accuracy and precision of Nd/Ca ratios were assessed by the analysis during each analytical session of gravimetrically prepared secondary consistency standards. Over the past 26 months, 50 analyses of a consistency standard with a Nd/Ca ratio of 1.1 μmol/mol, run at similar Ca concentrations to the samples analyzed here, gave an average Nd/Ca ratio that is within 1.1% of the gravimetric value with a standard deviation of 3.2%. As Nd/Ca ratios in our samples were between 2 and 10 times lower than the consistency standards, we will assume a conservative error of 10% in our results.

[13] Plankton tow Nd/Ca ratios, grouped by genus (globorotaliids/nongloborotaliids) and study areas, are compared to the closest available Nd concentration data for the water column, using the results published by *Jeandel* [1993], *Lacan and Jeandel* [2004], *Piepgras and Wasserburg* [1987], and *Tachikawa et al.* [2004] (Figure 1).

3. Results

[14] Nd/Ca ratios of tow samples (Table 1) are summarized in Table 2 and displayed in Figure 2. Ratios in oxidative-cleaned planktic foraminifera range from <0.01 μmol/mol for *G. bulloides* and *T.*

Table 1. Collection Data and Nd/Ca and Mn/Ca Ratios for Plankton Tow Samples

Species	Genus[a]	Size (μm)	Area	Station	Latitude (°N)	Longitude (°E)	Depth (m)	Nd/Ca (μmol/mol)	Mn/Ca (μmol/mol)
G. inflata	glob	250–355	SE Atlantic	TNO57-21	−41.0	8.0	63–142	0.23	1.3
G. inflata	glob	250–355	SE Atlantic	TNO57-21	−41.0	8.0	204–350	0.3	1.01
G. inflata	glob	250–355	SE Atlantic	TNO57-22	−43.0	12.0	27–122	0.06	1.2
G. truncatulinoides	glob	250–355	SE Atlantic	TNO57-11	−47.0	6.0	239–392	0.14	3.4
G. truncatulinoides	glob	250–355	SE Atlantic	TNO57-21	−41.0	8.0	63–142	0.26	3.8
G. truncatulinoides	glob	250–355	SE Atlantic	TNO57-21	−41.0	8.0	204–350	0.27	2.6
G. truncatulinoides	glob	355–500	SE Atlantic	TNO57-22	−43.0	12.0	222–295	0.12	3.1
G. bulloides	nonglob	150–250	SE Atlantic	TNO57-9	−47.0	7.0	0–75	0.02	0.58
G. bulloides	nonglob	150–250	SE Atlantic	TNO57-11	−47.0	6.0	0–800	0.02	2.2
G. bulloides	nonglob	150–250	SE Atlantic	TNO57-11	−47.0	6.0	0–75	0.01	0.89
G. bulloides	nonglob	250–355	SE Atlantic	TNO57-11	−47.0	6.0	0–75	0.02	1.2
G. bulloides	nonglob	150–250	SE Atlantic	TNO57-16	−50.0	6.0	0–83	0.07	1.5
G. bulloides	nonglob	150–250	SE Atlantic	TNO57-21	−41.0	8.0	0–63	0.04	3.6
G. bulloides	nonglob	150–250	SE Atlantic	TNO57-22	−43.0	12.0	62–67	0.01	1.5
G. bulloides	nonglob	250–355	SE Atlantic	TNO57-22	−43.0	12.0	62–67	0.01	0.37
G. bulloides	nonglob	150–250	SE Atlantic	TNO57-22	−43.0	12.0	27–122	0.01	0.91
G. bulloides	nonglob	150–250	SE Atlantic	TNO57-22	−43.0	12.0	0–27	0.01	0.36
G. bulloides	nonglob	250–355	SE Atlantic	TNO57-22	−43.0	12.0	0–27	0.004	0.51
N. incompta	nonglob	150–250	SE Atlantic	TNO57-16	−50.0	6.0	149–411	0.02	0.93
N. incompta	nonglob	150–250	SE Atlantic	TNO57-22	−43.0	12.0	62–67	0.06	1.1
N. incompta	nonglob	150–250	SE Atlantic	TNO57-22	−43.0	12.0	27–122	0.06	1.3
N. incompta	nonglob	150–250	SE Atlantic	TNO57-22	−43.0	12.0	0–27	0.05	1.0
N. pachyderma	nonglob	150–250	SE Atlantic	TNO57-9	−47.0	7.0	300–800	0.06	1.1
N. pachyderma	nonglob	150–250	SE Atlantic	TNO57-9	−47.0	7.0	0–75	0.04	0.75
N. pachyderma	nonglob	150–250	SE Atlantic	TNO57-11	−47.0	6.0	0–800	0.04	0.54
N. pachyderma	nonglob	150–250	SE Atlantic	TNO57-11	−47.0	6.0	392–783	0.03	0.25
N. pachyderma	nonglob	150–250	SE Atlantic	TNO57-11	−47.0	6.0	0–50	0.04	0.93
N. pachyderma	nonglob	150–250	SE Atlantic	TNO57-16	−50.0	6.0	149–411	0.03	Mn b.d.[b]
N. pachyderma	nonglob	150–250	SE Atlantic	TNO57-16	−50.0	6.0	0–83	0.04	2.6
N. pachyderma	nonglob	150–250	SE Atlantic	TNO57-16	−50.0	6.0	30–83	0.02	1.7
N. pachyderma	nonglob	150–250	SE Atlantic	TNO57-21	−41.0	8.0	63–350	0.04	1.0
N. pachyderma	nonglob	150–250	SE Atlantic	TNO57-21	−41.0	8.0	0–63	0.08	1.7
O. universa	nonglob	355–500	SE Atlantic	TNO57-22	−43.0	12.0	0–612	0.02	0.82
T. quinqueloba	nonglob	150–250	SE Atlantic	TNO57-9	−47.0	7.0	300–800	0.02	0.4
T. quinqueloba	nonglob	150–250	SE Atlantic	TNO57-11	−47.0	6.0	392–783	0.02	0.91
T. quinqueloba	nonglob	150–250	SE Atlantic	TNO57-16	−50.0	6.0	149–411	0.02	3.6
G. inflata	glob	355–500	NE Atlantic	POS334-69	36.0	−20.0	0–100	0.21	2.5
G. truncatulinoides	glob	355–500	NE Atlantic	POS334-72	36.0	−8.5	100–200	0.37	11
G. truncatulinoides	glob	355–500	NE Atlantic	POS334-72	36.0	−8.5	100–200	0.28	13
G. hirsuta	glob	355–500	NE Atlantic	POS334-69	36.0	−20.0	20–100	0.18	5.1
G. hirsuta	glob	>500	NE Atlantic	POS334-69	36.0	−20.0	80–100	0.25	15
G. hirsuta	glob	>500	NE Atlantic	POS334-70	37.0	−20.0	80–100	0.18	6.2

Table 1. (continued)

Species	Genus[a]	Size (μm)	Area	Station	Latitude (°N)	Longitude (°E)	Depth (m)	Nd/Ca (μmol/mol)	Mn/Ca (μmol/mol)
G. hirsuta	glob	>500	NE Atlantic	POS334-71	38.0	−20.0	60–80	0.21	5.4
G. hirsuta	glob	>500	NE Atlantic	POS334-72	36.0	−8.5	40–100	0.22	9.9
G. hirsuta	glob	355–500	NE Atlantic	POS334-72	36.0	−8.5	40–100	0.39	13
G. hirsuta	glob	355–500	NE Atlantic	POS334-72	36.0	−8.5	100–200	0.25	8.1
Nongloborotaliid mix	nonglob	mix	NE Atlantic	POS334-69	36.0	−20.0	0–100	0.12	1.4
Nongloborotaliid mix	nonglob	mix	NE Atlantic	POS334-70 + 71	–	–	0–100	0.17	2.1
Nongloborotaliid mix	nonglob	mix	NE Atlantic	POS334-72	36.0	−8.5	0–300	0.14	Mn b.d.[b]
N. incompta	nonglob	150–250	Norwegian Sea	–	64.0	5.50	8	0.12	3.5
N. incompta	nonglob	150–250	Norwegian Sea	–	64.0	5.50	8	0.12	2.8
N. incompta	nonglob	150–250	Norwegian Sea	–	66.8	8.3	8	0.09	3.8
N. incompta	nonglob	150–250	Norwegian Sea	–	66.8	8.3	8	0.08	4.0
N. incompta	nonglob	150–250	Norwegian Sea	–	69.5	11.5	8	0.07	5.2
N. incompta	nonglob	250–355	Norwegian Sea	–	64.0	5.5	8	0.12	3.7
N. incompta	nonglob	250–355	Norwegian Sea	–	64.0	5.5	8	0.12	2.9
N. incompta	nonglob	250–355	Norwegian Sea	–	66.8	8.3	8	0.11	6.0
N. incompta	nonglob	250–355	Norwegian Sea	–	66.75	8.3	8	0.09	4.0
N. incompta	nonglob	250–355	Norwegian Sea	–	69.5	11.5	8	0.07	5.4
N. incompta	nonglob	250–355	Norwegian Sea	–	69.5	11.5	8	0.07	5.2
G. inflata	glob	250–355	western Mediterranean	POS334-74	36.0	−2.0	100–300	0.42	54
G. inflata	glob	250–355	western Mediterranean	POS334-74	36.0	−2.0	100–300	0.32	46
G. inflata	glob	355–500	western Mediterranean	POS334-74	36.0	−2.0	100–300	0.33	52
G. inflata	glob	355–500	western Mediterranean	POS334-74	36.0	−2.0	100–300	0.32	48
G. inflata	glob	355–500	western Mediterranean	POS334-75	37.0	−0.5	0–40	0.32	19
G. inflata	glob	355–500	western Mediterranean	POS334-75	37.0	−0.5	40–100	0.17	9.3
G. inflata	glob	355–500	western Mediterranean	POS334-75	37.0	−0.5	100–300	0.2	12
G. inflata	glob	355–500	western Mediterranean	POS334-78	38.0	2.5	40–100	0.42	56
G. inflata	glob	355–500	western Mediterranean	POS334-78	38.0	2.5	100–200	0.37	58
G. inflata	glob	355–500	western Mediterranean	POS334-78	38.0	2.5	200–300	0.23	41
G. inflata	glob	250–355	western Mediterranean	POS334-78	38.00	2.5	40–300	0.4	48
G. inflata	glob	355–500	western Mediterranean	POS334-80	38.0	8.0	40–300	0.22	21
G. inflata	glob	355–500	western Mediterranean	POS334-80	38.0	8.0	0–300	0.26	28
G. inflata	glob	250–355	western Mediterranean	POS334-81	39.0	11.0	0–300	0.62	29
G. truncatulinoides	glob	>500	western Mediterranean	POS334-80	38.0	8.0	200–300	0.52	88
G. truncatulinoides	glob	355–500	western Mediterranean	POS334-80	38.0	8.0	200–300	0.56	84
G. truncatulinoides	glob	355–500	western Mediterranean	POS334-81	39.0	11.0	40–300	0.66	38
G. truncatulinoides	glob	>500	western Mediterranean	POS334-81	39.0	11.0	100–300	0.59	36
G. bulloides	nonglob	mix	western Mediterranean	POS334-74 + 75	–	–	0–300	0.06	2.9
G. bulloides	nonglob	mix	western Mediterranean	POS334-78 + 79	–	–	0–300	0.11	4.5
O. universa	nonglob	mix	western Mediterranean	POS334-74 + 78 + 79 + 80 + 81	–	–	0–300	0.05	0.45
Nongloborotaliid mix	nonglob	mix	western Mediterranean	POS334-80 + 81	–	–	0–300	0.14	2.8
Nongloborotaliid mix	nonglob	mix	western Mediterranean	POS334-74 + 78 + 79 + 80 + 81	–	–	0–300	0.08	8.7

[a] Glob, globorotaliid; nonglob, nongloborotaliid.
[b] Mn below detection limit.

Table 2. Minimum, Maximum, and Average Nd/Ca Ratios and K_d Values for Plankton Tow Samples

			Nd/Ca (μmol/mol)			K_d		
Area	Genus	N	Minimum	Maximum	Average	Minimum	Maximum	Average
SE Atlantic	nongloborotaliids	29	0.004	0.08	0.03	4	76	31
	globorotaliids	7	0.06	0.30	0.20	57	302	197
NE Atlantic	nongloborotaliids	3	0.12	0.17	0.14	93	132	111
	globorotaliids	10	0.18	0.39	0.25	140	302	197
NS South	nongloborotaliids	4	0.12	0.12	0.12	77	77	77
NS North	nongloborotaliids	7	0.07	0.11	0.08	78	122	92
Western Mediterranean	nongloborotaliids	5	0.05	0.14	0.09	20	57	36
	globorotaliids	18	0.17	0.66	0.39	70	270	158

quinqueloba in the SE Atlantic to 0.66 μmol/mol for *G. truncatulinoides* in the western Mediterranean. In all study areas, nongloborotaliid individuals generally present lower Nd/Ca ratios than globorotaliids. This feature is most conspicuous in the case of the western Mediterranean.

[15] Nd/Ca ratios in foraminiferal calcite have been compared to Nd/Ca ratios in seawater (Table 2 and Figure 3). K_d for nongloborotaliids ranges from 4 to 132, with an average of 49, while for globorotaliids it ranges from 57 to 302, with an average of 177. Figure 3 shows averages and ranges for each area and genus, plotted against the local range in Nd/Ca in seawater. There is little relationship between Nd/Ca in the foraminifera versus that in seawater for nongloborotaliids. For globorotaliids the regression yields an overall $K_d \sim 110$. The range in Nd/Ca ratios is larger in globorotaliids, and it is especially wide in the western Mediterranean.

[16] The cleaning test and shell size test results for core top samples show that Nd/Ca ratios are on average ~58% (std. dev. = 9.5%) lower in the "Cd method" splits, while no systematic differences are observed between size fractions. As for elements thought to be associated with possible "contaminant" phases, Mn/Ca and Fe/Ca ratios are on average 35% (std. dev. = 25%) and 64% (std. dev. = 27%) lower, respectively.

[17] Nd/Ca results have been plotted against Mn/Ca ratios in plankton tow samples (Figure 4) in order to examine any possible relationship, of at present unspecified origin, between these ratios. All samples have Mn/Ca ratios lower than the proposed contamination threshold of 100 μmol/mol [*Boyle*, 1983]. The samples with higher Mn/Ca ratios are the ones with higher Nd/Ca ratios, i.e., the globorotaliids. In the plot, there appears to be a relationship between these two variables, though with significant scatter. Mn/Ca ratios range from ~0 to 90 μmol/mol, while Nd/Ca ratios range from

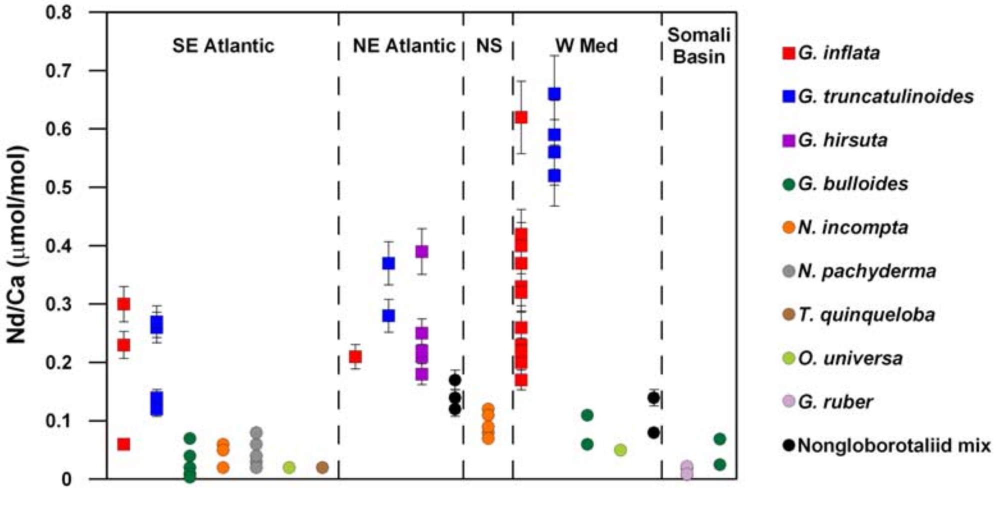

Figure 2. Plankton tow Nd/Ca ratios for the different species and study areas (NS, Norwegian Sea). Data for Somali Basin from *Pomiès et al.* [2002]. The different symbols represent the different genera analyzed (squares represent globorotaliids, and circles represent nongloborotaliids).

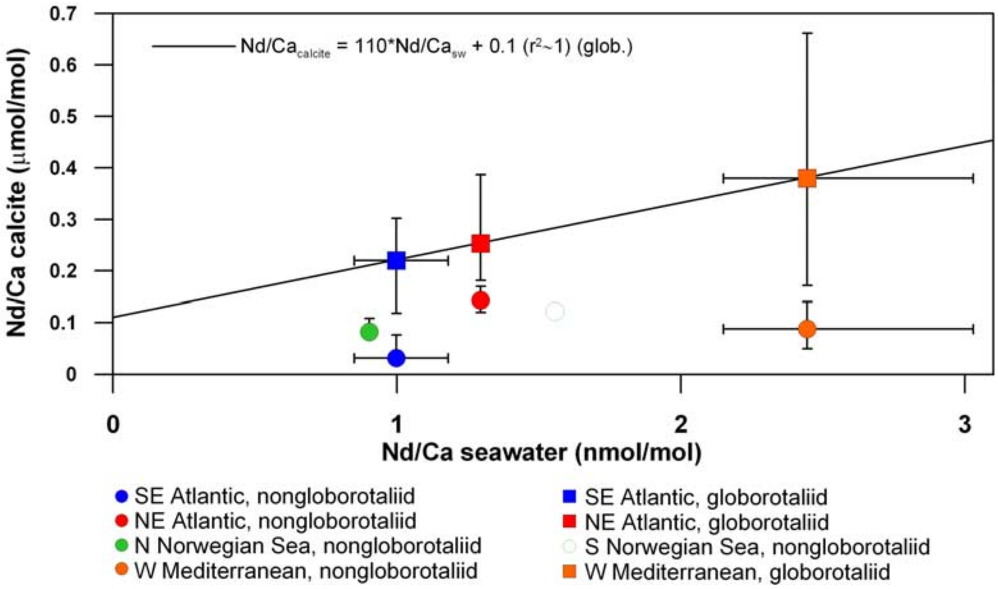

Figure 3. Nd/Ca ratios in foraminiferal calcite versus Nd/Ca ratios in seawater. Seawater data from *Jeandel* [1993], *Lacan and Jeandel* [2004], *Piepgras and Wasserburg* [1987], and *Tachikawa et al.* [2004] (see Figure 1 for more information). Nd/Ca ratios for seawater calculated from literature Nd concentration values and a Ca concentration in seawater of 0.01 moles/kg [*Vance and Burton*, 1999]. Each point represents the average Nd/Ca of all the samples from the specified genus and region, while the vertical "error bars" mark the range of Nd/Ca ratios for each case. Horizontal "error bars" represent the range of local seawater measurements (for the different stations and depths considered). The line is a linear regression through the globorotaliid mean values.

~0 to 0.7 μmol/mol. A linear regression through all the plankton tow data presented in this study yields the equation Nd/Ca (μmol/mol) = 0.006*Mn/Ca (μmol/mol) + 0.09 ($r^2 = 0.62$; $p < 0.001$). Figure 4 also shows data for the nongloborotaliid species *G. inflata* and *G. truncatulinoides* recovered from western Mediterranean core tops. These latter data present a similar relationship to that seen for the plankton tows.

[18] Figure 4 shows similarities between water column and core top globorotaliid samples in terms of Nd-Mn systematics. This feature is reinforced by Figure 5, where just Nd/Ca data for water column and core top samples of the globorotaliid species *G. inflata* and *G. truncatulinoides* along the western Mediterranean transect are compared. Nd/Ca ratios of core top samples are 0.12–0.50 μmol/mol while their plankton tow counterparts are 0.17–0.66 μmol/mol. In all cases, water column ratios are higher than those from corresponding core tops. These differences between water and sediment are probably due to differences in cleaning methods. The average reduction in Nd/Ca ratio between water column and core tops is 48 ± 8% (except 1 *G. truncatulinoides* sample, with only a 20% reduction), within the range of reduction associated with the "Cd method." *G. truncatulinoides* presents the highest ratios, both in the water column and in core tops. Nd/Ca data for core tops (Table 3) are summarized in Table 4.

4. Discussion

4.1. Comparison With Previous Plankton Tow Data

[19] Very few plankton tow Nd/Ca data have been published to date. The most thorough study [*Pomiès et al.*, 2002] presented 6 plankton tow and 21 sediment trap samples. But only 1 plankton sample was collected between 0 and 100 m depth while the other samples came from 402.9, 848.8 and 952 m depth, clearly well below the habitat of *G. ruber* and *G. bulloides*. The data given by *Vance and Burton* [1999] and *Vance et al.* [2004] were for plankton tow foraminifera collected at 0–70 m. For the Hawaii samples given by *Vance et al.* [2004]*G. sacculifer* and *O. universa* were analyzed, while the data given by *Vance and Burton* [1999] are for a mixed species sample from the North Atlantic.

[20] Our study comprises 83 plankton tow samples (8 different species), collected from 4 different hydrographic areas spanning 120° of latitude. All the samples come from the uppermost water column, ranging from 0 to 8 m in the Norwegian Sea to ~400–800 m in the deepest SE Atlantic samples.

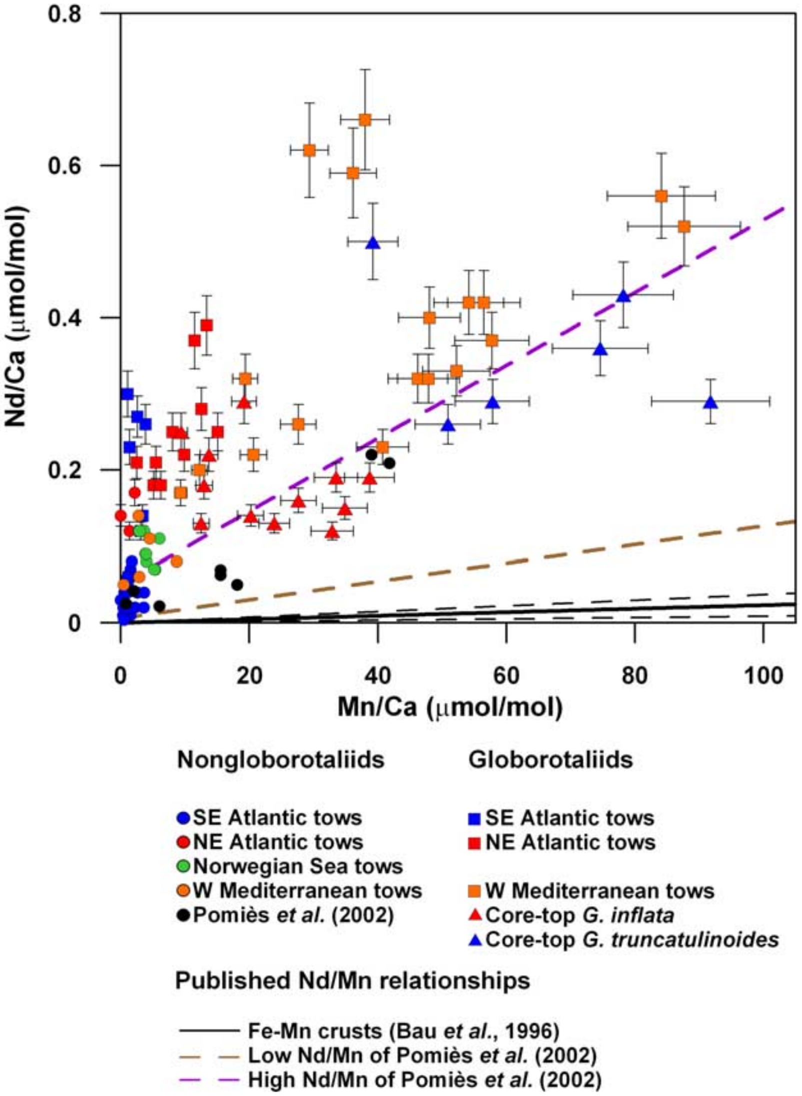

Figure 4. Nd/Ca versus Mn/Ca in plankton tow and core top samples. The different symbols are for the different genera analyzed (squares represent globorotaliids, and circles represent nongloborotaliids). Globorotaliid core top samples (triangles) are from the western Mediterranean area. Solid line labeled as "Fe-Mn crusts" represents the average Nd/Mn ratio of Fe-Mn crusts as measured by *Bau et al.* [1996], while the accompanying dashed lines show the standard deviation. Violet and brown dashed lines reproduce lines plotted by *Pomiès et al.* [2002, Figure 6], which represent the high Nd and low Nd secondary coatings (only composed of MnO_2) that might explain Nd/Ca ratios in their plankton tow samples. However, we should note that these lines represent Nd concentrations of 2000 and 8000 ppm, one order of magnitude higher than specified in the *Pomiès et al.* [2002] text and clearly much higher than Fe-Mn crusts. We assume a conservative error in Mn/Ca measurements of 10%.

The total plankton tow Nd/Ca range observed in the 4 study areas is in general agreement with previous work (Table 5). The total range seen here is 0.01–0.7 μmol/mol, versus 0.02 μmol/mol for *G. ruber* from the upper 100 m of the Indian Ocean [*Pomiès et al.*, 2002] and 0.35–0.38 μmol/mol for *G. sacculifer* and 0.71 μmol/mol for *O. universa* from the Pacific Ocean near Hawaii [*Vance et al.*, 2004]. The mixed species sample from the North Atlantic reported by *Vance and Burton* [1999] is slightly higher than our range at 0.85 μmol/mol.

4.2. Nd/Ca Ratios and Nd Distribution Coefficient (K_d) in Plankton Tows

[21] Mean K_ds in our data set are 49 for nongloborotaliids and 177 for globorotaliids. Our results for nongloborotaliids are consistent with *Pomiès et al.* [2002] data, although our range is wider. In contrast, data for globorotaliids are higher than *Pomiès et al.* [2002] observations, although significantly lower than data from *Vance et al.* [2004] and *Vance and Burton* [1999]. In the case

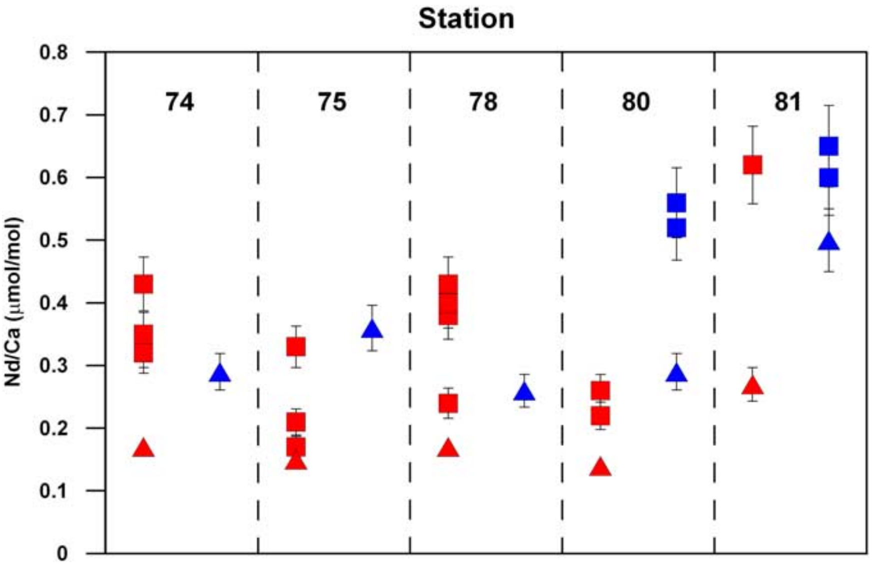

Figure 5. Nd/Ca ratios for plankton tow (squares) and core top (triangles) samples from the western Mediterranean transect. *G. inflata* (red) core top ratios are the average of two size fractions (250–355 μm and 355–500 μm), and *G. truncatulinoides* (blue) data are from the fraction 355–500 μm. Core top samples have been cleaned with both an oxidizing and reducing step, whereas tow samples have only been cleaned with an oxidizing step (see section 3 for further discussion).

of the latter two studies, given the similarities in the Nd/Ca ratios of their measured tow foraminifera to some of those measured here (see section 4.1), it is the low Nd contents of seawater that controls the high K_ds.

[22] One of the major arguments against the reliability of planktic foraminifera as recorders of the Nd isotopic composition of seawater has always been the high K_d found for this element in foraminifera [*Vance et al.*, 2004]. Inorganic experiments [*Zhong and Mucci*, 1995] yield very high partition coefficients (K_d = 120–2500), but these were conducted under very different conditions from natural environments and also lack the "vital effects" inherent in biogenic calcite. However,

Table 3. Collection Data and Nd/Ca and Mn/Ca Ratios for Core Top Samples

Species	Genus[a]	Size Fraction (μm)	Station	Latitude (°N)	Longitude (°E)	Core Depth (m)	Nd/Ca (μmol/mol)	Mn/Ca (μmol/mol)
G. inflata	glob	355–500	POS334-74	36.0	−2.0	1800	0.19	33
G. inflata	glob	250–355	POS334-74	36.0	−2.0	1800	0.14	20
G. inflata	glob	355–500	POS334-75	37.0	−0.5	2500	0.13	13
G. inflata	glob	250–355	POS334-75	37.0	−0.5	2500	0.18	13
G. inflata	glob	355–500	POS334-78	38.0	2.5	2700	0.22	14
G. inflata	glob	250–355	POS334-78	38.0	2.5	2700	0.13	24
G. inflata	glob	355–500	POS334-79	38.5	5.5	2700	0.19	39
G. inflata	glob	250–355	POS334-79	38.5	5.5	2700	0.16	28
G. inflata	glob	355–500	POS334-80	38.0	8.0	2600	0.15	35
G. inflata	glob	250–355	POS334-80	38.0	8.0	2600	0.12	33
G. inflata	glob	355–500	POS334-81	39.0	11.0	1100	0.29	19
G. inflata	glob	250–355	POS334-81	39.0	11.0	1100	0.25	9.4
G. truncatulinoides	glob	355–500	POS334-74	36.0	−2.0	1800	0.29	58
G. truncatulinoides	glob	355–500	POS334-75	37.0	−0.5	2500	0.36	75
G. truncatulinoides	glob	355–500	POS334-78	38.0	2.5	2700	0.26	51
G. truncatulinoides	glob	355–500	POS334-79	38.5	5.5	2700	0.43	78
G. truncatulinoides	glob	355–500	POS334-80	38.0	8.0	2600	0.29	92
G. truncatulinoides	glob	355–500	POS334-81	39.0	11.0	1100	0.50	39

[a] Glob, globorotaliid.

Table 4. Minimum, Maximum and Average Nd/Ca Ratios for Core Top Samples

Species	N	Nd/Ca (μmol/mol) Minimum	Maximum	Average
G. inflata	12	0.12	0.29	0.18
G. truncatulinoides	6	0.26	0.50	0.36

more recent work on REE in core top foraminifera from the SE Pacific [*Haley et al.*, 2005] supported the idea of high Nd K_d in planktic foraminifera. This study reports REE distribution coefficients between 100 and 500 for both planktic and benthic foraminifera, a range that is relatively similar to that found in our plankton tow data set. These K_ds were found to be consistent across the REEs in waters with very different REE concentrations. A possible explanation for this relatively high K_d could be the affinity of REEs for organic matter, such as the proteins used by foraminifera to acquire calcium ions [*Haley et al.*, 2005]. In this context, the concentration of any ion in the foraminifera, whose inventory is dominated by the organic phase, will depend on both its concentration in the water and its binding efficiency to the biomolecular agents of calcification. This argument would be consistent with the idea that the Nd that dominates foraminiferal isotopic analyses is most likely contained not in the carbonate lattice, but rather in the organic material, which is formed in the upper ocean [*Vance et al.*, 2004].

4.3. Nd/Ca-Mn/Ca Systematics

[23] As shown earlier, there is a statistically significant linear correlation between Nd/Ca and Mn/Ca ratios in our plankton tow data set (albeit with some scatter (Figure 4)). It is also evident from our data that the Nd-Mn systematics seen in the plankton tows are also observed in the core tops (Figure 4); that is, core top *G. inflata* and *G. truncatulinoides* Nd/Ca show a correlation with Mn/Ca ratios that is similar to that found in plankton tows. Core top samples underwent a reductive cleaning, so if any readsorption took place, it had little effect on Nd/Ca ratios. In fact, given that it is present in plankton tows as well as core tops, and whatever the reason for this correlation between Mn/Ca and Nd/Ca, it is acquired in the upper ocean and virtually unaffected during foraminiferal transport to the sedimentary

Table 5. Nd Contents of Plankton Tow Foraminifera

Location	Water Depth (m)	Species	Cleaning	Nd/Ca (μmol/mol)	Apparent K_d
Pacific Ocean (Hawaii)[a]	0–25	*O. universa*	none	0.71	~1300
		G. sacculifer	none	0.38	~700
		G. sacculifer	O[b]	0.35	~650
Atlantic Ocean[c]	0–70	mixed species	O	0.85	400–600
Indian Ocean (Somali Basin)[d]	20–952	*G. ruber*	LTA[e]+O	0.008–0.022	16–40
	402–848.8	*G. bulloides*	LTA[e]+O	0.025–0.069	21–53
SE Atlantic[f]	27–350	*G. inflata*	O*[g]	0.06–0.3	57–302
	63–392	*G. truncatulinoides*	O*	0.12–0.27	118–272
	0–122	*G. bulloides*	O*	<0.01–0.07	4–66
	0–411	*N. incompta*	O*	0.02–0.06	23–60
	0–800	*N. pachyderma*	O*	0.02–0.08	16–76
	0–612	*O. universa*	O*	0.02	24
	149–800	*T. quinqueloba*	O*	0.02	18
NE Atlantic[f]	0–100	*G. inflata*	O*	0.21	163
	100–200	*G. truncatulinoides*	O*	0.28–0.37	217–287
	0–200	*G. hirsuta*	O*	0.18–0.39	140–302
Norwegian Sea[f]	0–8	*N. incompta*	O*	0.07–0.12	77–122
Western Mediterranean[f]	0–300	*G. bulloides*	O*	0.06–0.11	25–45
	0–300	*O. universa*	O*	0.05	20
	0–300	*G. inflata*	O*	0.17–0.62	70–254
	40–300	*G. truncatulinoides*	O*	0.52–0.66	213–270

[a] *Vance et al.* [2004].
[b] O denotes organic clean.
[c] *Vance and Burton* [1999].
[d] *Pomiès et al.* [2002].
[e] Before any chemical cleaning, the samples were low-temperature ashed (LTA).
[f] This study.
[g] O* denotes strong oxidative cleaning (see section 2).

Table 6. Plankton Tow/Core Top Comparison

Location	Species	Origin	Cleaning	Nd/Ca (μmol/mol)
Pacific Ocean (Hawaii)[a]	*O. universa*	plankton tow	none	0.71
		core top	Red+Ox	1.01
Western Mediterranean[b]	*G. inflata*	plankton tow	high peroxide	0.17–0.62
		core top	Red+Ox	0.15–0.27
	G. truncatulinoides	plankton tow	high peroxide	0.52–0.65
		core top	Red+Ox	0.29–0.46

[a] *Vance et al.* [2004].
[b] This study.

record. The similarity between core top and plankton tow foraminifera in terms of their Nd/Ca ratios (Figure 5) confirms that found in the only other study where such a comparison has been made (Table 6).

[24] A priori, there are two potential causes for the Mn/Ca-Nd/Ca correlations. The first is that they are controlled by Fe-Mn oxide coatings. If this is the case the similarity of the Nd-Mn systematics in tows and core tops would suggest that these coatings are acquired in the upper water column. The second possibility is that Nd and Mn are acquired by another phase, perhaps organics [*Haley et al.*, 2005], in the upper water column during calcification.

[25] As noted by *Vance et al.* [2004] with reference to uncleaned sedimentary foraminifera, Nd/Mn ratio of Fe-Mn oxides is significantly different from the foraminifera data and appears to rule out the first explanation. Assuming a Nd/Mn ratio of a Fe-Mn coating similar to that of hydrogenetic crusts or Mn nodules ($\sim 2-4 \times 10^{-4}$ mol/mol [*Bau et al.*, 1996; *Wang et al.*, 1998]), the maximum contribution of a contaminant coating to Nd/Ca would be about 0.03 μmol/mol at a Mn/Ca of 100 μmol/mol. Thus, the reported concomitant increase of Nd/Ca and Mn/Ca is unlikely to be produced by a Fe-Mn coating. Oxic pore waters, the only pore waters which the core top foraminifera analyzed here have encountered, have very low Nd/Mn at around 1×10^{-5} mol/mol [*Haley et al.*, 2004]. Anoxic pore waters have higher Nd/Mn values, but even these waters average at least an order of magnitude lower than the analyzed foraminifera, at around $2-3 \times 10^{-4}$ mol/mol [*Elderfield and Sholkovitz*, 1987; *Haley et al.*, 2004]. *Pomiès et al.* [2002] suggest that a MnO_2 phase with Nd concentrations of 200–800 ppm (Nd/Mn = $1.2-4.8 \times 10^{-4}$ mol/mol) could explain the Nd/Ca ratios measured in their foraminifera. However, *Pomiès et al.* [2002, Figure 6], which compares the Mn/Ca and Nd/Ca of foraminifera tests with the Nd/Mn ratios of Fe-Mn crusts, considers Nd/Mn ratios in coatings 1 order of magnitude higher ($\sim 1.2-4.8 \times 10^{-3}$ mol/mol) than described in the *Pomiès et al.* [2002] text (Figure 4). In our data, the regression for plankton-towed samples suggests a Nd/Mn ratio of 6×10^{-3} mol/mol, while the Nd/Ca of foraminifera tests at Mn/Ca ~ 0 μmol/mol can be as high as 0.3 μmol/mol in globorotaliids, up to 6 times higher than *Pomiès et al.*'s [2002] data.

[26] These calculations assume that the cleaning process is as effective for Nd as it is for Mn and that none of the Nd released by the cleaning is readsorbed onto the foraminifera. Our plankton samples underwent a high-peroxide oxidative cleaning but not a reductive cleaning, so existing Fe-Mn oxides (if any) were not removed during the process. Therefore, no readsorption took place during the cleaning and the measured Mn/Ca is the original Mn content of the test and of the coexisting "contaminant" phases (if any) at the moment of collection. We note that such an assertion is consistent with the findings of *Vance et al.* [2004], who showed that the Nd/Mn ratios of sedimentary foraminifera that had not been cleaned were also 2 orders of magnitude in excess of Fe-Mn crusts.

[27] If contamination by Mn oxide phases is ruled out, then the high Nd contents in foraminifera, as well as the high Nd/Mn ratios, are still unexplained. We agree with the hypothesis put forward by *Vance et al.* [2004] and *Haley et al.* [2005], that organic matter associated with calcification may play a role. In such a scenario, the Nd/Mn ratio of foraminifera might reflect (1) the Nd/Mn ratio of the seawater in which they calcify and (2) the enrichment factor of Nd relative to Mn in the organic matter. The Nd/Mn ratio of world ocean surface waters is around 0.006 ± 0.002 (1 std. dev.) mol/mol (Table 7, and ignoring the two anomalous values at 0.0003 and 0.019 mol/mol), more than an order of magnitude greater than crusts. The Nd/Mn

.**Table 7.** Water Column Mn and Nd Concentrations and Nd/Mn Ratios

	Mn Data					Nd Data					
	Station	Position	Depth (m)	Concentration (nM)	Reference[a]	Station	Position	Depth (m)	Concentration (pM)	Reference[a]	Nd/Mn ($\times 10^{-3}$)
Indian Ocean	5	14°30′N, 67°E	40–60	2.01	1[b]	1605	14°30′N, 67°E	40–60	11	2	5.5
	8	22°30′N, 60°40′E	3–50	2.11	1[b]	1608	22°30′N, 60°40′E	3–50	9.7	2	4.6
	9	23°30′N, 59°E	4–60	2.68	1[b]	1609	23°30′N, 59°E	4–60	11.2	2	4.2
Pacific Ocean	GEOSECS 225	32°37′N, 161°55′E	3	2.46[c]	3[c]	TPS47 39-1	47°N, 161°08′E	3	15.9	4	6.5
						CM-5*	44°N, 155°E	surface	15.2	5	6.2
	GEOSECS 227	25°N, 170°5′E	21	0.98[c]	3[c]	TPS24 271-1	24°17′N, 150°28′E	0	5.41	4	5.5
	GEOSECS 324	22°59′S, 146°4′W	6	1.38[c]	3[c]	31	20°S, 160°W	30	0.411	6	0.29
Atlantic Ocean	78-016-8	53°N, 41°W	12	1.09	7[b]	Hudson 83-036, Station 11	52°05′N, 41°01′W	5	21.07	8	19
	Bermuda	32°15′N, 64°35′W	5	2.6	7[b]	AII 109-1, Station 30	36°15′N, 61°58′W	5	14.42	8	5.5
	10402	31°27′N, 24°34′W	24	1.1	9[b]	AII 109-1, Station 79	36°15′N, 19°57′W	5	9.29	8	8.4
	10554	31°30′N, 24°26′W	15	0.83	9[b]						11
	10404	34°23′N, 12°29′W	24	1.23	9[b]	AII 109-1, Station 95	36°17′N, 10°02′W	0	12.48	8	10
						10404	34°23′N, 12°29′W	13	12.4	10	10

[a] References are as follows: 1, *Saager et al.* [1989]; 2, *German and Elderfield* [1990]; 3, *Klinkhammer and Bender* [1980]; 4, *Piepgras and Jacobsen* [1988]; 5, *Amakawa et al.* [2004]; 6, *Piepgras and Wasserburg* [1982]; 7, *Yeats and Bewers* [1985]; 8, *Piepgras and Wasserburg* [1987]; 9, *Statham and Burton* [1986]; 10, *Greaves et al.* [1991].

[b] Dissolved Mn.

[c] Total dissolvable Mn.

ratio of our plankton tow data set is, on average, very similar at ~0.006 mol/mol. Organic material isolated from foraminiferal tests has been shown to be a heterogeneous mixture of proteins and polypeptides [*Robbins and Brew*, 1990], including the amino acids Aspartic acid, Serine, Glycine, Alanine and Glutamic acid [*King and Hare*, 1972; *Robbins and Brew*, 1990]. Metal complex equilibrium constants for the binding of Mn to these compounds (expressed as log K) are 3.2–3.7 [*Furia*, 1972; *Martell and Smith*, 1974]. The available data [*Cefola et al.*, 1962; *Makhijani and Sangal*, 1977; *Hancock et al.*, 1979; *Reddy and Rao*, 1986] (see also A. E. El'khilyali et al. and R. Deng et al. as cited by *Kremer et al.* [2005]) for the binding of Nd to these ligands (log K) cluster around 3.3–4.8 (n = 6), with one value at 5.7 and one at 6.5 [*Limaye and Saxena*, 1986]. These data are at least consistent with plankton tow and core top Nd/Mn ratios found in this study of about 0.006 mol/mol on average. Therefore, we hypothesize that the planktic foraminiferal Nd signal is linked to organic matter in the test, which is embedded in, and protected from diagenesis by [*Ren et al.*, 2009, and references therein], the calcite structure.

[28] This link between organic matter embedded in the tests and foraminiferal Nd content would explain and reconcile the features observed in this and previous studies, i.e., the high Nd concentration in tests, the correlation between Mn and Nd and, more importantly, the fact that foraminifera record an upper water column Nd isotopic signal, which is preserved from calcification to residence in marine sediments and not significantly affected by cleaning procedures.

4.4. Intergenus Differences

[29] Globorotaliids have Nd/Ca ratios 6 times higher (on average) than nongloborotaliids. The reason for this feature of the data is unclear at the moment. Though some potential reasons are discussed briefly below, the causes of this difference must remain speculative at present.

[30] It is possible that the lower Nd/Ca in nongloborotaliids is an artifact produced by the cleaning process, with the precleaning crushing step weakening the whole structure to a greater degree than for globorotaliids, allowing subsequent oxidative cleaning to remove internal organic layers. Globorotaliids have a test morphology characterized by thick walls, in contrast to the thinner and more porous walls of surface-living spinose nongloborotaliids.

[31] Alternatively, the difference between nongloborotaliids and globorotaliids may be a real feature originating in the water column, with two potential causes. Globorotaliids have thicker and denser tests, which may have more organic matter than nongloborotaliids. However, *King and Hare* [1972] showed that the total amino acid concentrations were comparable between different genera, with *G. bulloides* showing the highest values. *King and Hare* [1972] classified 16 species of planktic foraminifera according to their amino acid composition. The globorotaliids *G. truncatulinoides*, *G. inflata* and *G. hirsuta* are grouped together in "Factor 1" (rich in Alanine, Proline and Valine), while the rest of species analyzed in this study are grouped in "Factor III" (rich in Glycine, Serine and Glutamic Acid). It is possible that these different organic compounds have different affinities for REE.

5. Summary and Concluding Remarks

[32] We have presented the first extensive multispecific plankton tow Nd/Ca data set from several oceanic sites (SE Atlantic, NE Atlantic, Norwegian Sea, western Mediterranean), together with underlying core tops from the Mediterranean. Nd/Ca ratios in plankton-towed planktic foraminifera, cleaned only with an oxidative procedure, range from 0.01 to 0.66 μmol/mol. Where data for plankton tows and core tops are available, the tows and core tops give very similar Nd/Ca ratios. K_d values range from 4 to 302, clearly higher than for other trace elements in planktic foraminifera, which points to a location other than the carbonate lattice for Nd uptake. A relationship between Nd/Ca and Mn/Ca has been obtained, as in some other studies [*Pomiès et al.*, 2002]. We have shown that this relationship cannot be attributed to contamination by Fe-Mn oxide coatings in either our data or previous studies, because the Nd/Mn ratios of such phases are over an order of magnitude too small. Furthermore, readsorption during cleaning cannot explain the high Nd/Mn ratio of foraminifera because plankton tow data presented here did not undergo reductive cleaning.

[33] We suggest instead, following *Vance et al.* [2004] and *Haley et al.* [2005], that the Nd obtained from foraminiferal tests may be located in intratest organic material. This suggestion is at least consistent with the Nd/Mn ratios obtained from the foraminifera, the values in seawater, and the binding constants of Nd and Mn to the proteins located intratest. Moreover, such a suggestion helps explain some other aspects of Nd systematics

in foraminifera. First, the high binding constants to the organic matter (log K $\sim$ 4–5) could explain the high REE contents in all foraminifera. Second, the acquisition of Nd in the surface water column in this way would explain the fact that sedimentary planktic foraminifera reflect the Nd isotopic composition of the surface ocean. Third, *Vance et al.* [2004] found that the Nd isotopic composition of cleaned sedimentary foraminifera remained the same, despite the relative ferocity of the cleaning techniques applied. These observations suggest that the Nd inventory of foraminifera is dominated by a single reservoir that is partially, but not fully, accessed by each cleaning step. This is also consistent with an isotopically homogeneous pool of Nd that is bound to organic material located within the test, that can be partially broken down during cleaning, but which is only fully accessed when the calcite test itself dissolves. Finally, the protection that the calcite structure affords from diagenetic processes [*Ren et al.*, 2009] might explain the fact that down-core Nd isotopic records show clear relationships to other better established paleoceanographic proxies like δ^{18}O [*Burton and Vance*, 2000; *Scrivner et al.*, 2004; *Osborne et al.*, 2008].

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