Cd/Ca ratios of in situ collected planktonic foraminiferal tests

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[1] The Cd/Ca ratios of planktonic foraminiferal tests have been used to reconstruct surface water nutrient utilization and paleoproductivity. The reliability of this proxy has hitherto not been comprehensively studied, however. To fill this gap, we present novel Cd/Ca data for in situ sampled and sedimentary planktonic foraminifers of the species *Globigerinoides ruber*, *G. sacculifer*, *Globigerina bulloide*s, *Orbulina universa*, and *Globorotalia truncatulinoides* from the Arabian Sea and the North Atlantic. The Cd/Ca ratios obtained for *G. ruber* sampled from the live habitat generally display a correlation with seawater phosphate content, but no such trend is observed for *G. sacculifer*. This distinct behavior may reflect different ecological niches or species-specific incorporation of Cd into the calcite shells of the organisms. The Cd/Ca ratios of *G. ruber*, *G. sacculifer*, and *G. bulloides* from surface sediments are consistently higher than those obtained for live collected specimens of the same species. Postdepositional alteration of the tests is unlikely to be responsible for these systematic differences. Rather, they appear to reflect a combination of factors, including the formation of calcite crusts with high Cd contents, the different timescales that are represented by in situ and sedimentary foraminiferal tests, and the dominance of tests from periods of high productivity in sediments. Our results also reveal higher Cd/Ca ratios for live *G. ruber* than for settling tests of the same species. This suggests that planktonic foraminiferal shells are partially dissolved while they individually settle through the water column. Sedimentary tests, however, will be less affected by dissolution processes because these shells are primarily deposited in mass sinking events, which feature much higher settling velocities than those experienced by single settling shells.

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1. Introduction

[2] The geochemistry of cadmium in seawater has attracted significant attention over the past 30 years. This interest is based on the marine distribution of Cd, which resembles that of the macronutrient phosphate [e.g., *Boyle et al.*, 1976; *Bruland*, 1980]. Cadmium is furthermore incorporated into the tests of foraminifera in proportion to the Cd concentration of the ambient seawater [*Boyle*, 1981]. Hence, the Cd/Ca ratios of foraminiferal shells have been used in numerous paleoceanographic studies, as a water mass tracer and to investigate past changes in nutrient utilization. Measurements of Cd in planktonic foraminifers are of particular interest, because such data can provide information on surface water phosphate utilization, which in turn is linked to phytoplankton productivity [*Elderfield and Rickaby*, 2000; *Rickaby and Elderfield*, 1999].

[3] A number of results, however, have raised questions regarding the reliability of the Cd/Ca proxy. Artifacts from the contamination of the tests by ferromanganese coatings and other Cd-rich phases have hitherto been assessed only by indirect evidence [*Boyle*, 1988]. It has also been suggested that the dissolution of shells following deposition on the ocean floor may significantly alter the Cd/Ca ratios of foraminiferal tests [*McCorkle et al.*, 1995], analogous to the Mg/Ca values [e.g., *Rosenthal and Boyle*, 1993]. In addition, symbiont activity [*Mashiotta et al.*, 1997], Fe limitation (particularly in HNLC regions) [*Cullen*, 2006; *Frew et al.*, 2001], Zn concentration, and pCO_2 [*Cullen et al.*, 1999] might limit the use of the Cd/Ca proxy.

[4] The use of foraminiferal proxies is furthermore affected by the life cycle during which planktonic foraminifers migrate vertically through the water column. Juvenile individuals of shallow-dwelling species ascend into surface waters, whereas with maturity they descend into deeper waters to reproduce [*Hemleben et al.*, 1989; *Schiebel et al.*, 1997; *Schiebel and Hemleben*, 2005]. Planktonic foraminifers grow their tests by sequentially forming new chambers (primary calcite) and some species also precipitate a gametogenic calcite crust during reproduction and/or secondary calcite crusts in subsurface waters [*Bé*, 1980; *Duplessy et al.*, 1981; *Hemleben et al.*, 1989; *Schiebel et al.*, 1997]. For *G. sacculifer*, compositional differences between primary test walls and secondary calcite crust have been documented for $\delta^{18}O$ and Mg in specimens retrieved from plankton tows and laboratory-culturing experiments [*Duplessy et al.*, 1981; *Eggins et al.*, 2003; *Nürnberg et al.*, 1996; *Spero and Lea*, 1993]. Surface veneers that are enriched in Mg, Ba, Mn and Zn have also been documented for live sampled tests of *G. ruber* [*Eggins et al.*, 2003]. Consequently, different parts

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Table 1. Sampling Locations and Associated Seawater Parameters for in Situ Collected Planktonic Foraminifers Analyzed in This Study[a]

Sample	Cruise	Location	Station Number	Date	Latitude	Longitude	Net Number	Water Depth (m)	Species	Number	Test Size (μm)
5r/1/2/3/4	M 31/3	Arabian Sea	111/2	13.03.95	16.09°N	59.69°E	912	0–200	*G. ruber*	35	>200
4r/3/4	M 31/3	Arabian Sea	110/4	13.03.95	16.20°N	60.30°E	914	0–100	*G. ruber*	40	>200
4s/1/2	M 31/3	Arabian Sea	110/4	13.03.95	16.20°N	60.30°E	914	0–100	*G. sacculifer*	40	>250
4r/1	M 31/3	Arabian Sea	110/4	13.03.95	16.20°N	60.30°E	915	300–500	*G. ruber*	40	250–315
4r/2	M 31/3	Arabian Sea	110/4	13.03.95	16.20°N	60.30°E	915	500–700	*G. ruber*	20	250–315
3r	SO 119	Arabian Sea	WAST 7	24.05.97	16.20°N	60.31°E	1284	20–40	*G. ruber*	25	>315
7r	SO 119	Arabian Sea	WAST 7	25.05.97	16.20°N	60.31°E	1287	0–40	*G. ruber*	64	>250
7s	SO 119	Arabian Sea	WAST 7	25.05.97	16.20°N	60.31°E	1287	20–40	*G. sacculifer*	14	>500
1r/1	M 32/5	Arabian Sea	430	01.08.95	17.11°N	60.01°E	979	60–80	*G. ruber*	20	250–315
1r/2	M 32/5	Arabian Sea	430	01.08.95	17.11°N	60.01°E	979	60–80	*G. ruber*	14	>315
1s	M 32/5	Arabian Sea	430	01.08.95	17.11°N	60.01°E	979	60–80	*G. sacculifer*	15	>315
2r/1	M 33/1	Arabian Sea	WAST 601	30.09.95	16.15°N	60.48°E	1007	20–40	*G. ruber*	40	250–315
2r/2	M 33/1	Arabian Sea	WAST 601	30.09.95	16.15°N	60.48°E	1009	2000–2500	*G. ruber*	40	250–315
6b	M 36/5	N. Atlantic	354/72	30.09.96	48.60°N	22.38°W	1173	40–80	*G. bulloides*	41	250–315

[a]Station number, shipboard site number; WAST, western Arabian Sea station; net number, multinet number; and Number, number of specimens handpicked for analysis.

of a shell could display distinct Cd contents, which reflect the variable seawater conditions experienced by a foraminifer during its life cycle.

[5] The above concerns regarding the Cd/Ca proxy could be addressed by analyses of planktonic foraminifers that are sampled from the live habitat and comparison of these data with results obtained for samples from the deeper water column and from surface sediments collected at the same location. However, the precise determination of Cd/Ca ratios for in situ collected planktonic foraminifers is technically challenging, because (1) the amount of sample material available for analysis is generally limited and (2) planktonic foraminiferal calcite has extremely low Cd contents of ~0.002 to 0.1 μmol per mol Ca [*Lea*, 1999].

[6] In this study, we have carried out such comprehensive analyses on tests from tropical to transitional (non-HNLC) regions. To this end, we used a recently developed method [*Ripperger and Rehkämper*, 2007] to obtain Cd/Ca data for in situ sampled *Globigerinoides ruber*, *Globigerinoides sacculifer* and *Globigerina bulloide*s from the Arabian Sea and the North Atlantic. For comparison, we also analyzed the same species from core top samples taken at the same location. Our results reveal previously unidentified differences in Cd/Ca ratios between cytoplasm bearing tests (''live specimens''), empty settling tests (''dead specimens''), and shells from surface sediments, as well as species-specific variations.

2. Samples

2.1. In situ Samples

[7] The in situ collected planktonic foraminifers were sampled with plankton tows [*Schiebel et al.*, 1995] from both surface (0–100 m water depth, mainly ''live'' foraminifera) and subsurface waters (100–2500 m water depth, mainly empty settling tests) in the Arabian Sea and North Atlantic (Table 1).

[8] The samples from the western Arabian Sea station (WAST) at 16°N, 60°E were collected in March, August and September 1995 during the *Meteor* cruises M31/3, M32/5 and M33/1, as well as *Sonne* cruise SO119 in May 1997 [*Hiller*, 1996; *Schiebel and Bayer*, 1996; *Schiebel et al.*, 2004]. The North Atlantic was sampled in September 1996 during *Meteor* cruise M36/5 at the BIOTRANS area at 47°N, 20°W [*Schiebel et al.*, 2001].

[9] *Globigerinoides ruber* (white), *Globigerinoides sacculifer* (without sac chamber), and *Globigerina bulloides* were picked from the >200 μm size fraction to exclude juvenile specimens, and facilitate comparison of the new data with previously published results on, for example, stable isotope ratios. Depending on availability and shell size, 14 to 40 tests were analyzed, which is equal to an initial sample weight of about 200 to 500 μg of $CaCO_3$. Only one independent measurement was performed for the majority of in situ samples, because more material was not available for further analyses.

2.2. Surface Sediment Samples

[10] The same planktonic foraminifer species were analyzed from the top surfaces of the sediment cores SL 3011–1 (Arabian Sea [*Ivanova et al.*, 2003]) and MC 575 (North Atlantic [*Kurbjeweit*, 2000]). Sediment samples were obtained using a multicorer at the same locations as the in situ collected samples from the water column (Table 2). The samples were sieved over a 250 m screen and handpicked to obtain aliquots that comprised about 20 to 300 individuals, which is equivalent to an initial sample weight of about 0.8–4 mg $CaCO_3$. Two independent sample fractions were analyzed for each of the three species that were investigated.

[11] Additional specimens of *Orbulina universa* and *Globorotalia truncatulinoides* were analyzed from the North Atlantic core MC 575 (Table 2). Forty and 37 tests were picked from the size fraction >250 μm, resulting in initial sample weights of about 1.6 and 3 mg for *O. universa* and *G. truncatulinoides*, respectively.

[12] Mainly sedimentary planktonic foraminifers were used to validate the long-term reproducibility of the methods because in situ collected specimens were too rare to permit repeated analyses. Samples for method validation (*O. universa*) were picked from the size fraction >500 μm from the 0–40 cm interval of the Azores Front core KL 88 (Table 2) [*Schiebel et al.*, 2000]. The samples comprised

Table 2. Sampling Locations for Sediment Core Samples Analyzed in This Study

Sample	Core	Location	Latitude	Longitude	Water Depth (m)	Core Depth (cm)	Species	Specimens[a]	Test Size (μm)
1	KL 88	North Atlantic	34.78°N	27.66°W	2060	0–40	*O. universa*	46	>500
2/3/4	KL 88	North Atlantic	34.78°N	27.66°W	2060	0–40	*O. universa*	10	>500
5	KL 88	North Atlantic	34.78°N	27.66°W	2060	0–40	*O. universa*	12	>500
6/7/8	KL 88	North Atlantic	34.78°N	27.66°W	2060	0–40	*O. universa*	23	>500
9	SL 3011–1	Arabian Sea	16.53°N	55.33°E	2636	3	*G. ruber*	50	>250
10	SL 3011–1	Arabian Sea	16.53°N	55.33°E	2636	3	*G. ruber*	122	>250
11	SL 3011–1	Arabian Sea	16.53°N	55.33°E	2636	3	*G. sacculifer*	20	>500
12	SL 3011–1	Arabian Sea	16.53°N	55.33°E	2636	3	*G. sacculifer*	26	>500
13	MC 575	North Atlantic	47.18°N	19.57°W	4577	0–0.5	*G. bulloides*	50	>300
14	MC 575	North Atlantic	47.18°N	19.57°W	4577	0–0.5	*G. bulloides*	300	>250
15	MC 575	North Atlantic	47.18°N	19.57°W	4577	0–0.5	*O. universa*	40	>250
16	MC 575	North Atlantic	47.18°N	19.57°W	4577	0–0.5	*G. truncatulinoides*	37	>250

[a]Specimens, number of specimens handpicked for analysis.

10–23 specimens, which is equivalent to an initial sample weight of about 0.6 to 1.4 mg $CaCO_3$.

3. Oceanographic Setting of the Sampling Areas

[13] Physical properties and nutrient distribution in the Arabian Sea are largely influenced by the seasonal oscillation of the monsoon winds [*Webster et al.*, 1998]. The summer monsoon (southwest monsoon (SWM)) is characterized by strong upwelling and high nutrient concentrations along the Oman margin from May to October [*Bauer et al.*, 1991]. Upwelling ceases during October, and the winter monsoon (northeast monsoon (NEM)) affects the hydrography of the Arabian Sea from November to March. Relatively calm conditions prevail during the intermonsoon (IMS) in spring, from March to May. The surface water nutrient concentrations are lower during the NEM and IMS than during the SWM because the former periods feature less vigorous water mixing [*Garcia et al.*, 2006].

[14] The BIOTRANS area (47°N, 20°W) in the eastern North Atlantic is situated between the North Atlantic Current (NAC) and the Azores Current (AzC) [*Stramma*, 2001]. Phytoplankton productivity peaks in spring when the upper water column is thoroughly mixed. In summer, a well stratified surface water column causes nutrient depletion and less productive conditions than in spring [*Zeitzschel et al.*, 1998]. During autumn the mixed layer deepens again forced by storms. This process is accompanied by the entrainment of nutrients into the mixed layer and stimulation of phytoplankton and zooplankton production [*Schiebel et al.*, 2001; *Sellmer et al.*, 1998].

3.1. Seawater Parameters for in Situ Collected Planktonic Foraminifers

[15] Dissolved seawater phosphate concentrations and temperatures that prevailed during the calcification periods of the live collected foraminifers are listed in Table 3. At two of the six sites dissolved seawater phosphate concentrations and temperatures were determined from samples that were collected along with planktonic foraminifer assemblages (hereafter referred to as "in situ" seawater phosphate and temperature). These phosphate concentrations deviate significantly (by a factor of ~2–4) from the average monthly values given by *Garcia et al.* [2006] and *Locarnini et al.* [2006], but the relative differences between different months are similar. For consistency, we therefore used the phosphate and temperature data from *Garcia et al.* [2006] and *Locarnini et al.* [2006] throughout this study, if not explicitly stated otherwise. To this end, we calculated the mean phosphate and temperature values for the uppermost 75 m of the water column for each calcification month, to account for the overall depth habitat (~0–80 m) occupied by *G. ruber*, *G. sacculifer* and *G. bulloides* [*Schiebel et al.*, 1997, 2004]. Note that the calcification month does not

Table 3. Seawater Phosphate Contents and Temperatures for the Calcification Months of the in Situ Foraminifers[a]

Sample	Species	Calcification Month	Sampling Depth (m)	P 0–75 (μmol/L)	T 0–75 (°C)	P in situ 0–60	T in situ 0–60	Season
4s/1	*G. sacculifer*	February/March 1995	0–100	0.47	25.05	-	-	wNEM/IMS
4r/3, 5r	*G. ruber*	March 1995	0–200	0.49	25.23	-	-	wNEM/IMS
7s	*G. sacculifer*	April/May 1997	20–40	0.46	26.99	0.12	28.43	IMS/eSWM
3r, 7r	*G. ruber*	May 1997	0–40	0.43	27.56	0.12	28.43	IMS/eSWM
1r, 1s	*G. ruber*, *G. sacculifer*	July 1995	60–80	0.77	25.75	0.38	26.64	SWM
2r/1	*G. ruber*	September 1995	20–40	0.99	24.67	-	-	lSWM
6b	*G. bulloides*	September 1996	40–80	0.29	15.58	0.10	15.26	

[a]P, seawater phosphate concentration; T, seawater temperature; 0–75, mean phosphate and temperature values for the uppermost 75 m of the water column from *Garcia et al.* [2006] and *Locarnini et al.* [2006]; and in situ 0–60, mean phosphate concentration and temperature for the uppermost 60 m determined during the time of sampling [*Schiebel et al.*, 2004; *Zeitzschel et al.*, 1998]. Season denotes the Indian Ocean monsoons: wNEM, weak NE monsoon; IMS, intermonsoon; eSWM, early SW monsoon; SWM, SW monsoon; and lSWM, late SW monsoon.

Table 4. Seawater Phosphate Contents and Temperatures for the Bloom Months of the Foraminifers From Surface Sediments[a]

Sample	Species	Sampling Area	Bloom Month	P_{bm} (μmol/L)	T_{bm} (°C)	P Annual (μmol/L)	T Annual (°C)
SL 3011–1	*G. ruber*	Arabian Sea	July–September	1.16	21.29	0.95	24.02
SL 3011–1	*G. sacculifer*	Arabian Sea	March–May	0.60	25.93	0.95	24.02
MC 575	*G. bulloides*	N. Atlantic	May–June	0.32	13.54	0.33	14.04
MC 575	*O. universa*	N. Atlantic	July–August	0.23	15.51	0.33	14.04
MC 575	*G. truncatulinoides*	N. Atlantic	-	0.72	11.23	0.72	11.23

[a]P_{bm} and T_{bm} denote the seawater phosphate concentration and temperature for the bloom month. P annual and T annual denote the mean annual seawater phosphate content and temperature at the sampling site. All phosphate and temperature values were taken form *Garcia et al.* [2006] and *Locarnini et al.* [2006] and are average values for the uppermost 75 m, except for *G. truncatulinoides* where the seawater parameters correspond to 400 m water depth.

necessarily correspond to the sampling date, because the calcification period is 1 month for *G. sacculifer* and *G. bulloides*, and 2 weeks for *G. ruber* [*Bijma et al.*, 1990; *Erez et al.*, 1991; *Schiebel and Hemleben*, 2005].

3.2. Seawater Parameters for Surface Sediment Samples

[16] The seawater phosphate and temperature data for the sediment core top samples were also derived from *Garcia et al.* [2006] and *Locarnini et al.* [2006]. For the shallow-dwelling species *G. ruber*, *G. sacculifer*, *G. bulloides* and *O. universa* [*Schiebel et al.*, 1997, 2001, 2004], the seawater parameters were averaged for the uppermost 75 m of the water column of the corresponding time intervals, i.e., the most productive seasons ("bloom months," Table 4). During those highly productive periods, the upper water column is completely mixed, and nutriclines are not established [*Schiebel et al.*, 2001, 2004]. For the long-lived and deep dwelling species *G. truncatulinoides* [*Schiebel and Hemleben*, 2005], we used the annual mean phosphate and temperature values at 400 m depth.

4. Analytical Methods

4.1. General Techniques

[17] A detailed description of the analytical techniques is provided by *Ripperger and Rehkämper* [2007]. Only a brief summary is thus given here, plus more comprehensive accounts of procedures that are specific to this study.

[18] Following handpicking, the foraminiferal tests were crushed and cleaned with a leaching procedure [see *Ripperger and Rehkämper*, 2007] that is similar to techniques used in previous Cd/Ca studies [*Boyle and Rosenthal*, 1996; *Boyle and Keigwin*, 1985; *Martin and Lea*, 2002]. About 50% of the foraminiferal material was lost during cleaning of sediment core samples, but when applied to in situ collected foraminiferal shells the losses were typically larger at up to 80%. The latter observation appears to reflect that in situ sampled tests are more readily shattered into extremely small pieces during crushing and cleaning with ultrasonication. These small fragments either dissolved more readily during the treatment or were otherwise lost during solution transfers. In addition, the initial sample sizes were generally smaller for the in situ collected foraminifers than for the sediment samples, which may enhance the effect of calcite dissolution during leaching [*Boyle*, 1995].

[19] Following cleaning, the tests were dissolved in dilute HNO_3 and split in two aliquots. The major (95%) and minor (5%) aliquots were then spiked with a ^{110}Cd and ^{43}Ca tracer, respectively. The Ca aliquot did not require further processing. Following evaporation to dryness it was simply redissolved in an appropriate volume of 0.1 M HNO_3 to obtain a solution suitable for mass spectrometric analysis. Cadmium was separated at high yield (>90%) from the matrix elements by cation-exchange chromatography prior to the mass spectrometry.

[20] Repeated measurements indicate that the method is characterized by a total procedural Cd blank of 112 ± 44 fg (1 SD, n = 12), and a detection limit of 131 fg (3 SD of blank). All Cd concentration data were corrected for this blank contribution. For samples with 1 pg of Cd, a blank correction of this order of magnitude generates an uncertainty of about 4% for the Cd concentration. The Ca blank of 17 ± 6 ng (1 SD, n = 3) has a negligible effect on the measured Ca contents as it constituted only ~0.2% of the indigenous Ca present in the sample solutions.

[21] The isotope dilution concentration measurements were carried out with Nu Plasma MC-ICPMS instruments at ETH Zurich, using a multiple ion counting system for Cd, and multiple Faraday collectors equipped with 10^{11} Ω resistors for Ca. Sample introduction employed a CETAC MCN 6000 desolvator, which was used in conjunction with T1H nebulizers (CETAC) that were operated at flow rates of about 100–120 μl/min. A single Cd concentration measurement required about 4 min, during which about 400–500 μl of sample solution were consumed. The majority of in situ samples were analyzed as solutions with total Cd concentrations of ~3–15 pg/mL (ppt). Such analyses generally consumed about 0.5–2.5 pg of natural Cd and yielded total ion beam intensities of about (3–9) × 10^4 cps and (2–6) × 10^5 cps for ^{110}Cd and ^{111}Cd, respectively, depending on the spike-sample ratio. Each Ca analysis required about 6.5 min, during which ~650 μL of sample solution were consumed. In situ samples were analyzed as solutions with total Ca concentrations of about 1–2 μg/mL (ppm), which yielded total ion beam intensities of about 150 to 300 × 10^{-11} A.

4.2. Examination of Foraminiferal Cleaning Procedure

[22] The removal of secondary ferromanganese (Fe-Mn) oxide coatings and organic matter represent important steps to obtain reliable foraminiferal Cd/Ca records. Cleaning procedures therefore include both a reductive and an oxidative cleaning step [*Boyle and Rosenthal*, 1996; *Boyle and Keigwin*, 1985; *Martin and Lea*, 2002; *Ripperger and*

Table 5. Effect of the Reductive Cleaning Procedure on Mn/Ca and Cd/Ca Ratios[a]

Sample	Species	RCS	Mn/Ca (μmol/mol)	Cd/Ca (μmol/mol)
4s/1	*G. sacculifer*	yes	3	0.0192 ± 0.0002
4s/2	*G. sacculifer*	no	4	0.5032 ± 0.0127
4r/3	*G. ruber*	yes	66	0.0109 ± 0.0006
4r/4	*G. ruber*	no	4	0.3915 ± 0.0117

[a]RCS, reductive cleaning step included in cleaning procedure or not. The uncertainty of the Cd/Ca ratios denotes the total uncertainty (see section 4.3).

Rehkämper, 2007]. In principle, foraminiferal tests that were collected directly from the water column are not expected to have any Fe-Mn oxide coatings that would need to be removed by reductive cleaning. It is furthermore reasonable to assume that such samples may require more stringent oxidative cleaning because in situ collected foraminifers typically bear more organic matter than foraminifers from sediment cores [e.g., *Anand et al.*, 2003]. We therefore carried out experiments, which investigated whether different cleaning procedures are necessary for in situ collected and sedimentary foraminifers.

[23] The effect of the reductive cleaning procedure on in situ collected *G. ruber* and *G. sacculifer* was evaluated by analyses of four individually processed samples from 0 to 100 m water depth (Table 1, samples 4s/1/2 and 4r/3/4). One sample of each species (4s/1 and 4r/3) was subjected to the full cleaning procedure [*Ripperger and Rehkämper*, 2007], while the other two samples (4s/2 and 4r/4) were cleaned according to the standard cleaning protocol but without the reduction step. An intensified oxidative treatment was applied to all four samples, which consisted of five (normally two [see *Ripperger and Rehkämper*, 2007]) leaching steps.

[24] Two experiments were performed to investigate the potential impact of organic matter on the total Cd content of foraminifers. (1) The Cd concentrations of the oxidative cleaning solutions, which had been used to leach the samples 4s/1/2 and 4r/3/4 (Table 1), were determined. (2) The Cd/Ca ratios of in situ collected tests were determined after the tests had been subjected to the full cleaning procedure [*Ripperger and Rehkämper*, 2007], however, with a varying number of oxidative cleaning steps (2, 3, 4 or 5). Four individually processed sample fractions, each containing 35 specimens of *G. ruber* from 0 to 200 m depth, were used in this second experiment (Table 1, samples 5r/1/2/3/4).

4.3. Data Presentation

[25] All Cd/Ca and Mn/Ca data are reported in μmol/mol. The quoted uncertainties for the Cd/Ca data were obtained as follows. (1) If only a single analysis was available for a sample, the "total uncertainty" (TU) was obtained by propagating the individual uncertainties:

$$\text{total uncertainty} = R \cdot \sqrt{\sigma_B^2 + \sigma_{Cd}^2 + \sigma_{43Ca}^2 + \sigma_{42Ca}^2} \quad (1)$$

where R is the Cd/Ca ratio of the spiked sample in μmol/mol and σ_B, σ_{Cd}, σ_{43Ca}, and σ_{42Ca} denote the relative errors from the Cd blank uncertainty and from the uncertainty of the Cd and Ca concentrations, based on the within-run statistics of the $^{110}Cd/^{111}Cd$, $^{43}Ca/^{44}Ca$ and $^{42}Ca/^{44}Ca$ isotope data, respectively. (2) When several measurements were performed for a sample, the error denotes either 1 standard deviation (1 SD) or the total range of the individual data (hereinafter abbreviated as RI), depending on the number of independent analyses.

[26] The interspecimen variability of Cd/Ca data for foraminiferal samples is generally larger than the within-day uncertainty of the measurements [*Boyle*, 1995]. For this study, the best estimate of the interspecimen variability for surface sediments and in situ samples is given by the relative standard deviation (RSD) obtained for multiple analyses of (1) *O. universa* picked from the sediment core KL 88 and (2) in situ sampled *G. ruber* (4r/3, 5r), respectively (see section 5.2).

5. Results

5.1. Evaluation of Leaching Procedure

5.1.1. Experiments That Monitor the Removal of Fe-Mn Coatings

[27] The leaching experiments yielded similar Mn/Ca ratios for *G. sacculifer* (~3–4 μmol/mol) (Table 5) regardless of whether the cleaning procedure [*Ripperger and Rehkämper*, 2007] included the reductive cleaning step or not. For *G. ruber*, the sample without reductive cleaning (sample 4r/4) even yielded a significantly lower Mn/Ca ratio compared to that obtained for the reductively cleaned tests (sample 4r/3). In general, Mn/Ca values below 100 μmol/mol are considered indicative of sufficient removal of secondary Mn-oxide overgrowths [*Boyle*, 1983; *Martin and Lea*, 1998] and all four samples display Mn/Ca ratios (of <66 μmol/mol) below this threshold. This indicates that the in situ collected foraminifers have little or no Fe-Mn oxide coating, even though the samples were collected from the well oxygenated euphotic zone (0–100 m), where Mn would most likely form insoluble Mn-oxide, that can precipitate onto organic particulate matter [*Qasim*, 1982; *Pomies et al.*, 2002].

[28] It is noteworthy, however, that foraminiferal tests that were not subjected to a reductive cleaning display Cd/Ca ratios that are more than an order of magnitude larger compared to reductively cleaned samples (Table 5). This is most readily explained by (1) contamination of the tests with a Cd-bearing phase, which is not removed by acid or oxidative leaching, or (2) partial dissolution of Cd-rich organic matter during the reductive cleaning.

5.1.2. Experiments That Monitor the Removal of Organic Material

[29] In the first experiment, we monitored the Cd/Ca ratios of successive oxidative cleaning solutions that were siphoned off from the samples after leaching. These supernatants yielded decreasing Cd contents with increasing leach number for tests that had not been subjected to a previous reductive cleaning step (Figure 1a). In contrast, consistently low Cd contents of less than 1 pg were

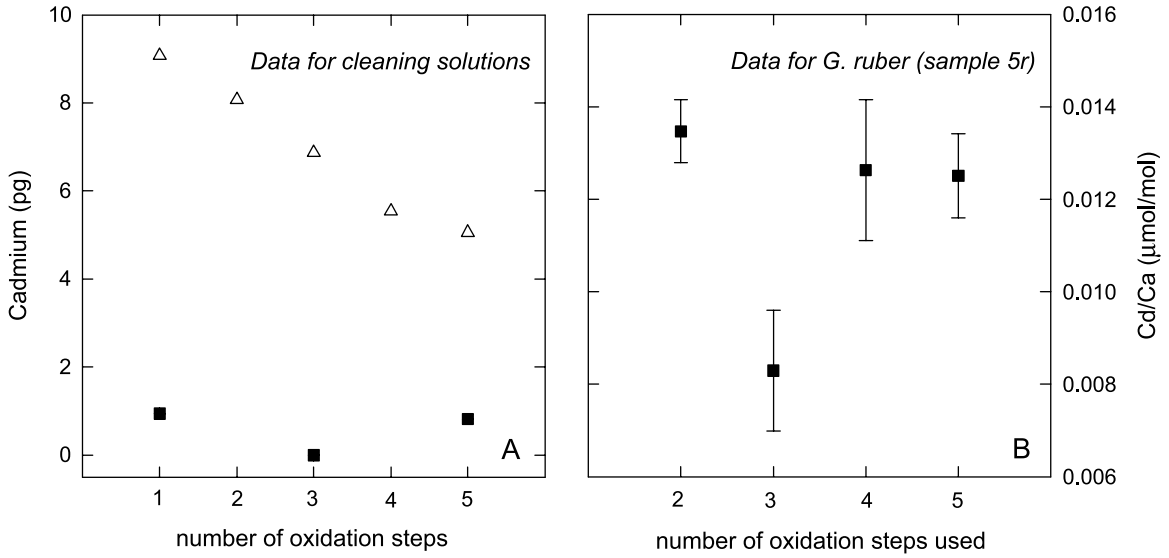

Figure 1. (a) Cd contents of oxidative cleaning solutions after they had been used for leaching of in situ collected foraminifers. Each oxidative treatment lasted for 10 min [*Ripperger and Rehkämper*, 2007], after which a fresh batch of cleaning solution was used. Squares represent data for samples subjected to the full cleaning procedure, including the reductive treatment [*Ripperger and Rehkämper*, 2007]. Triangles represent data for samples that underwent the standard cleaning protocol but without the reductive step. The error bars for the Cd data are smaller than the symbol size. (b) Measured Cd/Ca ratios for tests of *G. ruber* picked from a plankton net catch at 0–200 m depth. Each sample was treated with the standard cleaning protocol but with a different number of oxidative cleaning steps, each lasting 10 min. Error bars represent the total uncertainty (see section 4.3).

recorded for the supernatants of samples, which were cleaned according to our standard procedure, which includes reductive leaching [*Ripperger and Rehkämper*, 2007]. The observation that the oxidative cleaning solutions of nonreductively treated samples contain much more Cd (even after five successive 10 min leaches) than reductively cleaned tests, strengthens the conclusion that organic matter is at least partially removed by the reducing agent.

[30] In the second experiment, we monitored the Cd/Ca ratios of samples subjected to two, three, four or five oxidation steps. A low Cd/Ca ratio of 0.0083 ± 0.0013 (t.e.) was obtained for the tests that were treated with three oxidative cleaning steps, but the remaining fractions yielded a nearly constant (4% RSD) Cd/Ca ratio of 0.0129 μmol/mol (Figure 1b). This suggests that no improvement in cleaning is gained by the application of more than two oxidation steps. The slightly lower Cd/Ca ratio obtained for the sample that was leached 3 times can be attributed to interspecimen variability, as the sample fractions had not been homogenized before cleaning.

5.1.3. Summary of the Leaching Experiments

[31] The results of the leaching experiments indicate that the standard cleaning protocol described by *Ripperger and Rehkämper* [2007] is also suitable for cleaning of in situ collected tests. This conclusion is supported by the Mn/Ca ratios that were determined for all collected tests analyzed in this study. For this large group of samples, the Mn/Ca ratios varied between 3 and 108 μmol/mol, which does not significantly exceed the threshold value of 100 μmol/mol [*Boyle*, 1983; *Martin and Lea*, 1998]. A major advantage of using a cleaning procedure that is essentially identical to the standard Cd/Ca leaching protocol, is that this facilitates the comparison of data acquired for in situ collected samples with results for sedimentary foraminifers from this and previous studies.

5.2. Analytical Reproducibility and Natural Variability of Cd/Ca Ratios

[32] The long-term reproducibility of foraminiferal Cd/Ca data is based on multiple analyses, conducted over a period of 2 years, for *O. universa* tests picked from the sediment core KL 88 (Table 6). A total of 11 analyses were carried out and these used 8 independent sample fractions that were cleaned and processed separately. The measurements consumed about 5–11 pg and 0.5–1 μg of natural Cd and Ca, respectively, and yielded an average Cd/Ca ratio of 0.0307 ± 0.0038 (1 SD). This uncertainty, which is equivalent to an RSD value of ±12%, is more than an order of magnitude larger than the analytical reproducibility of ±0.7% that was determined in a previous study [*Ripperger and Rehkämper*, 2007]. Our result is comparable to the reproducibility of about 8% reported by *Rickaby et al.* [2000] for 4 and 6 replicate picks of foraminiferal tests from a sediment core. Taken together, these data support the finding of *Boyle* [1995], who concluded that the reproducibility of foraminiferal Cd/Ca ratios is limited by the interspecimen variability within a sediment sample ("natural variability"), if precise methods are available for the measurements.

[33] Repeated analyses were also performed for in situ collected foraminifers from a water depth of 0–200 m. A

Table 6. Reproducibility of Cd/Ca Ratios Obtained for Multiple Analyses of *O. universa* Picked From the Sediment Core KL 88[a]

Sample	n	Cd/Ca (μmol/mol)	Total Uncertainty (μmol/mol)
1[b]	4	0.0271	0.0002[c]
2	1	0.0261	0.0002
3	1	0.0333	0.0003
4	1	0.0309	0.0002
5	1	0.0362	0.0004
6	1	0.0295	0.0003
7	1	0.0275	0.0004
8	1	0.0348	0.0006
Average KL 88 *O. universa*	8	0.0307 ± 0.0038 (RSD 12%)	

[a]The average value calculated as unweighted mean of n independent measurements. The quoted uncertainty denotes 1 standard deviation. Total uncertainty is as defined in section 4.3.
[b]From *Ripperger and Rehkämper* [2007].
[c]One standard deviation.

total of five analyses were carried out for *G. ruber* (samples 5r and 4r/3, Table 7), and these utilized five independent sample fractions. The measurements yielded an average Cd/Ca ratio of 0.0116 ± 0.0020 (1 SD) and a RSD of ±18%. This RSD value is similar to but slightly worse than the reproducibility obtained for tests from sediment core sample KL 88 (Table 6), but the majority of analyses for in situ collected foraminifers consumed only ∼0.5 to 0.8 pg of natural Cd.

5.3. Cd/Ca Ratios of in Situ Collected Planktonic Foraminifers

[34] The Cd/Ca records that were acquired for the in situ collected planktonic foraminifers are summarized in Table 7. These analyses focused mainly on the spinose species *G. ruber* and *G. sacculifer* from the Arabian Sea. In order to compare the Cd/Ca ratios of live collected (cytoplasm bearing) foraminifers to those of dead specimens (settling, empty tests), the results were divided into three categories according to the depth range from which the foraminifers were collected. Category A samples were taken from the respective species-specific natural habitats and are hence expected to consist almost exclusively of live specimens. Category B samples include foraminifera collected from depth ranges that extend to levels marginally below the actual live habitats (0–200 m). Therefore, it can be assumed that these samples consist of live individuals and recently deceased specimens. As the ratio of living-to-dead individuals is estimated to be ∼10:1 at 100 m water depth [*Schiebel*, 2002], it is reasonable to combine the discussion of category A and B samples. Samples of category C were taken well below the natural habitat at depths of 300 to 2500 m and therefore contain mainly dead specimens.

5.3.1. Live Foraminifers: Categories A (0–80 m) and B (0–200 m)

[35] The live habitats of the analyzed species span a nearly identical depth range of ∼0–60 m for *G. sacculifer* and *G. bulloides* and ∼0–80 m for *G. ruber* [*Schiebel et al.*, 1997, 2004]. Samples of *G. ruber* and *G. sacculifer* were obtained during different monsoon seasons (Table 3), and the analyzed foraminifers are thus assumed to have calcified under different ecological (e.g., nutrient levels) and physical (e.g., light, temperature) conditions.

[36] The seasonal variations in ecological conditions (Figure 2a) are generally mirrored by the Cd/Ca ratios of the analyzed tests of live *G. ruber* (Figure 2b). Samples of *G. ruber* (4r/3 and 5r) that were collected in March 1995

Table 7. Cd/Ca Records Obtained for Samples of in Situ Collected Planktonic Foraminifers[a]

Sample	Species	Sampling Date	Water Depth (m)	n	Cd (pg)	Cd/Ca (μmol/mol)	Total Uncertainty	Blank Correction (%)
Category A (0–80 m Water Depth)								
3r	*G. ruber*	24.05.97	20–40	1	0.26	0.0040	0.0007	32
7r	*G. ruber*	25.05.97	0–40	1	1.1	0.0039	0.0002	9
Average 3r and 7r				2		0.0039 ± 0.0001 (RI)		
7s	*G. sacculifer*	25.05.97	20–40	1	3.8	0.0175	0.0002	3
1r/1	*G. ruber*	01.08.95	60–80	1	1.3	0.0320	0.0012	8
1r/2	*G. ruber*	01.08.95	60–80	1	3.0	0.0470	0.0010	4
Average 1r/1-2				2		0.0395 ± 0.0075 (RI)		
1s	*G. sacculifer*	01.08.95	60–80	1	2.2	0.0198	0.0005	5
2r/1	*G. ruber*	30.09.95	20–40	1	0.71	0.0162	0.0010	14
6b	*G. bulloides*	30.09.96	40–80	1	0.40	0.0085	0.0009	23
Category B (0–200 m Water Depth)								
5r/1[b]	*G. ruber*	13.03.95	0–200	1	1.8	0.0135	0.0004	6
5r/2[b]	*G. ruber*	13.03.95	0–200	1	0.59	0.0083	0.0007	16
5r/3[b]	*G. ruber*	13.03.95	0–200	1	0.76	0.0126	0.0008	13
5r/4[b]	*G. ruber*	13.03.95	0–200	1	1.3	0.0125	0.0005	8
4r/3[b]	*G. ruber*	13.03.95	0–100	1	0.77	0.0109	0.0006	13
Average 5r/1-4 and 4r/3				5		0.0116 ± 0.0020 (1 SD)		
4s/1b	*G. sacculifer*	13.03.95	0–100	1	5.2	0.0192	0.0002	2
Category C (300–2500 m Water Depth)								
4r/1	*G. ruber*	13.03.95	300–500	1	0.22	0.0034	0.0007	35
4r/2	*G. ruber*	13.03.95	500–700	1	0.27	0.0048	0.0008	29
2r/2	*G. ruber*	30.09.95	2000–2500	1	0.78	0.0041	0.0002	13

[a]The average Cd/Ca ratios calculated as unweighted means of n independent measurements. Total uncertainty is as defined in section 4.3. Cd (pg) denotes the amount of natural Cd determined in the sample solutions by isotope dilution.
[b]Samples that were treated with the standard cleaning protocol but using three (5r/2), four (5r/3) or five (5r/4, 4r/3, 4s/1) oxidation steps, respectively.

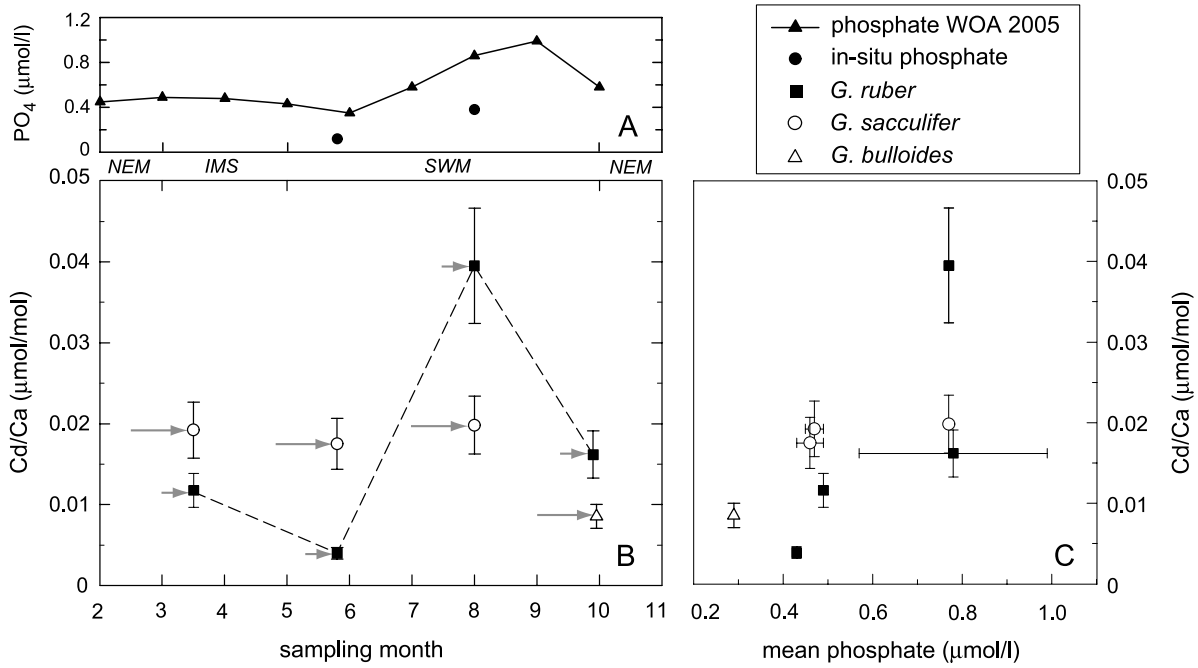

Figure 2. (a) Seawater phosphate concentration for the uppermost 75 m of the water column at 16°N and 60°E, derived from *Garcia et al.* [2006] (triangles) and seawater phosphate concentrations determined at the time of sampling (circles). (b) Cd/Ca ratios of live *G. ruber* (squares) and *G. sacculifer* (circles) collected in the Arabian Sea versus the sampling month. The arrows denote the life span (calcification period) of the two species, which is a fortnight for *G. ruber* and a full synodic lunar cycle for *G. sacculifer*. The different monsoon seasons are indicated in the upper part of Figure 2b. Also shown are data for the single in situ *G. bulloides* sample (triangle) from the North Atlantic. (c) Cd/Ca ratios of live *G. ruber* (squares), *G. sacculifer* (open circles), and *G. bulloides* (open triangles) versus mean seawater phosphate concentration for the upper 75 m of the water column. The horizontal error bars denote the range of seawater phosphate concentration that prevailed during the lifespan of the foraminifers. The uncertainty of the Cd/Ca data is given by the relative standard deviation (RSD) value of ±18% obtained for multiple analyses of *G. ruber* tests of category B (see section 4.3 and Table 7).

during the late NEM and beginning of the IMS, which constitutes a period that is generally characterized by low (near) surface seawater phosphate concentrations (~0.4 μmol/L, Figure 2a), exhibit an average Cd/Ca ratio of 0.0116 ± 0.0020 (1 SD, Figure 2b.). Live *G. ruber* (3r, 7r/1) collected toward the end of the IMS period and the onset of the SWM in May 1997 yielded an average Cd/Ca value of 0.0040 ± 0.0001 (1 SD), which is the lowest value obtained for live specimens from the Arabian Sea. In contrast, samples of live *G. ruber* (1r) taken during the fully developed SWM in August 1995, where the uppermost water column is characterized by a significantly higher phosphate content (~0.8 μmol/L, Figure 2a) exhibit the highest Cd/Ca ratio of 0.0395 ± 0.0075 (RI) determined for an in situ collected sample (Figure 2b). An intermediate Cd/Ca of 0.0162 ± 0.0010 (TU) was found for live *G. ruber* (2r/1) sampled during the late SWM, at end of September 1995. The majority of results obtained for *G. ruber* therefore exhibit a correlation of Cd/Ca with surface water phosphate concentrations (Figure 2c).

[37] No seasonal trend was observed for the Cd/Ca data obtained for live *G. sacculifer* (Figure 2b) even though the specimens were collected in the Arabian Sea together with *G. ruber*, in March (4s/1), August 1995 (1s), and May 1997 (7s). Tests of *G. sacculifer* from March and August display nearly identical Cd/Ca ratios of 0.0192 ± 0.0002 (TU) and 0.0198 ± 0.0005 (TU), respectively. A slightly lower value of 0.0175 ± 0.0002 (TU) was obtained for the live *G. sacculifer* sampled in May (Figure 2b).

[38] A Cd/Ca value of 0.0085 ± 0.0009 (TU) was determined for live specimens of *G. bulloides* (sample 6b, Figure 2b) collected in September 1996 from the North Atlantic, where phosphate concentrations are generally lower than in the Arabian Sea [*Garcia et al.*, 2006]. However, a comparison of this result with the data for the Arabian Sea samples is not straightforward, because of the different oceanographic settings.

5.3.2. Empty Tests of Settling Planktonic Foraminifers: Category C (300–2500 m)

[39] Category C samples are composed of only *G. ruber* tests from the Arabian Sea. These samples display consistently lower Cd/Ca ratios than their counterparts sampled from the live habitat on the same day (Table 7). In particular, tests collected from 300 to 500 m (4r/1) and

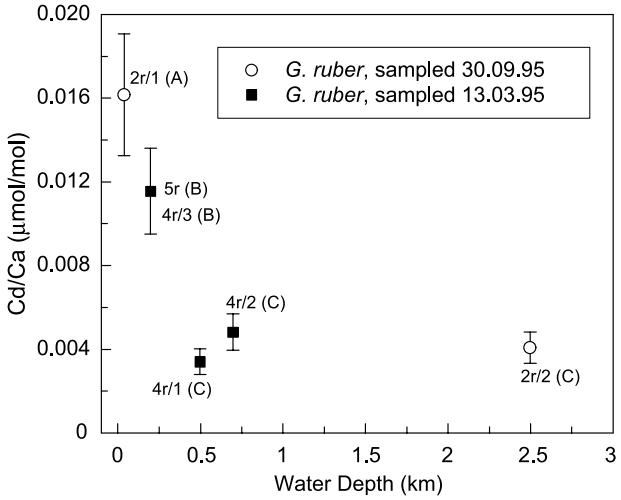

Figure 3. Cd/Ca ratios obtained for tests of in situ collected *G. ruber* versus sampling depth. The symbols are plotted at the deepest level of the depth interval over which the samples were collected and are labeled with sample number and category (Table 8). Samples taken on the same day are shown as identical symbols (circles, 30 September 1995; squares, 13 March 1995). The Cd/Ca ratios obtained for *G. ruber* collected from the live habitat (category A) and from depth intervals extending slightly below the live habitat (category B) are significantly higher than those obtained for *G. ruber* tests taken well below the live habitat (category C). The uncertainty of the average Cd/Ca value for the category B sample denotes 1 standard deviation (Table 8). The RSD value of ±18% obtained for multiple analyses of this sample was also used to characterize the uncertainty of category A and C samples, for which only one analysis was performed per sample (see section 4.3).

500–700 m depth (4r/2) have Cd/Ca ratios of 0.0034 ± 0.0007 (TU) and 0.0048 ± 0.0008 (TU), respectively, which are about a factor of 2–3 lower than the average value obtained for samples collected from 0 to 200 m water depth (4r/3 and 5r, Figure 3). A decrease of Cd/Ca ratio with depth is also evident from a comparison of results obtained for live *G. ruber* from 20 to 40 m (sample 2r/1) and empty shells (sample 2r/2) from the deepest sampling interval (2000–2500 m depth). The latter tests exhibit a Cd/Ca ratio that is about 5 times lower at 0.0041 ± 0.0002 (TU) compared to the live specimens (Figure 3).

5.4. Cd/Ca Ratios of Planktonic Foraminiferal Shells of Surface Sediments

[40] To facilitate a comparison of Cd/Ca ratios determined for in situ collected and sedimentary tests of planktonic foraminifers, we analyzed several sets of samples from similar locations (Tables 1 and 2). The Cd/Ca data for these surface sediment samples are summarized in Table 8. Tests of *G. ruber* and *G. sacculifer* from the top of sediment core SL 3011–1 yielded essentially identical average Cd/Ca ratios of 0.0603 ± 0.010 (RI) and 0.0568 ± 0.0084 (RI), respectively.

[41] Three different species were analyzed from the top of sediment core MC 575 from the North Atlantic. The lowest Cd/Ca of 0.0274 ± 0.0002 (TU) was determined for *O. universa* and this result is identical, within the error, to the Cd/Ca data obtained for the same species from North Atlantic sediment core KL 88 (Table 6). A somewhat higher Cd/Ca value of 0.0475 ± 0.0014 (RI) was measured for *G. bulloides*, which matches well with the Cd/Ca data obtained by *Rickaby and Elderfield* [1999] that predict a Cd/Ca ratio of about 0.04 to 0.06. The deep dwelling species G. *truncatulinoides* yielded the highest Cd/Ca of 0.0718 ± 0.0010 (TU).

6. Discussion

6.1. Incorporation of Cd Into the Shell Calcite of Live Foraminifers

[42] The incorporation of Cd from seawater into the tests of foraminifers can be described by a partition coefficient D_{Cd} [e.g., *Lea*, 1999]. However, different species collected at the same time and location may bear different Cd/Ca ratios as a result of different ecologic demands and characteristics of shell calcification. We therefore investigated whether the measured Cd/Ca ratios of planktonic foraminifers sampled from the water column show any correlation with seawater phosphate concentrations and estimated the partition coefficient for the different species.

Table 8. Results Obtained for Different Species of Planktonic Foraminifers Picked From Sediment Core Tops[a]

Sample	Species	n	Cd (pg)	Cd/Ca (μmol/mol)	Total Uncertainty	Blank Correction (%)
9	*G. ruber* (w)	1	5.2	0.0502	0.0006	2
10	*G. ruber* (w)	1	39	0.0704	0.0008	0.3
	Average SL 3011–1 *G. ruber*	2		0.0603 ± 0.0101		
11	*G. sacculifer*	1	4.6	0.0484	0.0009	2
12	*G. sacculifer*	1	17	0.0652	0.0007	0.7
	Average SL 3011–1 *G. sacculifer*	2		0.0568 ± 0.0084		
13	*G. bulloides*	1	2.1	0.0461	0.0011	5
14	*G. bulloides*	1	44	0.0488	0.0007	0.3
	Average MC 575 *G. bulloides*	2		0.0475 ± 0.0014		
15	*O. universa* MC 575	1	27	0.0274	0.0002	0.4
16	*G. truncatulinoides* MC 575	1	63	0.0718	0.0010	0.2

[a]The average values calculated as unweighted means of n independent measurements. The quoted uncertainties denote the total range of the individual data. Total uncertainty is as defined in section 4.3. Cd (pg) denotes the amount of natural Cd determined in the sample solutions by isotope dilution.

6.1.1. Correlation of Foraminiferal in Situ Cd/Ca Ratios With Seawater Phosphate

[43] Cataloged monthly average values of seawater phosphate derived from *Garcia et al.* [2006] were used in the following (see section 3.1). In most cases, uncertainties are not specified for the monthly phosphate values [*Garcia et al.*, 2006], but an indication of the magnitude of possible deviations can be obtained for the samples from the M 32/5 and SO 119 cruises (Table 1). In this case, the in situ phosphate concentrations are about a factor of 2–4 lower than the monthly mean values (Table 3). Such deviations of measured phosphate contents from the monthly averages are expected to be especially severe, if seawater phosphate displays large spatial or temporal gradients, as are typical for the Arabian Sea [*Webster et al.*, 1998].

[44] Despite of these uncertainties, the majority of Cd/Ca ratios obtained for live *G. ruber* display a good correlation with seawater phosphate (Figure 2c). Only one sample collected in late September 1995 (2r/1) does not unequivocally follow this trend. However, the seawater phosphate concentrations derived from *Garcia et al.* [2006] decrease by about a factor of 2 between September and October. The timing of this strong seasonal change in nutrient levels varies from year to year and the actual phosphate content at the time of sampling might therefore be better represented by the lower October phosphate concentration ($\sim$0.58 μmol/L [*Garcia et al.*, 2006]). This uncertainty in the seawater phosphate concentration is expressed in Figure 2c by the large horizontal error bar which spans the range between the September and the October value. Application of the October value places this Cd/Ca ratio on the trend defined by the other *G. ruber* data (Figure 2c) and a linear fit to this correlation suggests a relationship of $Cd/Ca \approx 0.10 * [P] - 0.04$.

[45] The results obtained for live *G. sacculifer* exhibit a different Cd/Ca to phosphate relationship than the *G. ruber* specimens from the same multinet samples. Inspection of Figure 2c reveals that *G. sacculifer* display nearly constant Cd/Ca values for phosphate contents between 0.4 and 0.8 μmol/L. The observed differences in Cd/Ca between *G. ruber* and *G. sacculifer* point toward species-specific mechanisms for the incorporation of Cd into foraminiferal tests, or possibly different ecological niches of these two species. An alternative explanation follows from the observation that *G. sacculifer* has a life span of approximately 4 weeks [*Bijma et al.*, 1990; *Schiebel et al.*, 2004], whereas the average reproduction cycle of *G. ruber* is 2 weeks only [*Almogi-Labin*, 1984; *Bijma et al.*, 1990; *Schiebel and Hemleben*, 2001]. The different Cd/Ca values of *G. ruber* and *G. sacculifer* might therefore reflect differences in the conditions of the ambient seawater during calcification of the shells.

6.1.2. Cadmium Partition Coefficients for the in Situ Collected Species

[46] It has been suggested, that the incorporation of Cd into shells of *G. bulloides* varies strongly with temperature, and this relationship was defined for temperatures of 4°C to 16°C [*Rickaby and Elderfield*, 1999]. Our result for a single sample live *G. bulloides* yields $D_{Cd} \approx 4$ at a temperature of about 15°C (see Appendix A and Table 3). This matches with the equation $D_{Cd} = 0.637 * \exp 0.15T$ of *Rickaby and Elderfield* [1999], which predicts $D_{Cd} \approx 6$ at 15°C, but at significantly higher Cd/Ca values of 0.04–0.06. This agreement of D_{Cd} values for Cd/Ca ratios that differ by about a factor of 6 is likely to be related to the low seawater phosphate concentration ($\sim$0.1 μmol/L, Table 3) that prevailed during the calcification of live *G. bulloides*. Using a cataloged monthly average seawater phosphate value for the uppermost 75 m ($\sim$0.3 μmol/L, Table 3) yields $D_{Cd} \approx 2$, which is no longer in accord with the equation given above. However, a D_{Cd} of about 2–4 for live *G. bulloides* matches well with results for cultured *G. bulloides* of $D_{Cd} \approx 2$–4 and 1.9, as published by *Delaney* [1989] and *Mashiotta et al.* [1997], respectively.

[47] The relationship between Cd incorporation and seawater temperature of *Rickaby and Elderfield* [1999] also does not hold for live *G. ruber* and *G. sacculifer*, which display D_{Cd} values of about 2 to 7 at significantly higher temperatures of 26.5°C to 28.5°C (Table 3). Owing to the small number of samples analyzed, the limited availability of in situ phosphate data, and the narrow temperature range, we cannot rule out or establish a temperature dependence of D_{Cd} for *G. ruber* and *G. sacculifer*. This implies, that any temperature-driven differences for the incorporation of Cd into foraminiferal shells will only be of minor importance for the in situ collected tests from the Arabian Sea (Table 1), as the variations in temperature are very small (Table 3).

6.2. Cd/Ca Ratios of Settling Shells

[48] The vertical sinking velocity of large foraminiferal shells (>200 μm) is up to 500 m per day [*Schiebel and Hemleben*, 2001]. Consequently, the settling time for the analyzed tests of *G. ruber* (category C, Table 7) between the live habitat in the upper 80 m and 2500 m is about 5 d. It can hence be assumed that both live specimens and empty tests, which were collected well below the live habitat on the same day, calcified under similar ecological conditions. Both types of samples should therefore display similar Cd/Ca ratios.

[49] Inspection of Figure 3 reveals, however, that settling shells (category C) of *G. ruber* collected from depths >300 m, display significantly lower Cd/Ca ratios than their counterparts from the live habitat. Preferential loss of Cd and/or selective dissolution of Cd-enriched calcite phases during sinking of the tests from warm surface waters through colder subsurface waters may be responsible for this observation. This assumption is supported by earlier findings, which suggest that the dissolution of calcite shells occurs primarily in the twilight zone, between 100 m and 1000 m water depth [*Schiebel*, 2002; *Schiebel et al.*, 2007] and such processes are known to alter the Mg/Ca ratios of planktonic foraminiferal tests [*Brown and Elderfield*, 1996; *Regenberg et al.*, 2006].

[50] Assuming an average loss of 19% of the original test calcite in subsurface waters [*Schiebel et al.*, 2007], and average Cd/Ca ratios of 0.022 and 0.004 μmol/mol in surface and subsurface waters, respectively (Table 7 and Figure 4), the Cd/Ca ratio of the dissolved part of the foraminiferal test would be about 0.1 μmol/mol, being well

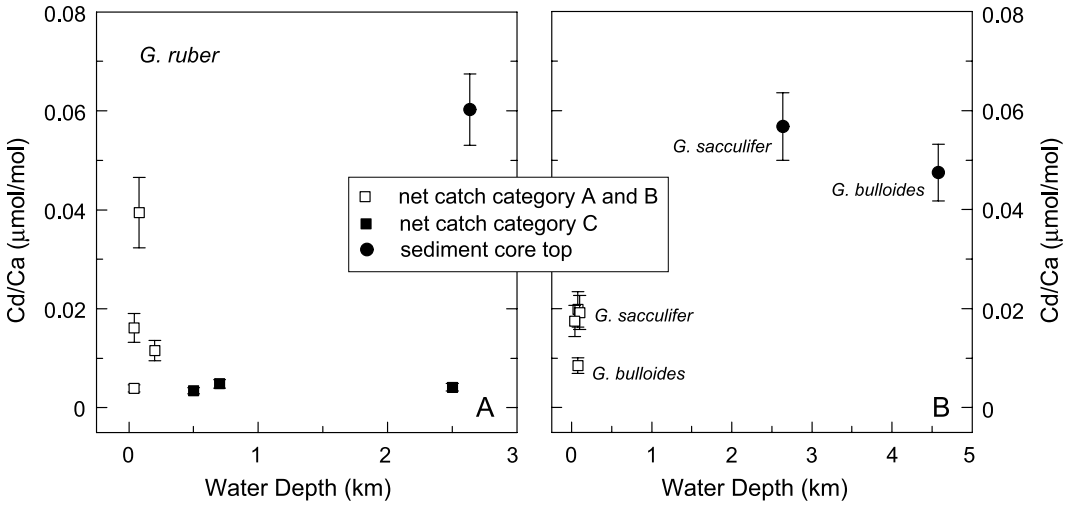

Figure 4. Cd/Ca ratios obtained for different species of foraminifera from plankton net tows (squares) and sediment core tops (circles) versus sampling depth. The in situ collected samples and corresponding sediment core tops are from approximately the same location. The symbols for the in situ collected samples are plotted at the deepest level of the depth interval over which the samples were collected (Table 8). (a) Cd/Ca ratios obtained for *G. ruber* tests from a sediment core top and from plankton net tows conducted in different months versus water depth (for detailed information see Table 8). (b) Cd/Ca ratios determined for *G. sacculifer* and *G. bulloides* versus water depth. The uncertainty of the Cd/Ca data obtained for fossil shells and in situ collected samples denotes the RSD obtained for multiple analyses of *O. universa* from sediment core KL 88 (±12%) and in situ sampled *G. ruber* (±18%, samples 4r/3 and 5r), respectively (for detailed information see section 4.3).

within a plausible range of Cd/Ca ratios (compare, e.g., Tables 7 and 8).

[51] A preferential enrichment of Cd at sites in the calcite structure of the shells, which are more susceptible to dissolution could account for the preferential loss of Cd relative to the major element Ca. This could be explained by different distribution coefficients of Cd into the different parts of the lamellar test wall (e.g., microgranular versus euhedral [*Hemleben et al.*, 1989, and references therein]). It is conceivable, that the incorporation of Cd into the outer calcite wall is less pronounced than into the inner wall, as the latter is placed closer to the foraminiferal cytoplasm (which may contain higher Cd concentrations than the shell). The inner test wall might also be more prone to dissolution effects, because of the random crystallographic orientation of the calcite crystals and because partial dissolution of tests could be related to changes in the microenvironment (e.g., decreasing pH) within the foraminiferal shells during bacterial remineralization of remaining cytoplasm [*Schiebel et al.*, 2007]. Alternatively, Cd could be enriched at crystal edges and/or lattice dislocations in the shell, which are likely to be more effected by dissolution processes.

6.3. Cd/Ca Ratios of in Situ Collected and Sedimentary Foraminiferal Tests

[52] A comparison of the Cd/Ca data reveals that foraminiferal tests from surface sediments have consistently higher Cd/Ca ratios than in situ collected specimens (Figure 4). In the following, we discuss this difference for both live foraminifers and settling shells, and we evaluate if the Cd/Ca ratios of sedimentary tests are biased by secondary alteration. Such an evaluation is of particular significance, as secondary alteration might render the Cd/Ca data of planktonic foraminiferal shells unsuitable for proxy studies.

6.3.1. Comparison of Cd/Ca Ratios Obtained for Live Foraminifers and Surface Sediments

[53] For the same species, foraminiferal tests from surface sediments exhibit Cd/Ca ratios that are about a factor of 1.5–15 higher compared to the shells of live foraminifers (Figure 4). It is possible that this difference reflects postdepositional alteration of the tests, for example by precipitation of Cd-rich mineral phases from pore waters. Pore waters of surface sediments from the NE Atlantic (0–0.5 cm) have Cd contents of 0.7–1.6 nmol/L [e.g., *Tachikawa and Elderfield*, 2002], which are about an order of magnitude higher than surface water Cd concentrations of the North Atlantic and Arabian Sea [e.g., *Ripperger et al.*, 2007; *Saager et al.*, 1992]. The results obtained for the sediment core MC 575 reveal, however, that planktonic foraminiferal species with different seasonal occurrences and depth habitats bear different sedimentary Cd/Ca ratios, which follow seawater phosphate concentrations (Tables 4 and 8 and Figure 5). This indicates that the Cd/Ca ratios of tests from surface sediments are not significantly overprinted by sedimentary pore waters but reflect primary (shell formation) processes.

[54] In particular, for most of the year *G. truncatulinoides* lives and calcifies its shell in deeper waters [*Schiebel and Hemleben*, 2005; *Schiebel et al.*, 2002] that are characterized by higher Cd concentrations than surface waters [e.g., *Bruland*, 1980; *De La Rocha*, 2003]. This signal is preserved in sedimentary tests of *G. truncatulinoides*, which

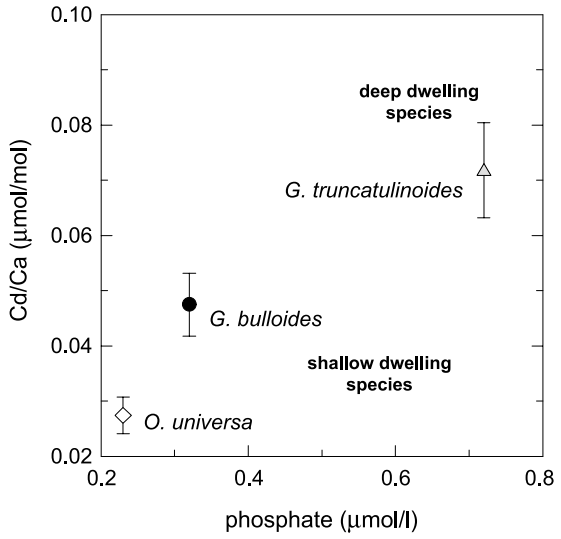

Figure 5. Foraminiferal Cd/Ca ratios obtained for three different species analyzed from the sediment core top MC 575 versus seawater phosphate concentration. The latter was derived from *Garcia et al.* [2006] and corresponds to the mean phosphate concentration prevailing during the species-specific bloom month and at the species-specific habitat.

display significantly higher Cd/Ca ratios than shells of the shallow dwelling species *G. bulloides* and *O. universa* from the same core top (Table 8 and Figure 5). The Cd/Ca ratio of *O. universa* tests was furthermore observed to be about 40% lower compared to *G. bulloides*. This offset may reflect the different ecological and trophic demands of these two species. *O. universa* is a tropical to subtropical species that generally calcifies after the spring bloom in North Atlantic [*Schiebel and Hemleben*, 2000], when surface waters are warm, well stratified and depleted in phosphate (Table 4). In contrast, *G. bulloides* is most frequent when vigorous mixing of the upper water column occurs and advection of phosphate-rich subsurface waters is observed [*Schiebel and Hemleben*, 2000]. It is also possible, however, that the different Cd/Ca ratios of *O. universa* and *G. bulloides* tests reflect a lower partition coefficient D_{Cd} for the symbiont-bearing species *O. universa* [*Mashiotta et al.*, 1997].

[55] In any case, these relatively small primary differences between *G. truncatulinoides*, *G. bulloides* and *O. universa* tests from the same core top (Figure 5) would probably not be visible, if the Cd/Ca ratios had been significantly modified by secondary alteration. In summary, we therefore regard secondary alteration as an unlikely explanation for the observed offsets of Cd/Ca data for in situ collected and sedimentary foraminiferal tests (Figure 4). The further discussion therefore focuses on three "primary" mechanisms that can account for these offsets and which have less severe consequences for the proxy application of Cd/Ca ratios.

[56] 1. Tests of live and sedimentary planktonic foraminifers may bear different calcite phases. It has been suggested that shells of planktonic foraminifers, such as *G. bulloides*, *G. sacculifer* and *G. ruber*, that underwent reproduction consist of two calcite types: a primary calcite that forms the chamber walls and a gametogenic (GAM) calcite crust, which is precipitated during reproduction [*Bé*, 1980; *Lohmann*, 1995; *Schiebel et al.*, 1997]. Such a layer of GAM calcite can add about 30% in weight to the primary calcite of a test, as shown for *G. sacculifer* [*Bé*, 1980]. The reproduction of the analyzed species typically takes place near the thermocline (~60–100 m [*Schiebel and Hemleben*, 2005]) where the Cd concentrations are somewhat higher than in shallow surface waters [e.g., *Boyle et al.*, 1976; *De La Rocha*, 2003; *Saager et al.*, 1992]. A GAM calcite crust or any other secondary calcite that forms at subsurface waters is therefore likely to be enriched in Cd relative to the primary calcite, based on the (reasonable) assumption that both types of calcite feature similar distribution coefficients for the incorporation of Cd.

[57] The shells from surface sediments analyzed in this study are assumed to bear both primary and GAM calcite phases, as the majority of tests are from adult (i.e., large tests sizes [*Hemleben et al.*, 1989, *Bijma et al.*, 1990]) specimens that likely underwent reproduction. The presence of GAM calcite crusts on tests of live foraminifers can also be assumed for adult (large) specimens. For *G. bulloides*, the reproduction rate of specimens with tests larger 150 μm is nearly 100% [*Schiebel et al.*, 1997], whereas for *G. sacculifer* the reproduction rate increases exponentially between a test size of ~300–400 μm and is about 80 to 100% for tests as large as about 500 μm [*Bijma and Hemleben*, 1994].

[58] Taking into account the test size of the analyzed live specimens, we can hence assume that the majority of *G. bulloides* specimens from sample 6b and most *G. sacculifer* specimens from samples 1s, 7s (test size >315 μm and >500 μm, respectively) underwent reproduction. In addition, spines were not observed on most of these large *G. bulloides* and *G. sacculifer* tests. This supports the conclusion that the majority of the in situ specimens underwent gametogenesis, as spines are generally resorbed during reproduction [*Bé*, 1980; *Hemleben et al.*, 1989]. Although these live collected *G. bulloides* and *G. sacculifer* tests are therefore likely to bear GAM crusts the Cd/Ca ratios of these samples are nonetheless about a factor of 3–5 lower compared to sedimentary tests (Figure 4). The same offset in Cd/Ca was observed for the live *G. sacculifer* tests of sample 4s/1 (Figure 4), but these shells are smaller (>250 μm) and some (but not all) of the specimens were observed to bear spines. This indicates that this sample is composed of tests both with and without GAM calcite [cf. *Bijma and Hemleben*, 1994].

[59] Taken together, our data thus indicate that the formation of GAM calcite crusts does not account for the observed offsets in Cd/Ca between the analyzed sedimentary and live *G. bulloides* and *G. sacculifer* tests. A more general conclusion should not be drawn from these data, however, given that the formation of GAM calcite and other secondary calcite crusts is species-specific. The *G. sacculifer* results must furthermore be viewed with caution, as the Cd/Ca ratios of these samples were not observed to correlate with seawater phosphate (Figure 2).

[60] 2. The two sets of samples cover different time periods. Planktonic foraminifers from surface sediments represent sedimentation over time periods of several hundred to thousands of years [*Barker et al.*, 2007; *Manighetti et al.*, 1995], and the Cd/Ca ratios of such samples thus integrate over long-term changes in Holocene climate, hydrography and the trophic state of surface waters. This includes periods of enhanced monsoon activity as well as variable seawater nutrient concentrations [*Burns et al.*, 2002; *Mayewski et al.*, 2004].

[61] 3. Foraminiferal shells that were calcified during seasons of enhanced planktonic bioproductivity are expected to dominate in surface sediments. In the Arabian Sea, *G. ruber* and *G. sacculifer* are most abundant during the late SWM and during late NEM to spring IMS, respectively [*Schiebel*, 2002; *Schiebel et al.*, 2004]. In the North Atlantic *G. bulloides* is most frequent during the spring [*Schiebel and Hemleben*, 2000; *Schiebel et al.*, 2001]. In all three cases, the maximum abundances of the foraminifers occur at times of enhanced nutrient, and by inference Cd, concentrations [*Garcia et al.*, 2006] that are characterized by enhanced phytoplankton production and associated with mass sinking events [*De La Rocha*, 2003; *Fowler and Knauer*, 1986; *Schiebel*, 2002].

[62] Most of the analyzed live collected samples, however, did not calcify during seasonal peaks of seawater phosphate and Cd contents and hence, they do not reflect the conditions that prevail during periods of mass production. In particular, this is true for (1) the tests of live *G. sacculifer* (sample 1s) that were collected in August in the Arabian Sea (Table 3) and (2) the tests of live *G. bulloides* from the North Atlantic (sample 6b), which calcified in late September when the seawater phosphate concentrations are lower than during peak production in spring [*Garcia et al.*, 2006]. In addition, we observed that the live *G. ruber* tests of sample 1r, which were collected in the Arabian Sea in August (Table 1) and that calcified during the fully developed SWM in July (Table 3), display the smallest offset to the sedimentary Cd/Ca value (Figure 4). The small offset may reflect that this single sample did not fully capture the maximum nutrient levels that prevailed during the maximum abundance of *G. ruber* from July to September (Table 3).

[63] In contrast, the proposed mechanism is not in accord with the observation that the live *G. sacculifer* samples 4s/1 and 7s were both obtained during times of enhanced productivity (March and May, Table 3) but display the same offset to the sedimentary Cd/Ca ratio (Figure 4) as the *G. sacculifer* sample 1s, which is from a less productive season (Table 3). It is possible, however, that this discrepancy is due to the nonsystematic behavior of *G. sacculifer*, which forms tests that do not display a correlation of Cd/Ca ratio with the seawater phosphate content (Figure 2).

[64] In summary, this suggests that the dominance of tests from time periods with high nutrient levels in the sedimentary record may account for some but not for all of the observed discrepancy in Cd/Ca ratios between live specimens and tests from sediment core tops. This discrepancy is most likely caused by a combination the mechanisms that were discussed above.

6.3.2. Comparison of Cd/Ca Ratios Obtained for Settling Shells and Surface Sediments

[65] The large difference in Cd/Ca between settling shells and tests from surface sediments (Figure 4) indicates that sedimentary shells are less affected by the dissolution processes, which are thought to reduce the Cd/Ca ratios of slowly settling individual tests (see section 6.2). The deposition of surface sediments is dominated by mass sinking events following maximum phytoplankton productivity [*Schiebel*, 2002]. Such mass sinking events are accompanied by high sinking velocities and a substantial fraction of the phytoplankton therefore reaches the ocean floor as relatively well preserved particles [*Fowler and Knauer*, 1986; *Schiebel*, 2002].

[66] The analyzed empty foraminiferal tests (of category C) were not collected during such mass sinking events, however. In general, mass dumps of plankton have only rarely been sampled with net hauls, because of their unpredictable and short-lived occurrence [*Schiebel*, 2002]. It is therefore reasonable to assume that the settling tests of this study were exposed to dissolution for a longer time, because of the much slower sinking velocities of single shells.

7. Summary and Conclusions

[67] In order to further the basic understanding of the Cd/Ca proxy and its application to planktonic foraminifers, we have determined Cd/Ca ratios for tests of *G. ruber*, *G. sacculifer* and *G. bulloides* from both plankton net tows and sedimentary core tops that were taken at the same location.

[68] Live (cytoplasm bearing) specimens of *G. ruber*, which were sampled in the Arabian Sea during different monsoon seasons, bear significantly different Cd/Ca ratios that appear to reflect seasonal changes in seawater phosphate concentrations. Such a correlation of Cd/Ca and seawater phosphate content is not observed for *G. sacculifer*. This indicates that vital effects or different ecological niches may be responsible for the different Cd/Ca systematics of *G. ruber* and *G. sacculifer*.

[69] The Cd/Ca data obtained for *G. ruber* reveal differences between live specimens and empty tests that were sampled from subsurface waters. The latter exhibit Cd/Ca values that are about 50 to 80% lower compared to shells sampled from their live habitat. This suggests that Cd is not homogenously distributed in foraminiferal shells and that the tests are partially dissolved while settling through the water column, with the dissolved part of the lamellar shells bearing Cd/Ca ratios about 25 times higher (on average 0.1 μmol/mol) than the undissolved part (on average 0.004 μmol/mol).

[70] The observation that live specimens of *G. ruber*, *G. sacculifer* and *G. bulloides* have significantly lower Cd/Ca ratios than tests from surface sediments is unlikely to be due to postdepositional alteration of the shells, for example by Cd-enriched pore waters. This conclusion is supported by the observation that fossil tests of different species, *G. bulloides*, *G. truncatulinoides*, and *O. universa*, from the same sediment core top show distinct differences in Cd/Ca that mirror the specific ecological demands of

these species. Such differences are not expected to be discernible if modification of the Cd/Ca ratios by secondary alteration would be an important process. A combination of different factors can, however, account for the distinct Cd/Ca systematics of sedimentary and live collected foraminiferal tests. (1) Samples from the water column and surface sediments may contain variable amounts of planktonic foraminifers that underwent reproduction and precipitated a gametogenic calcite crust within subsurface waters with elevated Cd concentrations. (2) Surface sediment samples integrate over longer time periods and the foraminifers may thus record long-term changes in Holocene climate and monsoon strength. (3) The majority of foraminiferal tests deposited in surface sediments were calcified during periods of high productivity and seawater nutrient concentrations [*Fowler and Knauer*, 1986], while most of the live collected samples are not representative of such times of maximum productivity. According to *Schiebel* [2002], about 97% of foraminiferal tests in surface sediments are produced during highly productive seasons.

[71] The large difference in Cd/Ca that is evident for sedimentary and settling shells of *G. ruber* indicates that the former are significantly less affected by the dissolution processes, which take place during settling of the shells through the water column. This distinct behavior is most readily explained by the different sinking velocities of the tests. The deposition of surface sediments takes place mainly during mass sinking events that follow phytoplankton blooms and they are associated with high sinking velocities. Dissolution is furthermore less pronounced for rapidly settling tests than for the individual slowly sinking tests that were analyzed as in situ samples in the present study [cf. *Schiebel*, 2002].

[72] Overall, the present investigation has enabled us to identify clear differences in foraminiferal Cd/Ca ratios for tests of live and deceased specimens, as well as surface sediments. The identification of the exact mechanisms responsible for these variations remains speculative at present and additional studies are needed to firmly establish the observed trends and their causes. Further progress is expected by increasing the sampling density of live collected foraminifers during the species-specific blooms. Analyses of empty tests from mass sinking events, as well as investigations of gametogenic calcification in laboratory-culturing experiments are also expected to yield new insights. Distinct chamber and chamber wall layer Cd contents may be resolvable with laser-ablation ICP-MS or ion probe analyses of individual shells, as has been demonstrated for other foraminiferal trace elements, such as Mg, Li, Mn, Ba, Zn and Sr [*Eggins et al.*, 2003; *Hathorne et al.*, 2003]. If such measurements would reveal differences in Cd/Ca of different parts of the shell (e.g., outer and inner calcite layers; primary calcite and GAM calcite crusts), different element ratios could be attributed to effects of shell formation and dissolution.

[73] Our data also support the conclusion that the Cd/Ca ratios of fossil foraminiferal shells can be used to reconstruct past seawater phosphate concentration at times of maximum productivity. In combination with knowledge of the ecological demands of particular species it may therefore be possible to make inferences on the extent of seasonal variations in nutrient utilization.

Appendix A

[74] For a trace element, the relationship between its concentration in the shell calcite of foraminifera and seawater can be described by a partition coefficient D [e.g., *Lea*, 1999]. For the incorporation of Cd into foraminiferal calcite, the partition coefficient D_{Cd} is defined as [see *Rickaby and Elderfield*, 1999]

$$D_{Cd} = \frac{\left(\frac{Cd}{Ca}\right)_{foram}}{\left(\frac{Cd}{Ca}\right)_{sw}} = \frac{\left(\frac{Cd}{Ca}\right)_{foram}}{\left(\frac{Cd}{P}\right)_{sw} \cdot \frac{[PO_4]_{sw}}{[Ca]_{sw}}} \quad (A1)$$

where $(Cd/Ca)_{foram}$ and $(Cd/Ca)_{sw}$ denote the Cd/Ca ratio of foraminifera and seawater, respectively; $[PO_4]_{SW}$ denotes the seawater phosphate concentration prevailing at the time of shell calcification. Here, we assumed a constant Ca^{2+} seawater concentration of $[Ca]_{SW} = 1.054 \times 10^4$ μmol/L [see *Rickaby and Elderfield*, 1999]. To facilitate a comparison of D_{Cd} values presented here with those of *Rickaby and Elderfield* [1999] we assumed a global average Cd/P ratio for seawater of 0.21 nmol/μmol [see *Rickaby and Elderfield*, 1999]. To calculate the D_{Cd} values presented in section 6.1.2, mean in situ seawater phosphate contents for the uppermost 60 m of the water column (see Table 3) were inserted for $[PO_4]_{SW}$ in equation (A1).

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References

Almogi-Labin, A. (1984), Population-dynamics of planktic foraminifera and pteropoda Gulf of Aqaba, Red-Sea, *Proc. K. Ned. Akad. Wet. Ser. B Palaeontol. Geol. Phys. Chem. Anthropol.*, *87*(4), 481–511.

Anand, P., et al. (2003), Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series, *Paleoceanography*, *18*(2), 1050, doi:10.1029/2002PA000846.

Barker, S., et al. (2007), Radiocarbon age offsets of foraminifera resulting from differential dissolution and fragmentation within the sedimentary bioturbated zone, *Paleoceanography*, *22*, PA2205, doi:10.1029/2006PA001354.

Bauer, S., G. L. Hitchcock, and D. B. Olson (1991), Influence of monsoonally-forced Ekman dynamics upon surface layer depth and plankton biomass distribution in the Arabian Sea, *Deep Sea Res., Part A*, *18*(5), 531–553, doi:10.1016/0198-0149(91)90062-K.

Bé, A. W. H. (1980), Gametogenic calcification in a spinose planktonic foraminifer *Globigerinoides*

sacculifer (Brady), *Mar. Micropaleontol.*, *5*, 283–310, doi:10.1016/0377-8398(80)90014-6.

Bijma, J., and C. Hemleben (1994), Population dynamics of the planktic foraminifer *Globigerinoides sacculifer* (Brady) from the central Red Sea, *Deep Sea Res., Part I*, *41*(3), 485–510, doi:10.1016/0967-0637(94)90092-2.

Bijma, J., et al. (1990), Lunar and semi-lunar reproductive cycles in some spinose planktonic foraminifers, *J. Foraminiferal Res.*, *20*(2), 117–127.

Boyle, E. A. (1981), Cadmium, zinc, copper, and barium in foraminifera tests, *Earth Planet. Sci. Lett.*, *53*, 11–35, doi:10.1016/0012-821X(81)90022-4.

Boyle, E. A. (1983), Manganese carbonate overgrowths on foraminifera tests, *Geochim. Cosmochim. Acta*, *47*, 1815–1819, doi:10.1016/0016-7037(83)90029-7.

Boyle, E. A. (1988), Cadmium: Chemical tracer of deepwater paleoceanography, *Paleoceanography*, *3*(4), 471–489, doi:10.1029/PA003i004p00471.

Boyle, E. A. (1995), Limits on benthic foraminiferal chemical analyses as precise measures of environmental properties, *J. Foraminiferal Res.*, *25*(1), 4–13.

Boyle, E. A., and L. D. Keigwin (1985), Comparison of Atlantic and Pacific paleochemical records for the last 215,000 years: Changes in deep ocean circulation and chemical inventories, *Earth Planet. Sci. Lett.*, *76*, 135–150, doi:10.1016/0012-821X(85)90154-2.

Boyle, E., and Y. Rosenthal (1996), Chemical hydrography of the South Atlantic during the last glacial maximum: Cd vs. δ^{13}C, in *The South Atlantic: Present and Past Circulation*, edited by G. Wefer et al., pp. 423–443, Springer, Berlin.

Boyle, E. A., et al. (1976), On the marine geochemistry of cadmium, *Nature*, *263*, 42–44, doi:10.1038/263042a0.

Brown, S. J., and H. Elderfield (1996), Variations in Mg/Ca and Sr/Ca ratios of planktonic foraminifera caused by postdepositional dissolution: Evidence of shallow Mg-dependent dissolution, *Paleoceanography*, *11*(5), 543–551, doi:10.1029/96PA01491.

Bruland, K. W. (1980), Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific, *Earth Planet. Sci. Lett.*, *47*, 176–198, doi:10.1016/0012-821X(80)90035-7.

Burns, S. J., D. Fleitmann, M. Mudelsee, U. Neff, A. Matter, and A. Mangini (2002), A 780-year annually resolved record of Indian Ocean monsoon precipitation from a speleothem from south Oman, *J. Geophys. Res.*, *107*(D20), 4434, doi:10.1029/2001JD001281.

Cullen, J. T. (2006), On the nonlinear relationship between dissolved cadmium and phosphate in the modern global ocean: Could chronic iron limitation of phytoplankton growth cause the kink?, *Limnol. Oceanogr.*, *51*(3), 1369–1380.

Cullen, J. T., T. W. Lane, F. M. M. Morel, and R. M. Sherrell (1999), Modulation of cadmium uptake in phytoplankton by seawater CO_2 concentration, *Nature*, *402*, 165–167, doi:10.1038/46469.

Delaney, M. L. (1989), Uptake of cadmium into calcite shells by planktonic foraminifera, *Chem. Geol.*, *78*(2), 159–165, doi:10.1016/0009-2541(89)90114-9.

De La Rocha, C. L. (2003), The biological pump, in *Treatise on Geochemistry*, vol. 6, *The Oceans and Marine Geochemistry*, edited by H. Elderfield, pp. 83–111, Elsevier, Oxford, U. K.

Duplessy, J. C., et al. (1981), Oxygen and carbon isotopic composition and biogeographic distribution of planktonic foraminifera in the Indian Ocean, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *33*, 9–46, doi:10.1016/0031-0182(81)90031-6.

Eggins, S., et al. (2003), Mg/Ca variation in planktonic foraminifera tests: Implications for reconstructing palaeo-seawater temperature and habitat migration, *Earth Planet. Sci. Lett.*, *212*, 291–306, doi:10.1016/S0012-821X(03)00283-8.

Elderfield, H., and R. E. M. Rickaby (2000), Oceanic Cd/P ratio and nutrient utilization in the glacial Southern Ocean, *Nature*, *405*, 305–310, doi:10.1038/35012507.

Erez, J., et al. (1991), On the live history of planktonic foraminifera: Lunar reproduction cycle in *Globigerinoides sacculifer* (Brady), *Paleoceanography*, *6*(3), 295–306, doi:10.1029/90PA02731.

Fowler, S. W., and G. A. Knauer (1986), Role of large particles in the transport of elements and organic-compounds through the oceanic water column, *Prog. Oceanogr.*, *16*(3), 147–194, doi:10.1016/0079-6611(86)90032-7.

Frew, R., et al. (2001), Macronutrient and trace-metal geochemistry of an in situ iron-induced Southern Ocean bloom, *Deep Sea Res., Part II*, *48*(11–12), 2467–2481, doi:10.1016/S0967-0645(01)00004-2.

Garcia, H. E., R. A. Locarnini, T. P. Boyer, and J. I. Antonov (2006), *World Ocean Atlas 2005*, vol. 4, *Nutrients (Phosphate, Nitrate, and Silicate)*, *NOAA Atlas NESDIS*, vol. 64, edited by S. Levitus, 396 pp., NOAA, Silver Spring, Md.

Hathorne, E. C., et al. (2003), Determination of intratest variability of trace elements in foraminifera by laser ablation inductively coupled plasma-mass spectrometry, *Geochem. Geophys. Geosyst.*, *4*(12), 8408, doi:10.1029/2003GC000539.

Hemleben, C., et al. (1989), *Modern Planktonic Foraminifera*, 363 pp., Springer, New York.

Hiller, B. (1996), Planktic foraminifera, in *Östliches Mittelmeer, Rotes Meer, Arabisches Meer, Cruise No. 31, 30 December 1994 – 22 March 1995*, edited by C. Hemleben et al., *Meteor Ber. 96–4*, pp. 165–169, Inst. für Meereskd., Univ. of Hamburg, Hamburg, Germany.

Ivanova, E., et al. (2003), Primary production in the Arabian Sea during the last 135000 years, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *197*, 61–82, doi:10.1016/S0031-0182(03)00386-9.

Kurbjeweit, F. (2000), Abundance, composition, diversity and biomass of deep sea benthic foraminifera, in *Ostatlantik 1998*, *Cruise No. 42*, edited by O. Pfannkuche, et al., *Meteor Ber. 00-1*, pp. 79–82, Inst. für Meereskd., Univ. of Hamburg, Hamburg, Germany.

Lea, D. W. (1999), Trace elements in foraminiferal calcite, in *Modern Foraminifera*, edited by B. K. Sen Gupta, pp. 259–277, Kluwer, Dordrecht, Netherlands.

Locarnini, R. A., A. V. Mishonov, J. I. Antonov, T. P. Boyer, and H. E. Garcia (2006), *World Ocean Atlas 2005*, vol. 1, *Temperature*, *NOAA Atlas NESDIS*, vol. 61, edited by S. Levitus, 182 pp., NOAA, Silver Spring, Md.

Lohmann, G. P. (1995), A model for variation in the chemistry of planktonic foraminifera due to secondary calcification and selective dissolution, *Paleoceanography*, *10*(3), 445–457, doi:10.1029/95PA00059.

Manighetti, B., et al. (1995), Chronology for climate change: Developing age models for the Biogeochemical Ocean Flux Study cores, *Paleoceanography*, *10*(3), 513–525, doi:10.1029/94PA03062.

Martin, P. A., and D. W. Lea (1998), Comparison of water mass changes in the deep tropical Atlantic derived from Cd/Ca and carbon isotope records: Implications for changing Ba composition of deep Atlantic water masses, *Paleoceanography*, *13*(6), 572–585, doi:10.1029/98PA02670.

Martin, P. A., and D. W. Lea (2002), A simple evaluation of cleaning procedures on fossil benthic foraminiferal Mg/Ca, *Geochem. Geophys. Geosyst.*, *3*(10), 8401, doi:10.1029/2001GC000280.

Mashiotta, T. A., et al. (1997), Experimental determination of cadmium uptake in shells of the planktonic foraminifera *Orbulina universa* and *Globigerina bulloides*: Implications for surface water paleoreconstructions, *Geochim. Cosmochim. Acta*, *61*, 4053–4065, doi:10.1016/S0016-7037(97)00206-8.

Mayewski, P. A., et al. (2004), Holocene climate variability, *Quat. Res.*, *62*(3), 243–255, doi:10.1016/j.yqres.2004.07.001.

McCorkle, D. C., P. A. Martin, D. W. Lea, and G. P. Klinkhammer (1995), Evidence of a dissolution effect on benthic foraminiferal shell chemistry δ^{13}C, Cd/Ca, Ba/Ca, and Sr/Ca: Results from the Ontong Java Plateau, *Paleoceanography*, *10*(4), 699–714, doi:10.1029/95PA01427.

Nürnberg, D., et al. (1996), Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures, *Geochim. Cosmochim. Acta*, *60*, 803–814, doi:10.1016/0016-7037(95)00446-7.

Pomies, C., et al. (2002), Neodymium in modern foraminifera from the Indian Ocean: Implications for the use of foraminiferal Nd isotope compositions in paleo-oceanography, *Earth Planet. Sci. Lett.*, *203*, 1031–1045, doi:10.1016/S0012-821X(02)00924-X.

Qasim, S. Z. (1982), Oceanography of the northern Arabian Sea, *Deep Sea Res., Part A*, *29*(9), 1041–1068, doi:10.1016/0198-0149(82)90027-9.

Regenberg, M., D. Nürnberg, S. Steph, J. Groeneveld, D. Garbe-Schönberg, R. Tiedemann, and W.-C. Dullo (2006), Assessing the effect of dissolution on planktonic foraminiferal Mg/Ca ratios: Evidence from Caribbean core tops, *Geochem. Geophys. Geosyst.*, *7*, Q07P15, doi:10.1029/2005GC001019.

Rickaby, R. E. M., and H. Elderfield (1999), Planktonic foraminiferal Cd/Ca: Paleonutrients or paleotemperature?, *Paleoceanography*, *14*(3), 293–303, doi:10.1029/1999PA900007.

Rickaby, R. E. M., et al. (2000), Cd in planktonic and benthic foraminiferal shells determined by thermal ionization mass spectrometry, *Geochim. Cosmochim. Acta*, *64*, 1229–1236, doi:10.1016/S0016-7037(99)00317-8.

Ripperger, S., and M. Rehkämper (2007a), A highly sensitive MC-ICPMS method for Cd/Ca analyses of foraminiferal tests, *J. Anal. At. Spectrom.*, *22*(9), 1275–1283, doi:10.1039/b704267.

Ripperger, S., et al. (2007b), Cadmium isotope fractionation in seawater—A signature of biological activity, *Earth Planet. Sci. Lett.*, *261*, 670–684, doi:10.1016/j.epsl.2007.07.034.

Rosenthal, Y., and E. A. Boyle (1993), Factors controlling the fluoride content of planktonic foraminifera: An evaluation of its paleoceanographic applicability, *Geochim. Cosmochim. Acta*, *57*, 335–346, doi:10.1016/0016-7037(93)90435-Y.

Saager, P. M., H. J. W. De Baar, and R. J. Howland (1992), Cd, Zn, Ni and Cu in the Indian Ocean, *Deep Sea Res., Part A*, *39*(1), 9–35, doi:10.1016/0198-0149(92)90017-N.

Schiebel, R. (2002), Planktic foraminiferal sedimentation and the marine calcite budget, *Global Biogeochem. Cycles*, *16*(4), 1065, doi:10.1029/2001GB001459.

Schiebel, R., and M. Bayer (1996), Particle flux in the benthic boundary layer, benthic foraminiferal habitats, and early diagenetic processes in deep sea environments, in *Biogeochemical Fluxes in the Deep-Sea and Investigations of Geological Structures in the Indian Ocean, Cruise No. 33, 22 September – 30 December 1995*, edited by K. Lochte et al., *Meteor-Ber. 96–5*, pp. 78–80, Inst. für Meereskd., Univ. of Hamburg, Hamburg, Germany.

Schiebel, R., and C. Hemleben (2000), Interannual variability of planktic foraminiferal populations and test flux in the eastern North Atlantic Ocean (JGOFS), *Deep Sea Res., Part II*, *47*(9–11), 1809–1852, doi:10.1016/S0967-0645(00)00008-4.

Schiebel, R., and C. Hemleben (2001), Protozoa, planktonic foraminifera, in *Encyclopedia of Ocean Sciences*, edited by J. Steele et al., pp. 2308–2314, Academic, San Diego, Calif.

Schiebel, R., and C. Hemleben (2005), Modern planktic foraminifera, *Palanontol. Z.*, *79*(1), 135–148.

Schiebel, R., B. Hiller, and C. Hemleben (1995), Impacts of storms on Recent planktic foraminiferal test production and $CaCO_3$ flux in the North Atlantic at 47°N, 20°W (JGOFS), *Mar. Micropaleontol.*, *26*(1–4), 115–129, doi:10.1016/0377-8398(95)00035-6.

Schiebel, R., et al. (1997), Population dynamics of the planktic foraminifer *Globigerina bulloides* from the eastern North Atlantic, *Deep Sea Res., Part I*, *44*(9–10), 1701–1713, doi:10.1016/S0967-0637(97)00036-8.

Schiebel, R., et al. (2000), Calcareous plankton and paleoceanography of the Azores Front-Current System, in *North Atlantic 1999*, *Cruise No. 45*, edited by F. Schott et al., *Meteor-Ber. 00-4*, pp. 104–108, Inst. für Meereskd., Univ. of Hamburg, Hamburg, Germany.

Schiebel, R., et al. (2001), Planktic foraminiferal production stimulated by chlorophyll redistribution and entrainment of nutrients, *Deep Sea Res., Part I*, *48*(3), 721–740, doi:10.1016/S0967-0637(00)00065-0.

Schiebel, R., et al. (2002), Impact of the Azores Front on the distribution of planktic foraminifers, shelled gastropods, and coccolithophorids, *Deep Sea Res., Part II*, *49*(19), 4035–4050, doi:10.1016/S0967-0645(02)00141-8.

Schiebel, R., et al. (2004), Distribution of diatoms, coccolithophores and planktic foraminifers along atrophic gradient during SW monsoon in the Arabian Sea, *Mar. Micropaleontol.*, *51*(3–4), 345–371, doi:10.1016/j.marmicro.2004.02.001.

Schiebel, R., et al. (2007), Planktic foraminiferal dissolution in the twilight zone, *Deep Sea Res., Part II*, *54*(5–7), 676–686, doi:10.1016/j.dsr2.2007.01.009.

Sellmer, C., et al. (1998), Planktological studies, in *Nordatlantik 1996*, edited by J. Mienert et al., *Meteor-Ber. 98-2*, pp. 197–200, Inst. für Meereskd., Univ. of Hamburg, Hamburg, Germany.

Spero, H. J., and D. W. Lea (1993), Intraspecific stable isotope variability in the planktic foraminifera *Globigerinoides sacculifer*—Results from laboratory experiments, *Mar. Micropaleontol.*, *22*(3), 221–234, doi:10.1016/0377-8398(93)90045-Y.

Stramma, L. (2001), Current systems in the Atlantic Ocean, in *Encyclopedia of Ocean Sciences*, edited by J. Steele et al., pp. 589–598, Academic, San Diego, Calif.

Tachikawa, K., and H. Elderfield (2002), Microhabitat effects on Cd/Ca and $\delta^{13}C$ of benthic foraminifera, *Earth Planet. Sci. Lett.*, *202*, 607–624, doi:10.1016/S0012-821X(02)00796-3.

Webster, P. J., et al. (1998), Monsoons: Processes, predictability, and the prospects for prediction, *J. Geophys. Res.*, *103*(14), 451–510.

Zeitzschel, T. P., et al. (1998), Hydrographical studies, in *Nordatlantik 1996*, edited by J. Mienert et al., *Meteor-Ber. 98-2*, pp. 181–185, Inst. für Meereskd., Univ. of Hamburg, Hamburg, Germany.

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