



U/Ca in benthic foraminifers: A proxy for the deep-sea carbonate saturation

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[1] The ocean plays a major role in the global carbon cycle, and attempts to reconstruct past changes in the marine carbonate system are increasing. The speciation of dissolved uranium is sensitive to variations in carbonate system parameters, and previous studies have shown that this is recorded in the uranium-to-calcium ratio (U/Ca) of the calcite shells of planktonic foraminifera. Here we test whether U/Ca ratios of deep-sea benthic foraminifera are equally suited as an indicator of the carbonate system. We compare U/Ca in two common benthic foraminifer species (*Planulina wuellerstorfi* and *Cibicides mundulus*) from South Atlantic core top samples with the calcite saturation state ($\Delta[\text{CO}_3^{2-}] = [\text{CO}_3^{2-}]_{\text{in situ}} - [\text{CO}_3^{2-}]_{\text{sat}}$) of the ambient seawater and find significant negative correlations for both species. Compared with planktonic foraminifera, the sensitivity of U/Ca in benthic foraminifera to changes in $\Delta[\text{CO}_3^{2-}]$ is about 1 order of magnitude higher. Although $\Delta[\text{CO}_3^{2-}]$ exerts the dominant control on the average foraminiferal U/Ca, the interest and intratest variability indicates the presence of additional factors forcing U/Ca.

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1. Introduction

[2] The seawater carbonate system plays a crucial role in the global carbon cycle. It controls variations in atmospheric carbon dioxide, and is influenced by chemical weathering, ocean circulation, carbon burial, and the dissolution of carbonate sediments [e.g., *Ridgwell and Zeebe, 2005*]. Seawater carbonate system parameters include all individual dissolved carbon species and pH, but the system can be determined when any two are known, including dissolved inorganic carbon (DIC) and alkalinity. The saturation of seawater with respect to calcite is described by the carbonate ion saturation state $\Delta[\text{CO}_3^{2-}]$ ($=[\text{CO}_3^{2-}]_{\text{in situ}} - [\text{CO}_3^{2-}]_{\text{sat}}$), where $[\text{CO}_3^{2-}]_{\text{sat}}$ (carbonate ion saturation) is mainly determined by pressure (and thus water depth) [*Zeebe and Wolf-Gladrow, 2001*].

[3] Reconstructions of carbonate system parameters over geological time have been based on the preservation state and mass of foraminiferal shells [*Broecker and Clark, 2001; Barker and Elderfield, 2002*], and the elemental and isotopic composition of calcareous microfossils. For example, boron isotopes in planktonic foraminifers and B/Ca in benthic foraminifers have been proposed as indicators for pH and $\Delta[\text{CO}_3^{2-}]$, respectively [*Sanyal et al., 1995; Pearson and Palmer, 2000; Yu and Elderfield, 2007; Hönisch et al., 2009*].

[4] Compared with these proxies, foraminiferal U/Ca ratios have received relatively little attention. In cultured planktonic foraminifers U/Ca was shown to decrease with increasing $[\text{CO}_3^{2-}]$ [*Russell et al., 2004*], and an influence of $[\text{CO}_3^{2-}]$ has also been proposed for cultured calcareous dinoflagellate cysts [*Gussone et al., 2010*]. Temperature may also influence the U/Ca of biogenic calcite [*Yu et al., 2008; Gussone et al., 2010*] and is potentially the dominant control on the U/Ca of coral aragonite [*Min et al., 1995; Shen and Dunbar, 1995; Felis et al., 2009*]. Although foraminiferal U/Ca is a promising marine carbonate system proxy, no calibrations have yet been conducted for deep-sea benthic species.

[5] Uranium exists in seawater in the form of multiple uranyl (UO_2^{2+}) carbonate complexes whose relative abundances depend on pH and $[\text{CO}_3^{2-}]$ [*Djogić et al., 1986; Krestou et al., 2003*] (Figure 1). It is difficult for the most abundant complex, $\text{UO}_2(\text{CO}_3)_3^{4-}$, to be incorporated into the calcite structure as a change in the uranyl coordination is required [*Reeder et al., 2000*]. *Russell et al.* [2004] suggested that $\text{UO}_2(\text{CO}_3)_2^{2-}$ and UO_2CO_3 may be preferentially incorporated. Since the concentrations

in seawater of these last two uranyl carbonate complexes increase with decreasing pH [*Djogić et al., 1986*] the relationship between biogenic U/Ca and the pH (and $[\text{CO}_3^{2-}]$) of the ambient water is negative [*Russell et al., 2004*]. Uranium speciation and solubility are additionally influenced by the redox state [*Barnes and Cochran, 1990*] (Figure 1).

[6] To explore the potential of U/Ca in two common species of benthic foraminifera (*Planulina wuellerstorfi*, *Cibicidoides mundulus*) for recording the deep-sea carbonate chemistry we analyzed specimens from core tops collected from five basins in the South Atlantic (Figure 2). Shell U/Ca is compared with bottom water $[\text{CO}_3^{2-}]$ and $\Delta[\text{CO}_3^{2-}]$ calculated from WOCE data [*WOCE Data Products Committee, 2002*] using the eWOCE Electronic Atlas [*Schlitzer, 2000*]. The potential influence of temperature on foraminiferal U/Ca was minimized by selecting sampling locations with a narrow range of bottom water temperatures (~ 1 to 4°C). Oxidic conditions prevail in the bottom water and the uppermost centimeter of the sediment (Figure 2). We therefore do not expect a major effect of the redox state on U/Ca in the epibenthic *P. wuellerstorfi* and shallow endobenthic *C. mundulus* employed in this study. We also investigate the intrashell U/Ca variability to test the presence of ontogenetic trends and additional controls on the uranium incorporation.

2. Material and Methods

[7] Foraminifer tests (size $> 250 \mu\text{m}$) of the benthic species *Planulina wuellerstorfi* (synonymous with *Cibicidoides wuellerstorfi*) and *Cibicidoides mundulus* were picked from a total of 23 South Atlantic core top samples over a depth range from 1805 to 4675 m (Figure 2 and Table 1). Most sampling sites are bathed in either North Atlantic Deep Water (NADW) or Antarctic Bottom Water (AABW) [*Stramma and England, 1999*]. Rose-Bengal-stained shells show that the individuals used here were recently living. Shells were visually unaltered (translucent, undissolved, cement-barren) and free of secondary mineral phases. *Planulina wuellerstorfi* is an epibenthic species preferring an elevated habitat above the water-sediment interface [*Lutze and Thiel, 1989*], while *Cibicidoides mundulus* is shallow endobenthic and occurs often within the uppermost centimeter of the sediment [*McCorkle et al., 1990*].

[8] We used laser ablation (LA)-ICP-MS to measure the element composition of the foraminifer

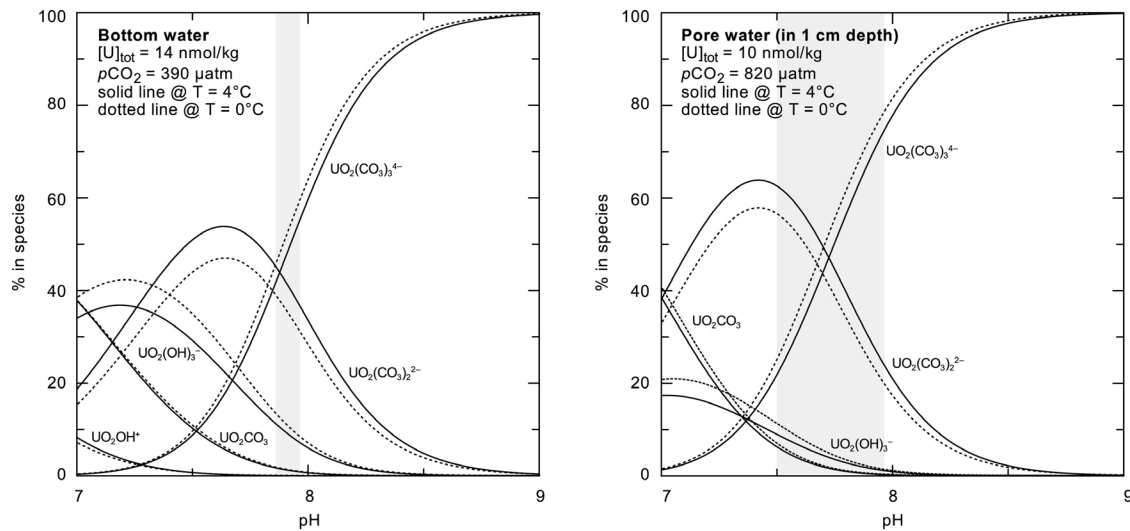


Figure 1. The speciation of uranium in seawater at ~3000 m water depth depending on pH and temperature. Plotted is (left) the U speciation for bottom water and (right) pore water conditions at 1 cm sediment depth. The total uranium concentration in pore water is depleted compared to bottom water due to authigenic U accumulation in the sediment through lower oxygen concentration (for comparison, see Figure 2), and $p\text{CO}_2$ is increased due to the decomposition of organic material in the sediment. The gray shaded areas indicate the pH ranges at the study sites.

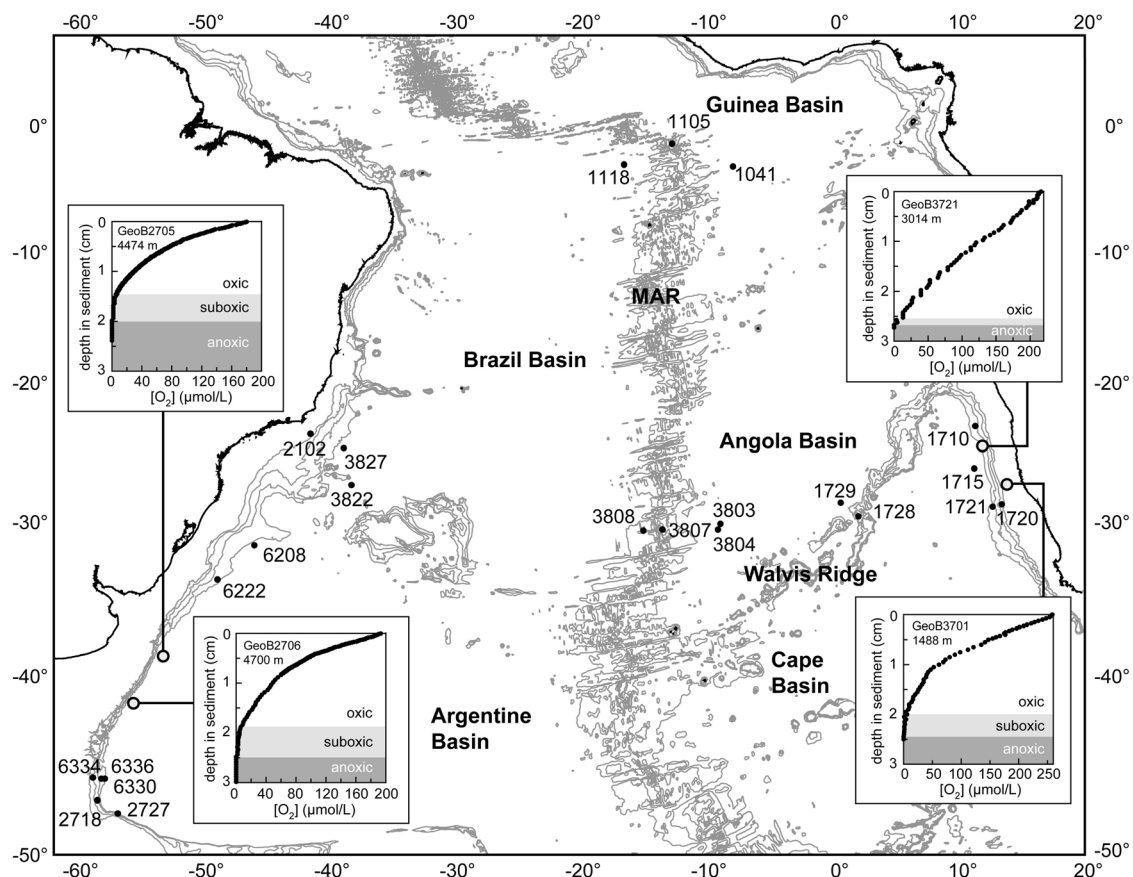


Figure 2. Positions of GeoB sampling sites and four nearby sites with available pore water oxygen concentrations [Hensen et al., 2004a, 2004b, 2004c, 2004d].

Table 1. Sampling Stations and Elemental Composition of Benthic Foraminifera^a

Meteor Cruise	GeoB Site ^b	Lat. °N	Long. °E	Depth (m)	Temp. (°C)	[CO ₃ ²⁻] (μmol/kg)	Δ[CO ₃ ²⁻] ^c (μmol/kg)	Planulina wuellerstorfi			Cibicides mundulus				
								U/Ca ± SE (nmol/mol)	D _U ^d	Mn/Ca ± SE (μmol/mol)	Al/Ca ± SE (μmol/mol)	U/Ca ± SE (nmol/mol)	D _U ^d	Mn/Ca ± SE (μmol/mol)	Al/Ca ± SE (μmol/mol)
M6/6	1041b	-3.48	-7.59	4035	2.51	106.67	14.29	8.88 ± 0.46	0.0064	4.31 ± 0.55	13.62 ± 5.44	N.D.	N.D.	N.D.	N.D.
M9/4	1105	-1.67	-12.43	3231	2.36	109.90	30.54	8.66 ± 0.75	0.0062	6.24 ± 0.53	4.94 ± 2.71	N.D.	N.D.	N.D.	N.D.
M9/4	1118b	-3.34	-16.26	4675	0.86	89.41	-14.85	22.93 ± 1.12	0.0165	3.43 ± 0.96	4.86 ± 2.10	16.89 ± 1.73	0.0122	7.94 ± 3.79	24.18 ± 9.85
M20/2	1710	-23.43	11.7	2987	2.57	103.04	27.26	10.68 ± 0.90	0.0077	4.64 ± 0.60	5.31 ± 1.31	11.55 ± 2.15	0.0083	9.41 ± 2.48	3.35 ± 2.47
M20/2	1715	-26.47	11.64	4095	1.43	96.40	2.97	14.75 ± 1.33	0.0106	25.73 ± 10.13	66.20 ± 24.75	N.D.	N.D.	N.D.	N.D.
M20/2	1720	-29	13.83	2011	2.95	101.08	38.07	6.05 ± 0.81	0.0044	6.42 ± 1.81	16.97 ± 9.42	N.D.	N.D.	N.D.	N.D.
M20/2	1721	-29.17	13.09	3045	2.43	101.22	24.61	10.80 ± 0.84	0.0078	25.25 ± 11.74	40.98 ± 16.02	N.D.	N.D.	N.D.	N.D.
M20/2	1728b	-29.84	2.41	2887	2.35	102.51	28.15	4.71 ± 0.28	0.0034	1.27 ± 0.72	6.19 ± 0.82	4.48 ± 0.44	0.0032	2.98 ± 1.13	11.70 ± 3.54
M20/2	1729	-28.89	1	4401	2.36	104.17	5.18	10.48 ± 0.62	0.0075	21.51 ± 6.87	73.82 ± 20.90	8.82 ± 0.82	0.0063	1.60 ± 0.31	5.98 ± 1.22
M23/2	2102	-23.98	-41.2	1805	3.88	93.72	33.11	5.58 ± 2.05	0.0040	30.65 ± 6.56	102.83 ± 25.97	3.38 ± 0.55	0.0024	0.91 ± 0.17	8.81 ± 8.81
M29/1	2718g	-47.31	-58.17	2991	1.20	89.49	13.66	13.48 ± 2.88	0.0097	38.89 ± 11.57	19.34 ± 7.20	14.51 ± 1.72	0.0104	2.07 ± 0.33	6.39 ± 2.42
M29/1	2727	-48.01	-56.54	2819	1.39	86.92	13.51	6.59 ± 0.94	0.0047	4.94 ± 1.20	17.54 ± 16.42	N.D.	N.D.	N.D.	N.D.
M34/3	3803	-30.35	-8.57	4173	2.43	105.39	10.57	7.32 ± 0.72	0.0053	18.38 ± 13.68	2.66 ± 0.32	9.65 ± 1.34	0.0069	1.00 ± 0.25	8.94 ± 4.53
M34/3	3804	-30.74	-8.77	3882	2.43	106.36	16.62	10.29 ± 1.00	0.0074	23.16 ± 10.78	17.18 ± 7.08	6.21 ± 0.66	0.0045	9.79 ± 4.24	6.13 ± 1.27
M34/3	3807	-30.75	-13.2	2515	2.51	103.33	34.02	4.66 ± 0.42	0.0034	4.21 ± 2.14	10.05 ± 4.27	N.D.	N.D.	N.D.	N.D.
M34/3	3808	-30.81	-14.71	3213	2.41	106.94	27.86	7.59 ± 0.81	0.0055	2.44 ± 0.80	0.48 ± 0.18	4.74 ± 0.31	0.0034	1.43 ± 0.22	3.89 ± 0.64
M34/3	3822	-27.63	-37.95	4273	0.43	86.62	-10.01	7.23 ± 0.68 ^e	0.0052	3.61 ± 0.98	17.61 ± 7.95	20.86 ± 3.26	0.0150	3.69 ± 0.39	43.45 ± 11.22
M34/3	3827	-25.03	-38.55	3842	1.53	100.87	11.80	11.43 ± 2.20	0.0082	2.72 ± 0.65	12.35 ± 3.61	15.68 ± 1.33	0.0113	6.15 ± 1.93	40.77 ± 13.41
M46/2	6208	-31.81	-45.67	3693	0.39	84.98	-1.62	13.44 ± 1.55	0.0097	2.60 ± 1.08	24.18 ± 18.57	N.D.	N.D.	N.D.	N.D.
M46/2	6222	-34.08	-48.62	3450	1.27	90.87	8.16	19.92 ± 1.99	0.0143	0.34 ± 0.57	43.03 ± 23.50	N.D.	N.D.	N.D.	N.D.
M46/3	6330	-46.15	-57.56	3874	0.43	85.67	-3.94	18.11 ± 1.55	0.0130	5.47 ± 1.04	0.51 ± 0.71	N.D.	N.D.	N.D.	N.D.
M46/3	6334	-46.09	-58.52	2597	1.57	90.65	20.26	13.96 ± 1.90	0.0100	4.87 ± 1.38	7.84 ± 4.93	6.78 ± 1.15	0.0049	1.68 ± 0.38	1.58 ± 3.17
M46/3	6336	-46.14	-57.84	3398	0.92	85.21	3.31	9.50 ± 0.93	0.0068	12.73 ± 0.99	19.65 ± 12.81	N.D.	N.D.	N.D.	N.D.

^aSE, standard error of the mean; N.D., not determined.

^bAll core top samples are from multicores, except box cores (labeled "b") and gravity cores (labeled "g").

^cCalculated from WOCE data using the equation of Jansen *et al.* [2002].

^dPartition coefficient D_U = (U/Ca_{shell})/(U/Ca_{seawater}) using a U/Ca_{seawater} = 1390 nmol/mol [Ku *et al.*, 1977].

^eOutlier not used in regressions.

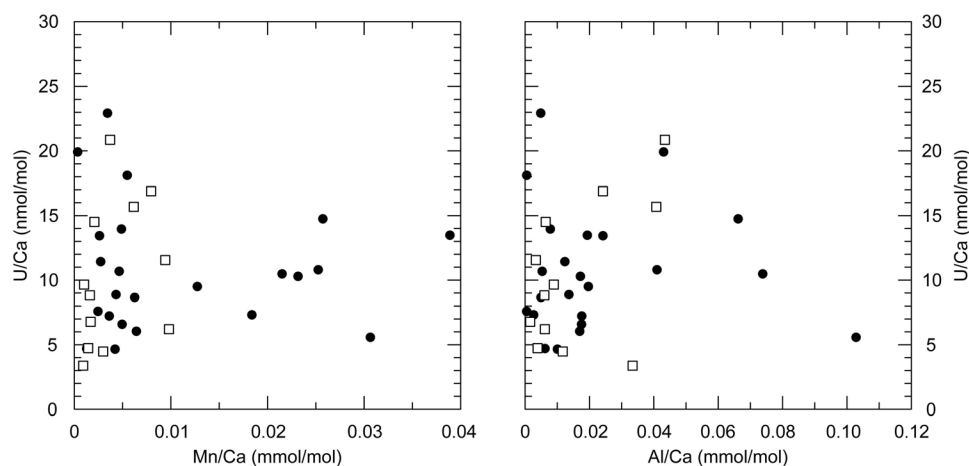


Figure 3. Shell U/Ca versus Mn/Ca and Al/Ca for *P. wuellerstorfi* (solid dots) and *C. mundulus* (open squares). Mn/Ca and Al/Ca remain low, and there are no correlations with U/Ca. For clarity, error bars are omitted.

tests. Following the protocols of Rathmann *et al.* [2004] and Raitzsch *et al.* [2008], we analyzed 3–5 individuals for each sediment sample and species, and 5 to 8 spot measurements were carried out on each test. The datum reported for one sample represents the average of all spot measurements. The whole shells were not chemically or physically treated before analysis. Instead, ablation sites were preablated for ~1 s in order to remove surface contaminations. Only the umbilical side of the shells, where pore density is lowest, was ablated while taking great care to avoid any pore fillings.

[9] Trace element composition was measured using a NewWave UP193 laser ablation system ($\lambda = 193$ nm) connected to a Thermo-Finnigan Element 2 sector field ICP-MS, using a pulse rate of 5 Hz, spot sizes of 50 and 75 μm , and irradiances between 0.16 and 0.24 GW/cm^2 . Each measurement was preceded by a 40 s gas blank, and the transient signals of ^{27}Al , ^{43}Ca , ^{55}Mn , ^{64}Zn , and ^{238}U were monitored. Al and Mn acted as indicators of sedimentary clay, ferromanganese coatings, and Mn-rich secondary carbonate. Zn was monitored in order to detect ablation of the sample holder consisting of a double-sided adhesive tape. Time resolved data were evaluated with the GeoProTM software (CETAC) using ^{43}Ca as internal standard. Signals were calibrated using the NIST 612 glass [Pearce *et al.*, 1997] that was measured before and after five measurements of each shell. Calibration of U/Ca in carbonate samples using the NIST 612 glass has been demonstrated to be accurate with a 193 nm laser [Hathorne *et al.*, 2008]. We analyzed a powder pellet of the Jct-1 calcium carbonate standard repeatedly and obtained a mean U/Ca value of 21.5 nmol/mol, indistinguishable from

the value of 21.1 nmol/mol reported by Inoue *et al.* [2004]. Assuming a homogeneous elemental distribution within the Jct-1 pellet the relative standard deviation (RSD) of 22% between spot measurements indicates the analytical uncertainty for single spot measurements. Average values for foraminifera samples are based on multiple spot measurements, where the relative standard error of the mean was typically 12%.

[10] Local in situ bottom water temperatures were obtained from CTD (conductivity-temperature-depth) data of the same cruises. For stations where CTD data were not available ($n = 8$), temperatures were derived from the World Ocean Atlas (WOA 2001) [Stephens *et al.*, 2002]. Carbonate ion concentrations were calculated from carbonate chemistry data derived from the eWOCE Electronic Atlas of WOCE data [Schlitzer, 2000] using the CO2SYS program [Lewis and Wallace, 1998; Pierrot *et al.*, 2006]. The carbonate ion saturation state was determined by subtracting the carbonate ion saturation [Jansen *et al.*, 2002] from the in situ carbonate ion concentration ($\Delta[\text{CO}_3^{2-}] = [\text{CO}_3^{2-}]_{\text{in situ}} - [\text{CO}_3^{2-}]_{\text{sat}}$).

3. Results

[11] Average U/Ca values (i.e., values averaged from multiple tests from the same sediment sample) range from 3 nmol/mol to 23 nmol/mol without differences between *P. wuellerstorfi* and *C. mundulus*. Mn/Ca is generally much lower than the 0.1 mmol/mol limit proposed by Boyle [1983] for trace element analysis of foraminifera (Table 1). In most cases Al/Ca is below detection limit, and in the other few cases (up to 0.1 mmol/mol) much lower than demonstrated

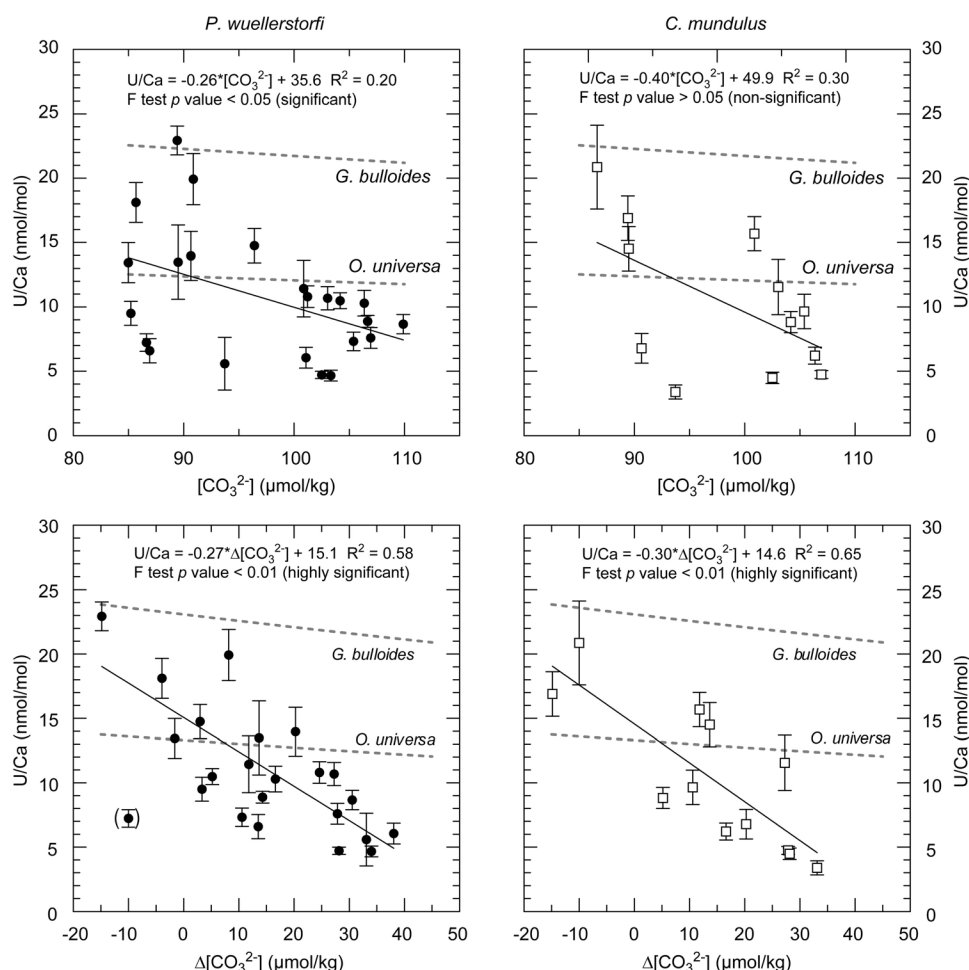


Figure 4. Benthic foraminiferal U/Ca versus bottom water (top) $[CO_3^{2-}]$ and (bottom) $\Delta[CO_3^{2-}]$ for (left) *P. wuellerstorfi* and (right) *C. mundulus*. Solid lines are linear fits through the data. The outlier in parentheses was excluded from the regression. Uncertainties for the regressions of U/Ca against $\Delta[CO_3^{2-}]$ are reported in equations (1) and (2). The dashed lines are the exponential regressions for the planktonic foraminifers *Orbulina universa* and *Globigerina bulloides* reported by Russell *et al.* [2004].

by Barker *et al.* [2003] for uncleaned samples (>0.5 mmol/mol). In addition, Mn/Ca and Al/Ca show no relationship with U/Ca (Figure 3). Together with the excellent shell preservation this suggests that the samples were not affected by sedimentary clay contamination or the growth of authigenic minerals linked to the redox state of the pore or bottom water.

[12] In both species U/Ca decreases with increasing $[CO_3^{2-}]$ (Figure 4) but we found a much higher significance in the correlation between U/Ca and $\Delta[CO_3^{2-}]$:

[13] *Planulina wuellerstorfi* (one outlier removed)

$$U/Ca = (-0.27 \pm 0.04) \cdot \Delta[CO_3^{2-}] + 15.1 \pm 1.4; \quad R^2 = 0.58 \quad (1)$$

Cibicides mundulus

$$U/Ca = (-0.30 \pm 0.06) \cdot \Delta[CO_3^{2-}] + 14.6 \pm 1.8; \quad R^2 = 0.65 \quad (2)$$

where U/Ca is in nmol/mol and $\Delta[CO_3^{2-}]$ in $\mu\text{mol/kg}$.

[14] The relationships are significant for ordinary least square linear regression and show similar slopes and intercepts in both species. Negative correlations also exist between shell U/Ca and temperature (Figure 5) although this may result from the correlation of temperature and $\Delta[CO_3^{2-}]$ (see discussion).

[15] Based on our data, $\Delta[CO_3^{2-}]$ explains 58% (*P. wuellerstorfi*) and 65% (*C. mundulus*) of the mean U/Ca. On average, U/Ca deviates by about \pm

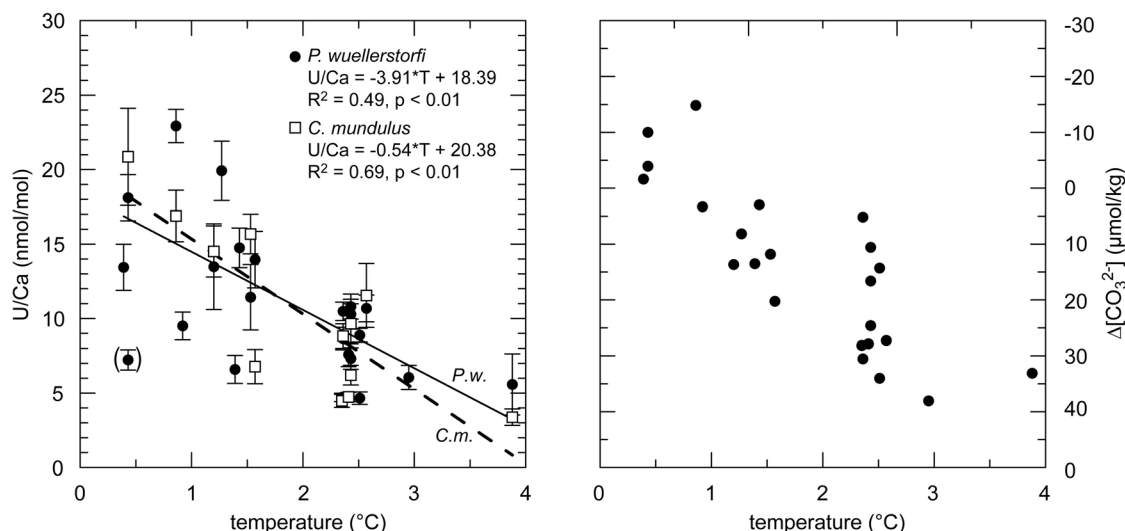


Figure 5. (left) Linear regressions of U/Ca in *P. wuellerstorfi* (solid dots and line) and *C. mundulus* (open squares and dashes line) with temperature. The outlier in parentheses was excluded from the regression. (right) Bottom water $\Delta[\text{CO}_3^{2-}]$ plotted against temperature for the sampling locations. The relationship between $\Delta[\text{CO}_3^{2-}]$ and temperature is probably the reason for the correlation of U/Ca with temperature.

3 nmol/mol from the regression lines (based on the regression residuals). For a U/Ca of 10 nmol/mol this translates to errors for reconstructed $\Delta[\text{CO}_3^{2-}]$ of about $\pm 15 \mu\text{mol/kg}$ for *P. wuellerstorfi* and $\pm 10 \mu\text{mol/kg}$ for *C. mundulus*.

[16] Differences in U/Ca between spot measurements are greater than the analytical uncertainty indicating considerable heterogeneity in the intrate uranium distribution. Occasionally, U/Ca may vary by a factor of five within the same shell. A sample subset had all chambers analyzed to test for the presence of ontogenetic trends (Figure 6). In some specimens U/Ca increases from the older toward the younger chambers, while others show a decrease or no trend at all. On average, there is no consistent link between the ontogenetic stage and the U/Ca of a chamber. Intra and intershell U/Ca variability compare well, with average relative standard deviations (RSD) of $\sim 28\%$ in both cases and for both species. This number can be used to extrapolate the uncertainty of U/Ca averaged from multiple shells. Estimated standard errors of the means are 13% for 5 shells, 9% for 10 shells, and 6% for 20 shells.

4. Discussion

4.1. Influence of $\Delta[\text{CO}_3^{2-}]$ and Temperature on U/Ca

[17] In the benthic foraminifera investigated here U/Ca decreases with increasing $\Delta[\text{CO}_3^{2-}]$. This has

also been observed in culture experiments with the planktonic foraminifer species *Orbulina universa* (symbiont-bearing) and *Globigerina bulloides* (symbiont-barren) [Russell et al., 2004]. However, by comparison U/Ca of *P. wuellerstorfi* and *C. mundulus* is about ten times more sensitive to changes in $\Delta[\text{CO}_3^{2-}]$ (Figure 4). The $\Delta[\text{CO}_3^{2-}]$ range covered by our data (-10 to $40 \mu\text{mol/kg}$) is lower than that examined in the culturing experiments of Russell et al. [2004] (~ 30 to $430 \mu\text{mol/kg}$). Further, these authors found an exponential relationship between U/Ca and $[\text{CO}_3^{2-}]$, rather than a linear one. We can therefore not rule out the possibility that our linear U/Ca versus $\Delta[\text{CO}_3^{2-}]$ calibrations are valid only within the $\Delta[\text{CO}_3^{2-}]$ range covered by our study (-10 to $40 \mu\text{mol/kg}$) and that an exponential relationship would be more appropriate for a larger $\Delta[\text{CO}_3^{2-}]$ range.

[18] Given that benthic foraminiferal U/Ca in our study is correlated with $\Delta[\text{CO}_3^{2-}]$, rather than with $[\text{CO}_3^{2-}]$, raises the question of the factor that controls the uranium uptake into shell calcite. In aragonite (e.g., coral skeletons), the aqueous uranium species $\text{UO}_2(\text{CO}_3)_3^{4-}$ is preferentially incorporated into the crystal structure due to its coordination and geometry, whereas in calcite a change in the coordination of this species is required to fit into the calcite lattice [Reeder et al., 2000]. Therefore, it was suggested that the aqueous species $\text{UO}_2(\text{CO}_3)_2^{2-}$ instead of $\text{UO}_2(\text{CO}_3)_3^{4-}$ is incorporated [Russell et al., 2004]. Since the relative concentration of $\text{UO}_2(\text{CO}_3)_2^{2-}$ decreases with increasing pH and

thus $[\text{CO}_3^{2-}]$ (Figure 1), this may explain the inverse relationship between planktonic U/Ca and pH. This change in aqueous U speciation with pH may also explain why U/Ca in *O. universa* is lower than in *G. bulloides* (Figure 4) since the photosymbionts in *O. universa* increase the pH at the shell surface. Russell et al. [2004] also considered that at higher pH the adsorption of uranium onto different mineral and organic surfaces, which precedes the incorporation into calcite, is inhibited, thus lowering the overall uranium concentration in calcite at higher pH. Alternatively, at lower $[\text{CO}_3^{2-}]$ the calcification rate is slower, which may enhance the U incorporation because the uranyl carbonate complex has more time to adjust sterically to fit into the calcite lattice [Russell et al., 2004]. However, since we obtain a more significant correlation of U/Ca with $\Delta[\text{CO}_3^{2-}]$ than with $[\text{CO}_3^{2-}]$ (Figure 4), we argue that it is the calcite saturation state, rather than the carbonate ion concentration, that influences U/Ca in the benthic foraminifer species investigated here.

[19] Temperature influences the dissociation constants of aqueous uranium species and therefore potentially affects the availability of $\text{UO}_2(\text{CO}_3)_2^{2-}$ that is incorporated into shell calcite. The temperature change from 0 to 4°C increases the concentration of $\text{UO}_2(\text{CO}_3)_2^{2-}$ by about 15% (Figure 1). Based on this result and the empirical data by Yu et al. [2008], we would expect a positive correlation between temperature and U/Ca in our samples. However, the observed correlation is negative, which suggests the influence of a common forcing on U/Ca and temperature, rather than a direct influence of temperature on U/Ca. Both temperature and $\Delta[\text{CO}_3^{2-}]$ drop with increasing water depth, and decreasing temperatures further reduce $\Delta[\text{CO}_3^{2-}]$. Thus temperature and $\Delta[\text{CO}_3^{2-}]$ in the field are positively related (Figure 5). Since U/Ca is primarily driven by $\Delta[\text{CO}_3^{2-}]$, it is also inversely related with temperature. As outlined above, the influence of temperature (if any) on U/Ca would be positive, but is insufficient to overcome the dominant $\Delta[\text{CO}_3^{2-}]$ forcing.

4.2. Potential Influence of Pore Water on U/Ca

[20] The magnitude of intratest U/Ca variability is high given the rather constant environmental con-

ditions in the deep sea (Figure 6). The variability is too large to be explained by local changes in bottom water $\Delta[\text{CO}_3^{2-}]$ alone. It has been shown that the elemental composition of infaunal benthic foraminifera may be influenced by pore water rather than bottom water chemistry [Rathmann and Kuhnert, 2008]. However, *P. wuellerstorfi* is an epibenthic species [Lutze and Thiel, 1989] and not exposed to pore water. On the contrary, *C. mundulus* is most abundant within the uppermost centimeter of sediment, but can occur over a relatively large sediment depth range [McCorkle et al., 1990; Rathburn and Corliss, 1994]. While aqueous [U] is conservative in oxygenated ocean waters, it is sensitive to the redox conditions in environments with low oxygen content through reduction of the soluble U(VI) to the insoluble U(IV) [see McManus et al., 2005, and references therein]. Such a uranium removal from pore water via authigenesis in reducing sediments is controlled by several factors and combinations including organic carbon (TOC) rain and $[\text{O}_2]$ of bottom water [e.g., McManus et al., 2005; Morford et al., 2009]. The TOC flux is an important factor in controlling [U] both by delivering uranium to the sediment and by its accumulation within the sediment via diagenesis caused by the consumption of oxygen associated with the degradation of organic matter [e.g., McManus et al., 2005, and references therein]. Conversely, an increase in bottom water $[\text{O}_2]$ and/or a decrease in TOC rain may increase the oxygen penetration into the sediment resulting in a remobilization of uranium once accumulated as insoluble U within the sediment [e.g., Zheng et al., 2002].

[21] Similarly, variations in TOC rain and oxygen penetration depth also change pore water $[\text{CO}_3^{2-}]$ through the addition of CO_2 from organic matter degradation. The resulting pH change controls the aqueous U speciation within the sediment and thus the relative concentration of $\text{UO}_2(\text{CO}_3)_2^{2-}$ preferentially incorporated into calcite (Figure 1). Consequently, shell U/Ca of infaunal species should record pore water rather than bottom water conditions due to steep gradients in pH, $[\text{CO}_3^{2-}]$ and $[\text{O}_2]$.

[22] However, to better constrain the link between such variations in pore-water chemistry and foraminiferal U/Ca we need to have data of uranium pore-water profiles, which are unfortunately not

Figure 6. (top) Photograph of *P. wuellerstorfi* showing ablation holes in different chambers. (bottom left) U/Ca from spot measurements in individual shells of *P. wuellerstorfi*. (right) U/Ca from spot measurements in individual shells of *C. mundulus*; f is the final (youngest) chamber of the shell, f-2 the third youngest, and so forth. Averages are marked by gray bars. The analytical error shown here ($\pm 22\%$ RSD) is based on measurements of a carbonate standard (see section 2).

available for the South Atlantic. Hence we examined two study sites (EN433) from the middle Atlantic Bight (~36°N, 74°W) reported by *Morford et al.* [2009], which exhibit a geochemical setting similar to our study sites (TOC, bottom-water [O₂] and O₂ penetration depth). At the sites studied by *Morford et al.* [2009], pore-water [U] decreases by between 17 and 41% within the first centimeter of sediment. Based on this decrease in [U] we calculated the U speciation at two different settings, one at bottom-water and one at pore-water conditions at 1 cm sediment depth (Figure 1) using PhreePlot (D. G. Kinniburgh and D. M. Cooper, PhreePlot: Creating graphical output with PHREEQC, 2009, available at <http://www.phreeplot.org/>) that is based on the computer program PHREEQC [Parkhurst and Appelo, 1999]. Interestingly, the relative abundance of $\text{UO}_2(\text{CO}_3)_2^{2-}$ in pore waters is higher than in bottom waters, although the total uranium concentration is lower by 41%. The effect of the higher relative abundance of $\text{UO}_2(\text{CO}_3)_2^{2-}$ on foraminiferal U/Ca may counteract or even cancel out the lower total uranium concentration in pore waters. Hence, it seems not surprising that U/Ca of *C. mundulus* is similar to that of *P. wuellerstorfi*.

[23] Nevertheless, the pH range of pore water within the sediment depth inhabited by *C. mundulus* is more variable than that of bottom water (Figure 1). Since *C. mundulus* migrates vertically through the sediment, we would expect higher scatter in the calibration against bottom water $\Delta[\text{CO}_3^{2-}]$ and a higher intratest U/Ca variability compared with *P. wuellerstorfi*. However, we observe similar relationships between U/Ca and bottom water $\Delta[\text{CO}_3^{2-}]$ for both species with comparable scatter, and intrashell U/Ca variability is equally high.

[24] We propose two explanations that do not exclude one another:

[25] 1. The intratest U/Ca variability is not environmentally forced, but results from enigmatic biological factors. This is analogous to Mg/Ca in benthic foraminifera, where the bulk shell composition is primarily governed by temperature [e.g., *Martin et al.*, 2002], but intratest Mg/Ca typically varies by ±20–50% from the average value and therefore exceeds the range that can be explained by temperature changes [*Rathmann et al.*, 2004; *Toyofuku and Kitazato*, 2005; *Hintz et al.*, 2006].

[26] 2. *Cibicidoides mundulus* primarily calcifies at the sediment surface where it is exposed to bottom water rather than pore water. The reason for this behavior is speculative, but may include more favorable conditions for secreting calcite (i.e.,

higher pH) than within the sediment. The hypothesis of calcification at the surface is supported by the foraminiferal boron isotopic composition ($\delta^{11}\text{B}$), which is predominantly controlled by the pH of ambient seawater during calcification. It has been recently shown that $\delta^{11}\text{B}$ of *C. mundulus* is nearly identical to that of *P. wuellerstorfi*, irrespective of water depth and the geographical position of the sites studied [*Rae et al.*, 2011]. Correspondingly, we assume that also the mean U/Ca ratios of *C. mundulus* primarily reflect bottom water rather than pore water conditions.

5. Conclusions

[27] We have shown that variations in the average U/Ca of the shells of two common benthic foraminifera (*Planulina wuellerstorfi*, *Cibicidoides mundulus*) are most likely driven by the carbonate ion saturation state of the ambient seawater. The lack of any obvious influence of pore water on U/Ca of the shallow infaunally living *C. mundulus* suggests that this species secretes its shell at the sediment surface and thus records bottom water rather than pore water conditions. Additional biological factors force U/Ca variability between shells from the same sediment sample and also on the microscale between chambers of the same specimen. The range of $\Delta[\text{CO}_3^{2-}]$ covered by our calibrations is characteristic for the deep sea, and we therefore consider U/Ca in the above species as a promising proxy for the reconstruction of past changes in the deep marine carbonate system.

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