Key Points:
- We investigate controlling factors on U/Ca and U/Mn of two benthic foraminiferal species from core-top and downcore samples
- Our data reveal no significant correlation between core-top (lattice-bound) U/Ca and carbonate system parameters
- Downcore (shell + coating) U/Mn and U/Ca are proposed to indicate past sedimentary redox conditions

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An evaluation of benthic foraminiferal U/Ca and U/Mn proxies for deep ocean carbonate chemistry and redox conditions

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Abstract The deep ocean is thought to have played a crucial role in modulating atmospheric CO_2 changes, and thus reconstructions of deep ocean conditions can place important constraints on the past global carbon cycle. Some previous studies suggested that foraminiferal U/Ca could be used to infer seawater carbonate chemistry changes, but others showed complications from diagenesis and temperature. A recent downcore study suggested that foraminiferal U/Mn may be used for sedimentary redox-conditions, but no core-top work has been done to investigate factors affecting U/Mn. We investigate controlling factors on U/Ca and U/Mn in two benthic foraminiferal species from 120 global core-tops and three Atlantic sediment cores. Our core-top data reveal no significant correlation between core-top benthic U/Ca and carbonate system parameters. The lack of an influence of deep-water $[CO_3^{2-}]$ on U/Ca is further supported by our downcore results. Together, our data highlight complications to use benthic U/Ca for deep-water carbonate chemistry reconstructions. Although no correlation is found between core-top U/Mn and hydrographic data, high-resolution U/Mn and U/Ca in core TNO57-21 show similar patterns to authigenic U (aU) and vary in tandem with atmospheric CO_2 on millennial timescales. Changes in U/Mn, U/Ca and aU in TNO57-21 may reflect postdepositional diagenesis linked to sedimentary oxygen, which is controlled by subantarctic surface productivity and ventilation of deep South Atlantic in the past. We suggest that benthic U/Mn and U/Ca may be used as auxiliary indicators for past sedimentary redox-conditions and along with other proxies could reflect deep-water oxygenation.

1. Introduction

Understanding mechanisms responsible for past atmospheric CO_2 concentration variations is one of unresolved challenges in paleoceanography. The deep ocean is the largest carbon reservoir of the atmosphere-land biosphere-ocean system, and marine processes (such as the biological pump) that alter deep-water carbon content have exerted profound influences on atmospheric CO_2 fluctuations on glacial-interglacial timescales [*Broecker*, 1982; *Sigman and Boyle*, 2000]. Reconstructions of the marine carbonate system are therefore important to understand marine carbon cycling and the ocean's role in controlling atmospheric CO_2 changes in the past [*Gottschalk et al.*, 2015; *Yu et al.*, 2010, 2014, 2016].

The chemical composition of foraminiferal carbonate from deep-sea sediments has been widely used to reconstruct physicochemical properties of seawaters from which shells precipitate [*Boyle and Keigwin*, 1985/1985; *Russell et al.*, 1994, 1996, 2004; *Yu and Elderfield*, 2007; *Yu et al.*, 2007b,a]. Among proxies used, U/Ca in foraminiferal carbonates have been proposed to reconstruct changes in marine carbonate chemistry. U/Ca in cultured planktonic foraminifera (*Orbulina universa* and *Globigerina bulloides*) show strong negative relationships with seawater carbonate ion concentration ($[CO_3^{2-}]$) [*Russell et al.*, 2004]. The application of these relationships to *Globigerinoides sacculifer* U/Ca records in two cores from the Caribbean Sea and the eastern equatorial Atlantic [*Russell et al.*, 2004] suggests that surface-water $[CO_3^{2-}]$ was ~80–110 μmol/kg higher during the Last Glacial maximum (LGM) than during the Holocene, qualitatively consistent with reconstructions based on other proxies [*Barker and Elderfield*, 2002; *Foster*, 2008; *Henehan et al.*, 2013; *Sanyal and Bijma*, 1999]. However, U/Ca variations in *Globigerina bulloides*, *Neogloboquadrina pachyderma* (d), and *Globorotalia inflata* have been reinterpreted to reflect a temperature effect, based on U/Ca measurements of the North Atlantic core-top samples [*Yu et al.*, 2008a]. For both core-top and downcore samples [*Russell et al.*, 1996; *Yu*

et al., 2008a], U/Ca in planktonic foraminifera (*G. sacculifer, G. ruber, G. bulloides, N. pachyderma* (d), and *G. inflata*) show strong positive correlations with Mg/Ca, a proxy for calcification temperature [*Elderfield and Ganssen*, 2000; *Hastings et al.*, 1998; *Lea et al.*, 1999; *Nürnberg et al.*, 1996], corroborating a temperature effect on foraminiferal U/Ca. Furthermore, *Salmon et al.* [2016] found positive correlations between planktonic shell U/Ca and shell size, implicating biological controls on the U incorporation. More recent studies suggested that downcore planktonic U/Ca is affected by postdepositional authigenic coating, which has much higher U/Ca than lattice-bound U [*Boiteau et al.*, 2012].

In cultured shallow benthic foraminifera (*Ammonia spp.), Keul et al.* [2013] suggested seawater [CO_3^{2-}] to be the dominant parameter controlling U/Ca. Using core-top samples from the South Atlantic, *Raitzsch et al.* [2011b] showed that U/Ca in *Cibicidoides wuellerstorfi* and *Cibicidoides mundulus* are negatively correlated with carbonate saturation state ($\Delta[CO_3^{2-}] = [CO_3^{2-}] - [CO_3^{2-}]_{sat}$, where [$CO_3^{2-}]_{sat}$ represents saturated [CO_3^{2-}]). Compared to planktonic studies, less data are available for benthic foraminifera, and the U/Ca-$\Delta[CO_3^{2-}]$ calibration is currently restricted to the South Atlantic with no downcore reconstruction.

Since authigenic U and Mn in foraminiferal coatings are sensitive to sedimentary redox conditions [*Boiteau et al.*, 2012], *Gottschalk et al.* [2016] measured foraminiferal U/Mn from a South Atlantic core to infer changes in deep-water [O_2] during the last ∼70 ka. Their downcore U/Mn correlated with apparent ventilation ages (benthic-planktonic and benthic-atmospheric ^{14}C age offsets), and broadly synchronized with variations in deep-water oxygenation [*Gottschalk et al.*, 2016; *Jaccard et al.*, 2016]. However, given sparse downcore and core-top studies on U/Mn, its feasibility for sedimentary redox-condition reconstructions and potential controlling factors warrants further evaluation.

In this study, we measured core-top U/Ca and U/Mn in two benthic species (*C. wuellerstorfi* and *C. mundulus*) collected from globally distributed samples to assess their controlling factors. For these core-top data, we investigate possible influences from (i) different cleaning procedures and (ii) various hydrographic parameters including bottom water temperature, [O_2], [CO_3^{2-}] and $\Delta[CO_3^{2-}]$ [*Boiteau et al.*, 2012; *Raitzsch et al.*, 2011b; *Russell et al.*, 2004; *Yu et al.*, 2008a]. We then present new downcore U/Ca and U/Mn records from three Atlantic sediment cores, to test the feasibility of using these ratios for paleoreconstructions (deep ocean carbonate chemistry and redox conditions) by comparing with previous published records.

2. Samples and Methods

2.1. Foraminiferal Samples

Specimens of *C. wuellerstorfi* and *C. mundulus* were picked from 120 core-top samples from the Atlantic, Indian, and tropical Pacific Oceans (Figure 1 and supporting information Tables S1 and S2). All core tops were verified to be the Late Holocene (0–5 ka) in age using published benthic and planktonic foraminiferal δ^{18}O and radiocarbon dates [*Elderfield et al.*, 2006; *Yu and Elderfield*, 2007]. Downcore profiles of U/Ca and U/Mn were measured in *C. wuellerstorfi* from BOFS 8K (52.5°N, 22.1°W, 4045 m) and TNO57-21 (41.1°S, 7.8°E, 4981 m), and in *C. mundulus* from BOFS 17K (58.0°N, 16.5°W, 1150 m) (Figure 1 and supporting information Tables S3–S5). The chronologies for BOFS 8K and BOFS 17K are from *Barker et al.* [2004], and the age model of TNO57-21 is from *Barker and Diz* [2014] and *Yu et al.* [2014]. The average sedimentation rates at BOFS 8K, BOFS 17K, and TNO57-21 are ∼7.5, ∼4.5, and ∼15 cm/ka, respectively.

Sediment samples were disaggregated in deionized water and washed through 63 μm sieves. Approximately 10–15 tests were picked from the 250–500 μm size fraction for each sample. Foraminiferal shells were treated with two cleaning procedures to explore cleaning effects on U/Ca and U/Mn. The "Cd-cleaning" method is based on *Rosenthal et al.* [1997] modified from the procedure developed by *Boyle and Keigwin* [1985/1985]. This method aims to remove extraneous contaminants from clays, organic matter, and Mn-Fe oxide coatings by a sequence of cleaning steps, including deionized water/methanol rinses, oxidative organic removal, reductive cleaning of Mn-Fe oxide coatings, and weak acid leaching. By contrast, the "Mg-cleaning" method omits the reductive cleaning step, which induces biases for Mg/Ca measurements by preferential dissolution of Mg-rich carbonates [*Barker et al.*, 2003]. About ∼35% of core-tops were cleaned by the "Cd-cleaning" method, while the rest by the "Mg-cleaning" method. Downcore samples from BOFS 8K and BOFS 17K were cleaned by the "Cd-cleaning" method. Shells from core TNO57-21 were cleaned by the "Mg-cleaning" method to detect postdepositional diagenetic effects on benthic U/Ca and U/Mn [*Boiteau et al.*, 2012].
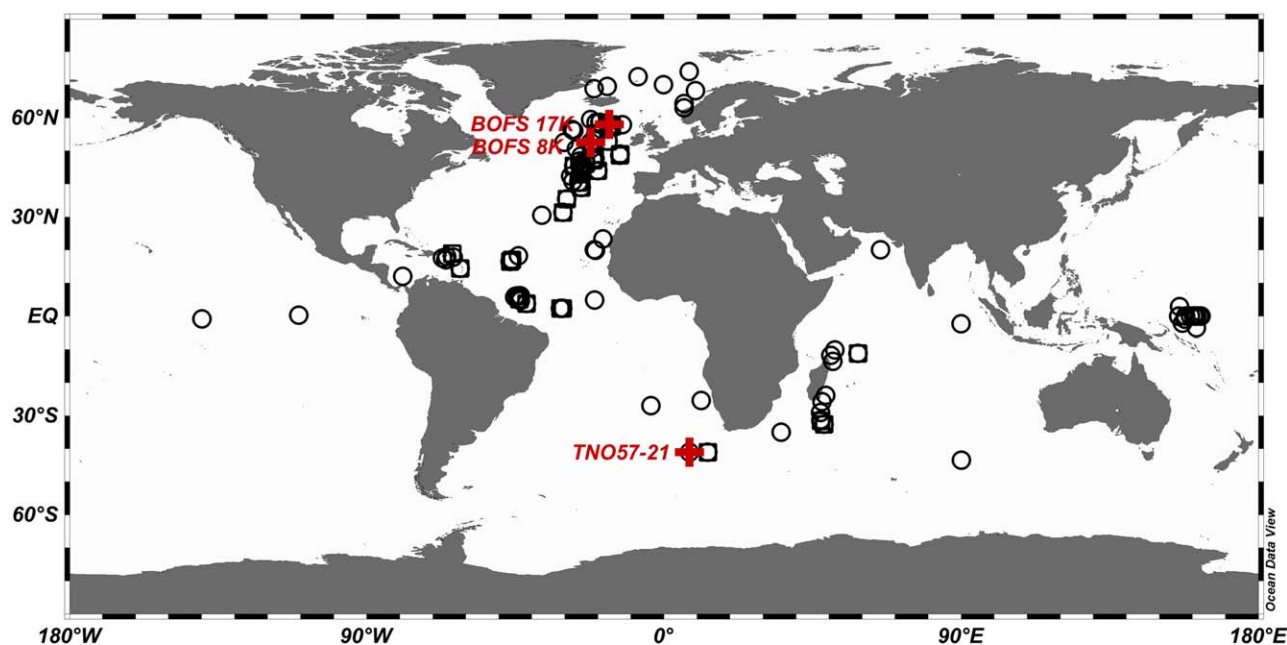
Figure 1. Locations of core-top (*C. wuellerstorfi*: black circles, *C. mundulus*: black squares) and downcore (red crosses) samples used in this study.

Shell U/Ca, Mn/Ca, and Al/Ca ratios were analyzed by inductively coupled plasma mass spectrometer (ICP-MS) according to the method by *Yu et al.* [2005]. The precisions for U/Ca, Mn/Ca, Al/Ca, and U/Mn are $< 2.5\%, < 1\%, < 3.5\%$, and $< 3.5\%$, respectively. Al/Ca are below ~ 5 μmol/mol, indicating minimal effects from clay minerals.

2.2. "Shell" (Lattice-Bound) Versus "Bulk" (Shell + Coating) Ratios

Foraminiferal shells buried in sediments are subjected to postdepositional diageneses, accumulating authigenic U-Mn-rich coatings [*Boiteau et al.*, 2012]. Moreover, concentrations of U and Mn in authigenic coatings are much higher than those in foraminiferal carbonates ("shell") [*Boiteau et al.*, 2012; *Boyle*, 1983]. Hence, it is necessary to evaluate whether our core-top and downcore samples are influenced by authigenic coatings.

Previous studies indicated that U/Ca of culturing and sediment trap samples ("shell") typically ranges from 3 to 23 nmol/mol [*Raitzsch et al.*, 2011b; *Russell et al.*, 2004], comparable with our core-top U/Ca (3–16 nmol/mol). Furthermore, with the exception of three samples, our core-top benthic Mn/Ca ratios are well below the accepted 100 μmol/mol threshold [*Boyle*, 1983] (supporting information Figure S1). Most core-top samples show Mn/Ca ratios of 0–50 μmol/mol, similar to those of sediment-trap foraminiferal carbonates. This indicates that our core-top U/Ca and Mn/Ca are negligibly affected by authigenic coatings, and hence can be regarded as "shell" (lattice-bound) ratios.

By contrast, U/Ca of downcore foraminiferal tests reach 300–700 nmol/mol [*Boiteau et al.*, 2012; *Gottschalk et al.*, 2016], much higher than "shell" U/Ca revealed by core-top samples. In addition, Mn/Ca of downcore samples are mostly > 100 μmol/mol, corroborating strong influences from authigenic coatings. The elevated U/Ca and Mn/Ca of our downcore samples indicate that these ratios reflect "bulk" (shell + coating) compositions.

2.3. Hydrographic Data for Core-Top Samples

We estimated total dissolved inorganic carbon (DIC), oxygen, alkalinity, salinity, temperature, and anthropogenic CO_2 for deep waters close to the core-tops using the Global Ocean Data Analysis Project (GLODAP) data set [*Key et al.*, 2004]. The anthropogenic CO_2 contribution was removed from DIC. We calculated preindustrial $[CO_3^{2-}]$, pH, and the saturation states (Ω) for calcite by CO2sys program [*Pelletier et al.*, 2005]. The carbonate saturation state was determined by $\Delta[CO_3^{2-}] = [CO_3^{2-}] - [CO_3^{2-}]_{sat}$ [*Jansen et al.*, 2002]. The choice

of dissociation constants is the same as previous studies [*Dickson*, 1990; *Mehrbach et al.*, 1973; *Yu and Elderfield*, 2007]. Benthic U/Ca and U/Mn ratios, along with the estimated hydrographic data, for core-top and downcore samples are given in supporting information Tables S1–S5.

3. Effects From Cleaning, Species, and Dissolution on Core-Top U/Ca and U/Mn

3.1. Cleaning Effects

We investigated influences of different cleaning methods on benthic U/Ca and U/Mn by comparing results from 21 *C. wuellerstorfi* and 8 *C. mundulus*, whose shells were separately subject to the "Cd-cleaning" and "Mg-cleaning" methods (Figures 2a and 2b). All samples, cleaned either with or without the reductive step, have Mn/Ca <100 μmol/mol (supporting information Figure S1). Consistent with previous studies [*Barker et al.*, 2003; *Yu et al.*, 2007a], both U/Ca ratios cleaned by the two methods are linearly correlated. Compared to samples subject to the "Mg-cleaning" method, U/Ca ratios are significantly decreased, by ~30%, when the reductive step was included (Figure 2a). In contrast, U/Mn ratios show comparable values between the two cleaning methods (Figure 2b).

Two possibilities have been proposed to explain the decline of benthic U/Ca by the "Cd-cleaning" method: (1) removal of contaminating phases like Fe-Mn oxides and manganese carbonate overgrowths [*Barker et al.*, 2003; *Yu et al.*, 2007a], and (2) preferential dissolution of U-Mn enriched carbonates [*Yu et al.*, 2007a]. To explore which explanation is more reasonable, we calculated the decline of U/Ca that could be caused by the removal of Fe-Mn oxide coatings (supporting information Tables S6 and S7). We assume that the U/Mn of Mn-rich contaminations attached to foraminiferal shells is the same as in discrete Fe-Mn nodules [*Yu et al.*, 2007a]. Our results reveal that only ~3% of the observed decline of U/Ca induced by the reductive step may be attributed to Mn-rich contaminations. Considering the low Mn/Ca ratios (mostly <100 μmol/mol; supporting information Figure S1) of our core-top samples due to the short time for postdepositional diagenesis, removal of Fe-Mn oxides does not appear to be the main reason for the observed U/Ca decline during the reductive step, unless contaminating phases associated with foraminiferal carbonate have much higher U/Mn (at least 30 times) than those of Fe-Mn nodules. *Barker et al.* [2003] argued that the reductive treatment causes partial dissolution of foraminiferal carbonate with high Mg. If high-Mg shell fragments are also enriched with U [*Yu et al.*, 2008a], partial dissolution during the reductive step should result in a decrease in U/Ca. *Yu et al.* [2007a] suggested that the reductive step preferentially dissolves U-Mn enriched carbonates. However, a previous study suggested that authigenic coatings on downcore shells are not completely eliminated by the Mg-cleaning [*Hasenfratz et al.*, 2017]. Given relatively low U/Ca and Mn/Ca in our core-tops, U/Ca cleaned by the "Mg-cleaning" method may not strongly reflect coating signal due to the short burial time in sediments. Therefore, we suggest that most (> 95%) of U/Ca decreases during the reductive step associated with core-top samples are probably driven by preferential dissolution of foraminiferal carbonates enriched in uranium, although further work is needed to pin down the chemical compositions of possible contaminating phases.

3.2. Interspecies Offsets and Dissolution Effects

Irrespective of cleaning methods used to clean our samples, *C. wuellerstorfi* shows higher U/Ca than *C. mundulus* with the exception of four samples (~20% of the samples), while U/Mn ratios display roughly similar values between the two species except for two samples (Figures 2c and 2d). In line with previous studies [*McCorkle et al.*, 1990; *Rae et al.*, 2011; *Raitzsch et al.*, 2011a; *Yu et al.*, 2013; *Zeebe et al.*, 2003], we attribute the U/Ca offsets between two species to influences of biological processes on the U incorporation into foraminiferal carbonates.

To investigate possible dissolution effects, we compared U/Ca and U/Mn in Rose Bengal stained ("recently" living shells, subject to minimal dissolution) and coexisting unstained shells presumably subject to some degree of dissolution on the seafloor (Figures 2e and 2f). Although cleaned by different methods, these paired samples show similar U/Ca and U/Mn values, and thus suggest little influences of dissolution on these ratios [*Yu and Elderfield*, 2007]. We note that our samples shown in Figures 2e and 2f are mainly from the North Atlantic where dissolution is expected to be weak due to saturated deep waters ($\Delta[CO_3^{2-}] = $ ~10–35 μmol/kg). Furthermore, little dissolution is also indicated by planktonic U/Ca [*Yu et al.*, 2008a]. Considering that benthic shells are more immune to dissolution relative to planktonics, we assume little dissolution effect on U/Ca and U/Mn of our samples here.
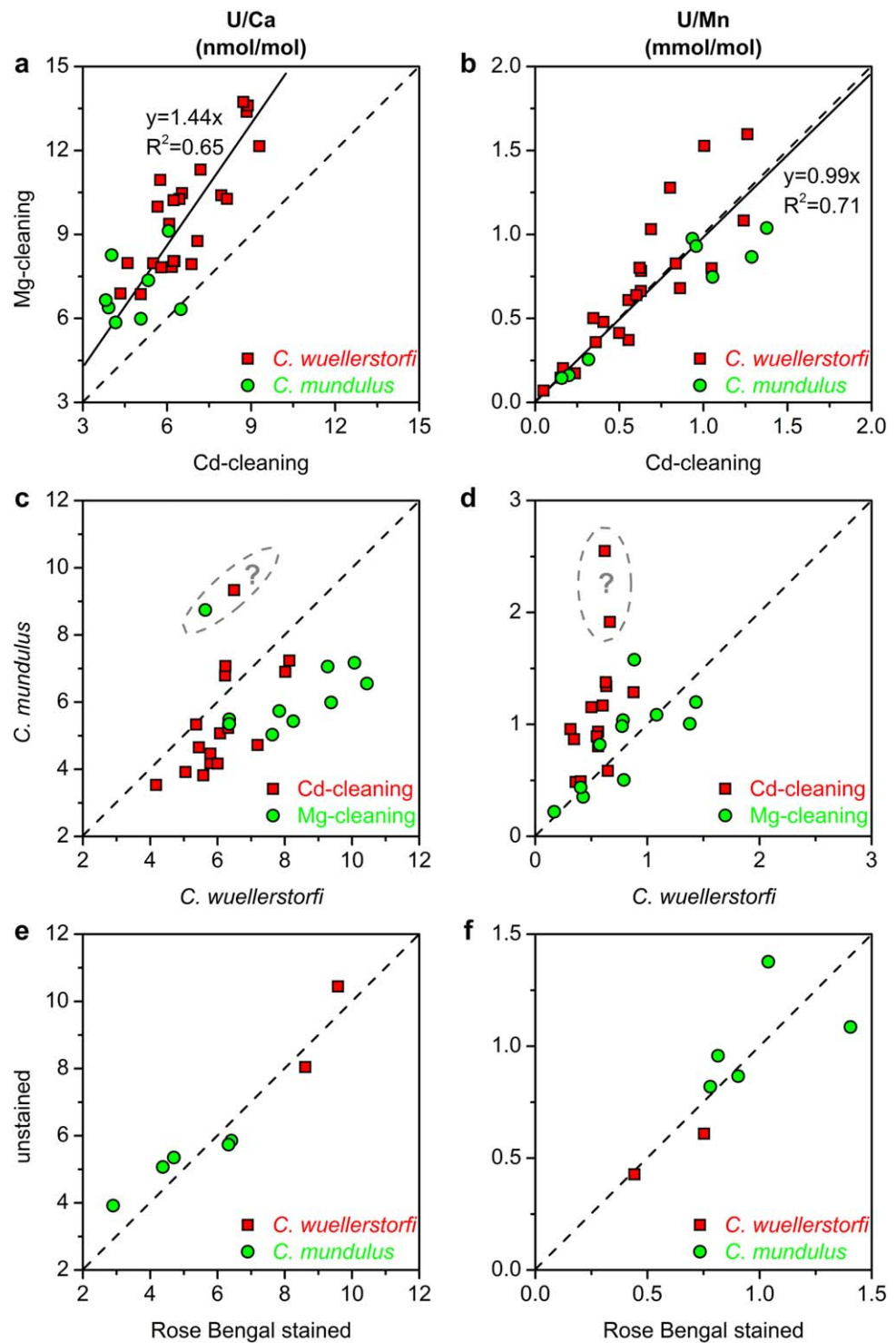
Figure 2. Effects from cleaning, species, and dissolution. (a and b) U/Ca and U/Mn cleaned by "Mg-cleaning" and "Cd-cleaning" methods; (c and d) U/Ca and U/Mn in coexisting *C. wuellerstorfi* and *C. mundulus*; (e and f) U/Ca and U/Mn in coexisting Rose Bengal stained and unstained shells. Dash lines: y = x; solid lines: linear best fits forced through the origin.

4. Controlling Factors on Benthic U/Ca

4.1. Core-Top U/Ca

Overall, core-top samples show U/Ca ranges of 3–16 and 3–10 nmol/mol in *C. wuellerstorfi* and *C. mundulus*, respectively. Our U/Ca fall within the ranges previously reported for benthic (4–23 nmol/mol) and

planktonic (3–15 nmol/mol) foraminifera [*Raitzsch et al.*, 2011b; *Russell et al.*, 1994, 1996, 2004; *Yu et al.*, 2008a]. Using a $U/Ca_{seawater} = 1390$ nmol/mol [*Ku et al.*, 1977], the empirical distribution coefficient D_U ($D_U = U/Ca_{calcite}/U/Ca_{seawater}$) varies from 0.002 to 0.011 for both species, comparable with D_U (0.002–0.016) from previous studies [*Raitzsch et al.*, 2011b; *Russell et al.*, 1994, 2004].

Due to their wide hydrographic distribution (Figure 1), our core-top samples provide an opportunity to assess influence factors on U/Ca in two benthic foraminiferal species. We first investigated a possible influence from seawater $[CO_3^{2-}]$. In seawater, uranium mainly exists as carbonate complexes including $UO_2(CO_3)$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$, whose relative abundances depend on seawater $[CO_3^{2-}]$ [*Djogić et al.*, 1986; *Russell et al.*, 2004]. If only $UO_2(CO_3)_2^{2-}$ is incorporated into foraminiferal carbonates [*Russell et al.*, 2004], a negative correlation between foraminiferal U/Ca and seawater $[CO_3^{2-}]$ may be expected, as shown by previous studies [*Raitzsch et al.*, 2011b; *Russell et al.*, 2004]. However, Figures 3a and 3b show no correlation between benthic U/Ca and deep-water $[CO_3^{2-}]$. In core-top specimens of *C. wuellerstorfi* and *C. mundulus* from the South Atlantic, *Raitzsch et al.* [2011b] showed a strong correlation between U/Ca and $\Delta[CO_3^{2-}]$, rather than $[CO_3^{2-}]$ itself. However, we do not observe this relationship for our core-top data, which span a greater range of $\Delta[CO_3^{2-}]$, irrespective of cleaning methods used to clean our shells (Figures 3c and 3d). Considering the much larger data set and wider range in $[CO_3^{2-}]$ and $\Delta[CO_3^{2-}]$ at our core-top sites, the lack of any correlation of benthic foraminiferal U/Ca with deep-water $[CO_3^{2-}]$ or $\Delta[CO_3^{2-}]$ leads us to suggest that
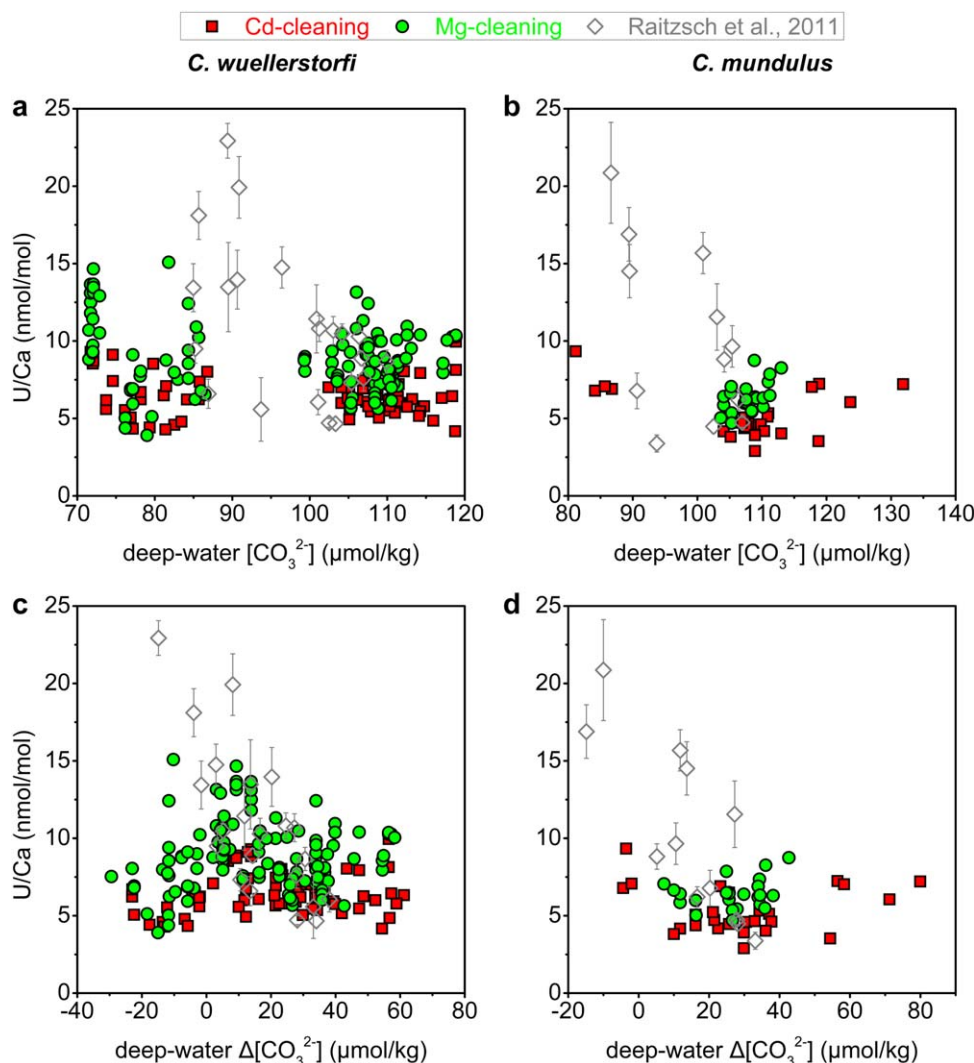

Figure 3. Core-top benthic U/Ca versus (a and b) deep-water $[CO_3^{2-}]$ and (c and d) $\Delta[CO_3^{2-}]$. South Atlantic data (gray diamonds) are from *Raitzsch et al.* [2011b].
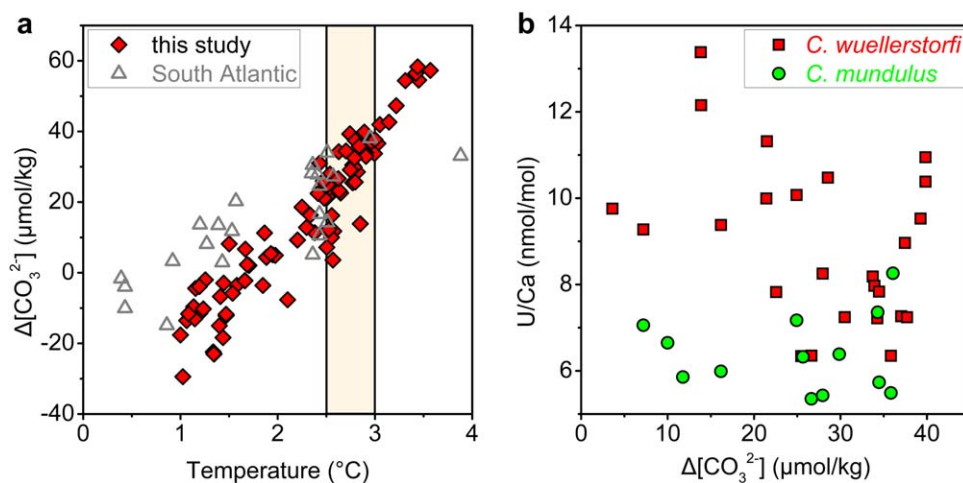
Figure 4. (a) Deep-water $\Delta[CO_3^{2-}]$ versus temperature for core-top locations. Shaded band highlights core-top sites with temperatures from 2.5 to 3°C (used for b). (b) Benthic U/Ca versus $\Delta[CO_3^{2-}]$ for core-tops from temperature of 2.5–3°C.

the U incorporation into *C. wuellerstorfi* and *C. mundulus* is not significantly affected by the deep-water carbonate chemistry (Figure 3 and supporting information Table S8).

There could be three possible explanations for the discrepancy between our and previous studies [*Raitzsch et al.*, 2011b]. First, the poor U/Ca-$\Delta[CO_3^{2-}]$ correlation in our study might be that effects from $\Delta[CO_3^{2-}]$ (a negative U/Ca-$\Delta[CO_3^{2-}]$ correlation [*Raitzsch et al.*, 2011b]) and temperature (a positive U/Ca-T correlation [*Yu et al.*, 2008a]) on U/Ca are canceled out. We investigated possible interactions between different controls over benthic U/Ca. The ambient deep-water temperatures at our core-top sites are positively correlated with $\Delta[CO_3^{2-}]$ (Figure 4a). To separate these two factors, we investigated benthic U/Ca for core-tops from a narrow temperature range of 2.5–3°C. Within the 0.5°C range, there is still no correlation between benthic U/Ca and $\Delta[CO_3^{2-}]$ (Figure 4b). Therefore, our core-top data suggest that it is not feasible to deduce deep-water carbonate chemistry even with constraints on temperature changes.

Second, U/Ca measurements of uncleaned foraminiferal shells by LA-ICP-MS in the previous study [*Raitzsch et al.*, 2011b] might not completely eliminate Mn-rich contaminations in the inner surface of shells [*Hasenfratz et al.*, 2017; *Pena et al.*, 2005], resulting in anomalously high U/Ca of samples under reducing conditions. Compared with high $[CO_3^{2-}]$ water masses, water masses with low $[CO_3^{2-}]$ are generally associated with relatively low O_2 content, high respiration of organic carbon, and hence more reducing conditions. Therefore, one possibility for the relatively high U/Ca ratios of core-top samples associated with low $[CO_3^{2-}]$ by [*Raitzsch et al.*, 2011b] could be attributed to authigenic accumulations of U in the inner layer of foraminiferal shells.

Third, the ranges of $[CO_3^{2-}]$ and $\Delta[CO_3^{2-}]$ covered by our core-tops are twice as large as the previous study [*Raitzsch et al.*, 2011b]. An exponential relationship between U/Ca and $[CO_3^{2-}]$ within a much larger $[CO_3^{2-}]$ range (30–430 μmol/kg) was found in culturing studies [*Russell et al.*, 2004]. Thus, it is likely that U/Ca-$\Delta[CO_3^{2-}]$ correlations in *Raitzsch et al.* [2011b] are not applicable to the larger $\Delta[CO_3^{2-}]$ range in our study.

We also explored potential influences of temperature and $[O_2]$ on benthic U/Ca. As shown in Figure 5 and supporting information Table S8, benthic U/Ca shows no significant correlations with either temperature or deep water $[O_2]$. It suggests that these two parameters impose little influences on benthic U/Ca.

4.2. Downcore U/Ca

To further evaluate the feasibility of benthic foraminiferal U/Ca as a proxy for deep-water carbonate chemistry reconstruction, we considered data from three cores with different carbonate chemistry histories (Figure 6). Core BOFS 17K (58.0°N, 16.5°W, 1150 m) today is predominantly influenced by the high-$[CO_3^{2-}]$ North Atlantic Deep Water (NADW). Benthic B/Ca data suggested that deep-water $[CO_3^{2-}]$ at this site was ~25 μmol/kg higher during the LGM than during the Holocene [*Yu et al.*, 2008b]. This is consistent with the formation of low-nutrient and high-δ^{13}C Glacial North Atlantic Intermediate Water (GNAIW) and more elevated surface-water $[CO_3^{2-}]$ at the source region during the LGM [*Marchitto and Broecker*, 2006; *Oppo and Lehman*,
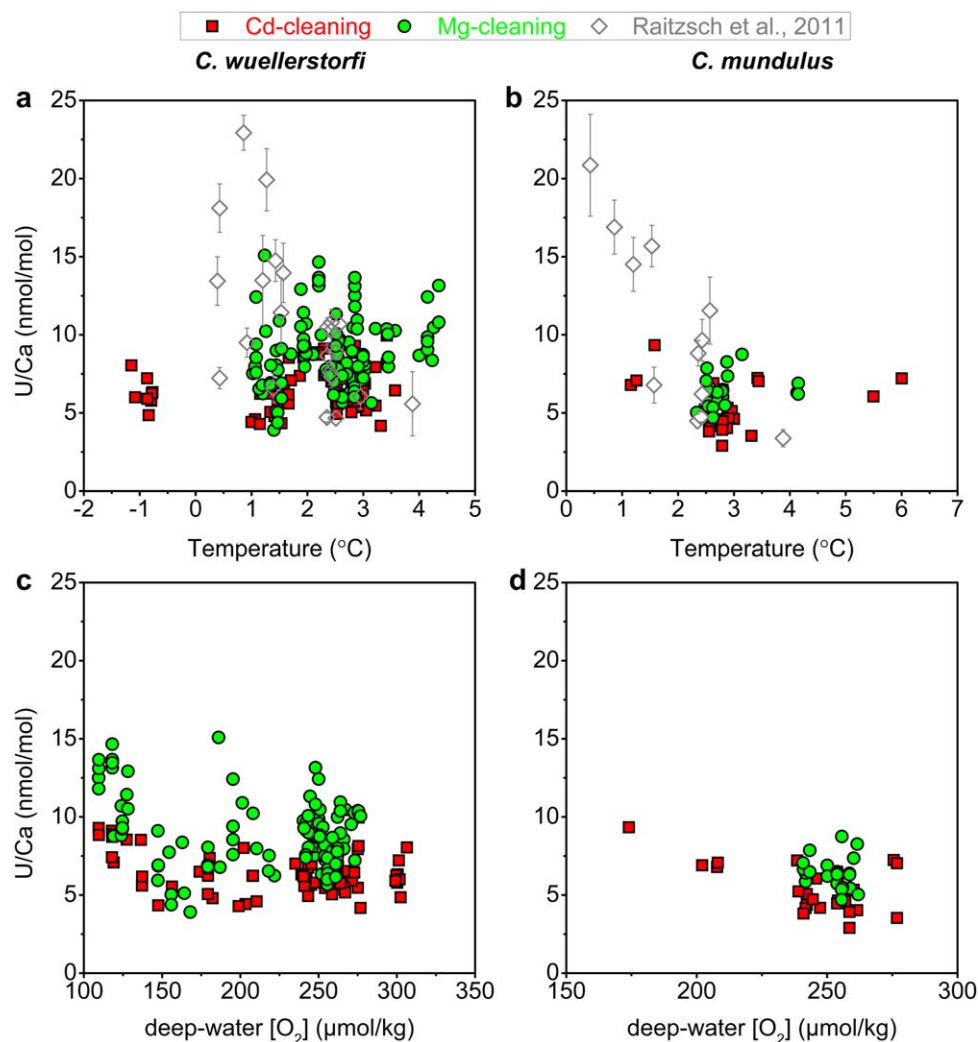
Figure 5. Core-top benthic U/Ca versus (a and b) temperature and (c and d) deep-water [O$_2$]. South Atlantic data (gray diamonds) are from *Raitzsch et al.* [2011b].

1993]. By contrast, deep water at BOFS 8K (52.5°N, 22.1°W, 4045 m) had lower [CO$_3^{2-}$] during the LGM than during the Holocene, due to enhanced northward penetration of low-[CO$_3^{2-}$] deep waters from the South Atlantic during the LGM as indicated by lower δ^{13}C and higher Cd/Ca in benthic foraminifera [*Curry and Oppo*, 2005; *Marchitto and Broecker*, 2006]. At site TNO57-21 (41.1°S, 7.8°E, 4981 m), both sediment CaCO$_3$ content and *C. wuellerstorfi* B/Ca suggested comparable deep-water [CO$_3^{2-}$] between the LGM and the Holocene with a deglacial [CO$_3^{2-}$] peak centered around 10 ka (Figure 6C).

We applied the core-top U/Ca-Δ[CO$_3^{2-}$] relationships from *Raitzsch et al.* [2011b] to convert benthic U/Ca from our cores into deep-water [CO$_3^{2-}$] (Figure 6), and compared these trends to those in published B/Ca and δ^{13}C records from the same cores. In BOFS 17K (Figure 6A), U/Ca-derived [CO$_3^{2-}$] decreased from the LGM to the Holocene, but it showed a smaller LGM-Holocene amplitude (~10 μmol/kg) and large offsets (~50 μmol/kg lower) from B/Ca-derived [CO$_3^{2-}$]. In addition, U/Ca-derived [CO$_3^{2-}$] displays a negative excursion centered around 6.5 ka, which is not found in benthic B/Ca and δ^{13}C. In BOFS 8K (Figure 6B), [CO$_3^{2-}$] calculated from U/Ca show comparable values (within ~5 μmol/kg) between the LGM and the Holocene, with minima at ~17 and ~27 ka, which are not revealed by B/Ca and δ^{13}C. Thus, glacial northward penetration of low-[CO$_3^{2-}$] southern-sourced deep waters is not reflected by benthic U/Ca in BOFS 8K. In the deep South Atlantic, benthic U/Ca in core TNO57-21 suggests a large [CO$_3^{2-}$] increase (~80 μmol/kg) from the LGM to the Holocene, in contrast to trends in benthic B/Ca and sediment CaCO$_3$ content [*Sachs and Anderson*, 2003;
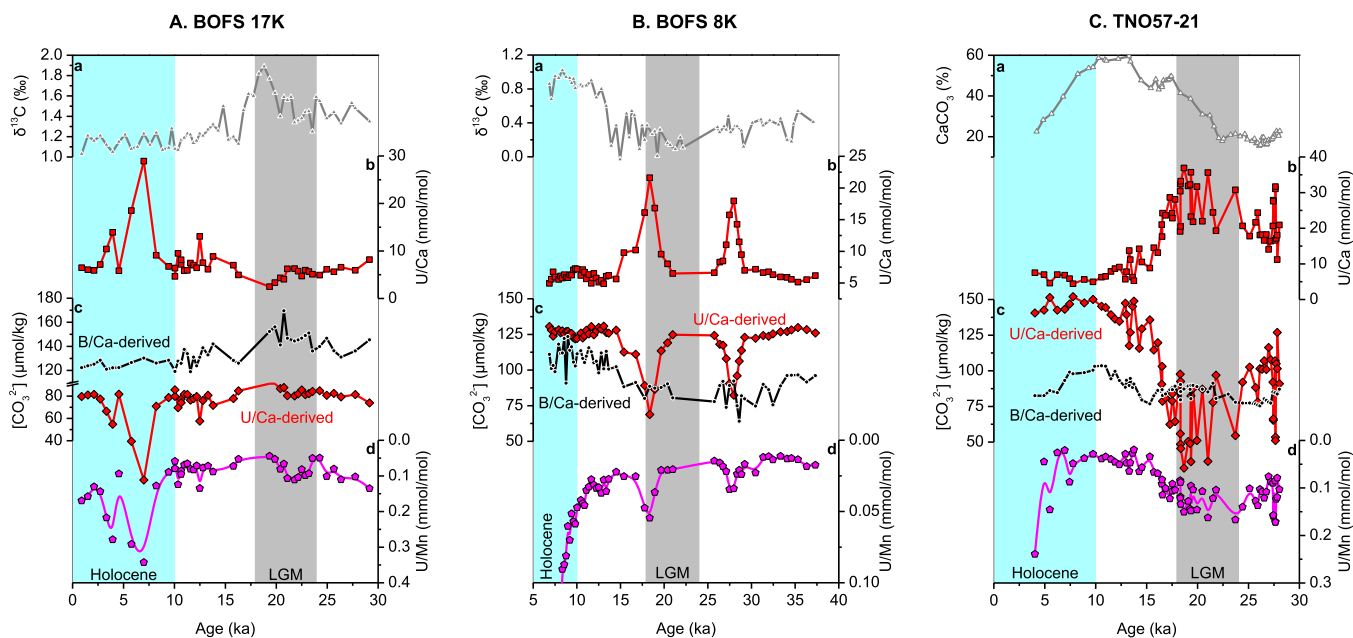
Figure 6. Downcore results. (A) BOFS 17K, (B) BOFS 8K, (C) TNO57-21. For BOFS17K, from top to bottom shows: (a) *Cibicidoides* genera δ^{13}C [*Bertram et al.*, 1995], (b, d) *C. mundulus* U/Ca, U/Mn with b-spline smoothing, (c) [CO_3^{2-}]; For BOFS 8K, from top to bottom shows: (a) *C. wuellerstorfi* δ^{13}C [*Barker et al.*, 2004], (b, d) *C. wuellerstorfi* U/Ca, U/Mn with b-spline smoothing, (c) [CO_3^{2-}]; for TNO57-21, from top to bottom shows: (a) sediment carbonate content [*Sachs and Anderson*, 2003], (b, d) *C. wuellerstorfi* U/Ca, U/Mn with b-spline smoothing, (c) [CO_3^{2-}]. Deep-water [CO_3^{2-}] are calculated by previous calibrations [*Raitzsch et al.*, 2011b; *Yu and Elderfield*, 2007].

Yu et al., 2014] (Figure 6C). Overall, deep-water [CO_3^{2-}] derived from U/Ca are inconsistent with values derived from benthic B/Ca and past ocean circulation changes based on other proxies [*Curry and Oppo*, 2005; *Marchitto and Broecker*, 2006; *Yu et al.*, 2008b,].

It is worth noting that cleaning methods used in our study cannot completely remove U-rich contaminations in downcore samples and bias actual foraminiferal carbonate U/Ca. Nevertheless, combined with core-top data, we conclude that U/Ca from *C. wuellerstorfi* and *C. mundulus* should not be used for deep-water carbonate chemistry reconstructions.

5. Core-Top U/Mn

Under some conditions, U and Mn may be removed from pore waters in the form of authigenic foraminiferal coatings during postdepositional diagenesis [*Lea et al.*, 2005; *Pedersen and Price*, 1982]. U removal from pore waters and accumulation as foraminiferal coatings occur below the oxygen penetration depths where organic matter is consumed by iron and sulfate reduction [*Cochran et al.*, 1986; *McManus et al.*, 2005], whereas Mn in foraminiferal coatings can be dissolved into pore waters under reductive sedimentary environment [*Boiteau et al.*, 2012]. In sediments and pore waters, oxidants are consumed in sequence of $O_2 >$ manganese oxides $>$ iron oxides $>$ sulfate [*Froelich et al.*, 1979]. To be specific, soluble U^{6+} is reduced to insoluble U^{4+} and is precipitated from pore waters where iron and sulfate reduction happened, while under reducing conditions, insoluble Mn^{4+} can be dissolved into pore waters as Mn^{2+}, which then reprecipitate as Mn-carbonates or Mn oxides under oxic conditions [*Tribovillard et al.*, 2006]. Accumulations of authigenic U and Mn are controlled by oxygen penetration depth in sediments, which is determined by overlying deep water [O_2] and organic carbon export to the sediment. Hence U and Mn in foraminiferal coatings may indicate overlying deep water [O_2] and organic carbon export, or the combination of these two factors. Recently, *Gottschalk et al.* [2016] argued that bulk (shell + coating) U/Mn of briefly cleaned foraminifera (subjected only to clay removal and silicate picking) can be used as a qualitative proxy of sedimentary redox conditions, which are affected by respiration of organic matter (biogenic matter flux from surface) within sediments and availability of the oxygen from the overlying deep waters [*Boiteau et al.*, 2012; *McManus et al.*, 2005].
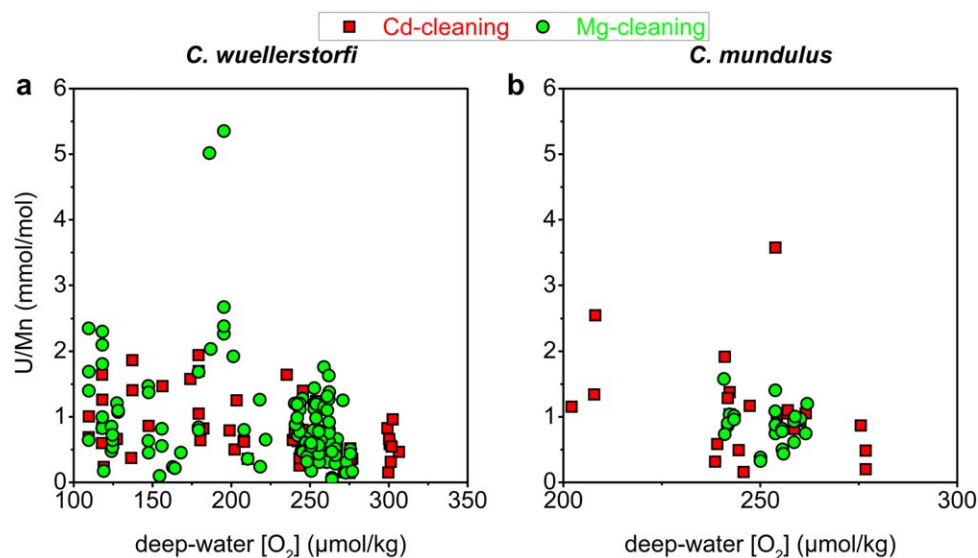
Figure 7. Core-top benthic U/Mn versus deep-water [O_2].

We first investigated possible influences of deep-water [O_2] on benthic U/Mn using our core-top samples. With the exception of three samples, core-top U/Mn ratios are < 3 mmol/mol, within the U/Mn range of the previously published downcore record [*Gottschalk et al.*, 2016]. Figure 7 shows no significant correlation of core-top U/Mn with deep-water [O_2]. The lack of U/Mn-[O_2] correlation may be due to: (1) "Mg-cleaning" or "Cd-cleaning" methods performed in our study have effectively removed U-Mn enriched authigenic coatings, and/or (2) core-top samples are barely subjected to postdepositional diagenetic processes relative to downcore samples [*Boyle*, 1983]. In addition, it is noteworthy that our core-top [O_2] ranges from 100 to 300 μmol/kg, which is much higher than the level of deep water [O_2] (∼25 μmol/kg) for U precipitation [*Zheng et al.*, 2002]. Hence it cannot fully cover the variability of oxygen required to test the influence on U/Mn (or U/Ca). Although core-top U/Mn (and U/Ca) cannot strongly reflect postdepositional diagenesis due to efficient cleaning procedures and/or the lack of early diagenetic processes, it is still worthwhile to see possible influencing factors on "lattice-bound" U/Mn using core-top samples. Our core-top U/Mn data suggest that shell U/Mn is not affected by any particular parameter (Figure 7). Nevertheless, previous studies suggest that downcore U/Mn variations driven mainly by authigenic coatings may be attributable to sedimentary redox changes.

6. U/Mn for Sedimentary Redox Conditions

Downcore samples experienced stronger postdepositional diagenetic processes and accumulated much more authigenic Mn-U-rich coatings, which are difficult to remove even by the reductive cleaning [*Boyle*, 1983; *Pena et al.*, 2005]. Therefore, downcore U/Mn and U/Ca for shells even after some cleaning can still reflect authigenic coating signals, which can be linked to sedimentary redox-conditions [*Boiteau et al.*, 2012; *Gottschalk et al.*, 2016].

Here, we explore the use of downcore U/Mn for sedimentary redox-condition reconstructions. Compared to the Holocene, glacial U/Mn in core BOFS 17K showed decreased values (Figure 6A), consistent with improved ventilation of the middepth North Atlantic by GNAIW during the LGM [*McManus et al.*, 2004; *Oppo and Lehman*, 1993]. In the early Holocene, an U/Mn peak is observed at ∼7 ka, but due to the limited measurements, we refrain ourselves from discussing its paleoceanographic implications. The peak might have been caused by some U-rich detritus sediments transported to the site at ∼7 ka. At site BOFS 8K (Figure 6B), the glacial water mass was possibly ventilated by southern-sourced waters [*Curry and Oppo*, 2005]. This would reduce ventilation and hence deep-water [O_2], which in turn should raise glacial U/Mn in this site [*Gottschalk et al.*, 2016]. The relatively low U/Mn during the early LGM (24–20 ka) in BOFS 8K therefore suggests reduced glacial respiration of organic matter, consistent with reduced organic carbon export caused by enhanced stratification in the polar glacial North Atlantic [*Radi and de Vernal*, 2008; *Wary et al.*,

2015]. During the late LGM (20–18 ka), increased U/Mn could arise from depleted deep water [O_2] caused by poorly ventilated southern-sourced waters. Changes in U/Mn during the LGM indicate alternative control of organic carbon export and deep water [O_2] on U/Mn. During Heinrich Stadial 1 (HS1, ~18–14.5 ka), Pa/Th suggests a reduced AMOC, which would have facilitated organic matter accumulation in the deep North Atlantic [*McManus et al.*, 2004]. The decreased U/Mn during HS1 in BOFS 8K may reflect the increased deep water [O_2] from the South Atlantic when the ventilation of the Southern Ocean was increased at that time [*Gottschalk et al.*, 2016; *Jaccard et al.*, 2016]. This demonstrates that U/Mn, along with other proxies, may be used to infer past deep water conditions that are useful for paleoceanography studies.

In core TNO57-21, benthic U/Mn showed elevated values during the LGM relative to the mid-Holocene. This is consistent with more reducing pore-water conditions, caused by increased surface export productivity in the Sub-antarctic Zone [*Sachs and Anderson*, 2005] and reduced ventilation of the deep South Atlantic during the LGM [*Gottschalk et al.*, 2016; *Jaccard et al.*, 2016]. A more reducing environment would facilitate the accumulation of U on authigenic foraminiferal coatings, resulting in the increase of benthic U/Mn. The increased U/Mn values in the late Holocene are possibly caused by low Mn/Ca of near core-top samples [*Boyle*, 1983] (Figures 6C and 8c).
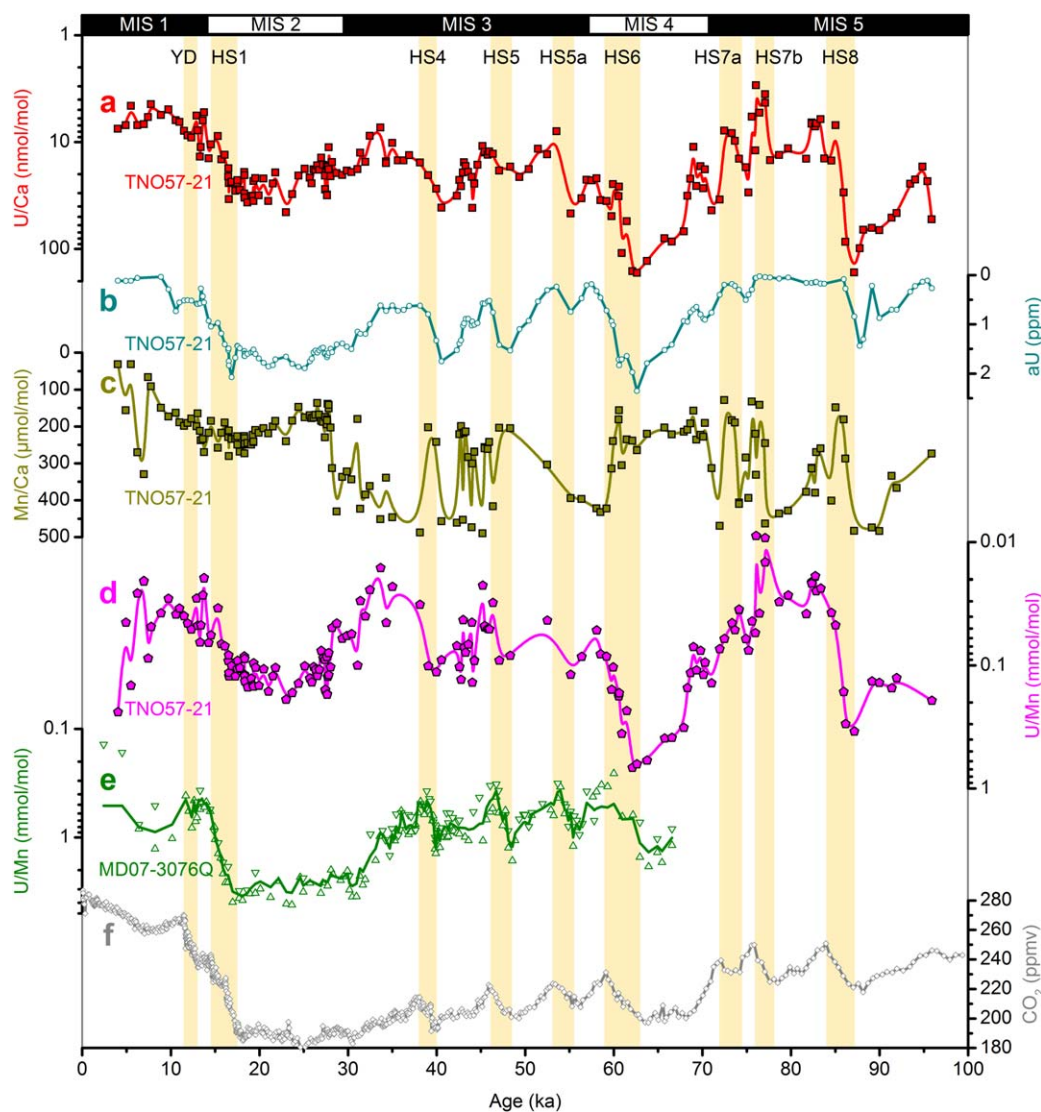

Figure 8. TNO57-21 records. *C. wuellerstorfi* (a) U/Ca, (c) Mn/Ca, and (d) U/Mn cleaned by the "Mg-cleaning" method with b-spline smoothing. (b) Authigenic uranium (aU) [*Sachs and Anderson*, 2003, 2005]. (e) U/Mn of *Uvigerina* spp. (triangles), *G. bulloides* (inverse triangles) and their mean (green line) from the core MD07-3076Q [*Gottschalk et al.*, 2016]. (f) Atmospheric CO_2 [*Ahn and Brook*, 2014; *Bereiter et al.*, 2015; *Marcott et al.*, 2014; *Monnin et al.*, 2001]. Yellow bars represent major Heinrich Stadials (HS) [*Rashid et al.*, 2003; *Rasmussen et al.*, 2003]. All records are shown on the AICC2012 age scale [*Veres et al.*, 2013].

Our high-resolution *C. wuellerstorfi* U/Mn record also reveals millennial-scale changes during the last ~100 ka. In TNO57-21 (Figures 8a–8d), U/Mn covaries with U/Ca and sedimentary aU, suggesting that all these records are strongly affected by diagenesis. Compared with U/Ca, Mn/Ca roughly shows opposite changes on glacial-interglacial timescales, displaying decreased values in glacial periods (MIS 2 and 4) and relatively high and more fluctuant values during interglacial periods (MIS 3 and 5). The comparison of U/Ca and Mn/Ca of TNO57-21 corroborates opposite diagenetic behaviors of U and Mn showed in previous studies [*Boiteau et al.*, 2012; *Gottschalk et al.*, 2016], suggesting that deep water masses in the Southern Ocean are characterized by depleted O_2 and enriched nutrient during glacial periods. Our U/Mn record from TNO57-21 shows a similar pattern to U/Mn from MD07-3076Q [*Gottschalk et al.*, 2016] (Figures 8d and 8e). During Heinrich Stadials, intensified vertical mixing and improved ventilation of the deep South Atlantic (increasing deep-water O_2 supply), accompanied by decreased organic carbon fluxes (decreasing respiration), would raise deep-water and sediment oxygenation conditions [*Anderson et al.*, 2009; *Gottschalk et al.*, 2016; *Stephens and Keeling*, 2000]. This would lower authigenic U accumulation on foraminiferal coatings, and hence benthic U/Mn (Figures 8b–8e). Compared with MD07-3076Q, consistently lower U/Mn in TNO57-21 may be attributed to more effective cleaning method ("Mg-cleaning"). Nevertheless, parallel patterns in two records suggest that the use of "Mg-cleaning" method has little influence on the temporal U/Mn variations. Similar variations in U/Mn, U/Ca and aU in TNO57-21 suggest that benthic U/Mn are sensitive to sedimentary redox conditions via postdepositional diagenetic processes, supporting the previous findings that benthic U/Mn can be used as an auxiliary indicator for past sedimentary redox changes [*Boiteau et al.*, 2012; *Gottschalk et al.*, 2016]. Compared to *Gottschalk et al.* [2016], our long record shows decreased U/Mn during HS 7 and 8, consistent with increased ventilation of the deep South Atlantic during Heinrich Stadials. Therefore, during the last 100 ka, TNO57-21 benthic U/Mn changed in tandem with atmospheric CO_2 on millennial timescales: U/Mn decreased when atmospheric CO_2 increased (Figures 8d–8f). Covariations of U/Mn in TNO57-21 and atmospheric CO_2 suggest that the deep South Atlantic plays an important role in the global carbon cycle during the last ~100 ka. Furthermore, U/Mn appears to show an obvious peak during MIS 4, which is larger than the LGM, suggesting that the ventilation of the deep South Atlantic was poorer during the MIS 4 than during the LGM.

7. Conclusions

Based on measurements of core-top samples from the global ocean, core-top (dominantly lattice-bound) U/Ca in *C. wuellerstorfi* and *C. mundulus* show no correlation with deep-water $[CO_3^{2-}]$, $\Delta[CO_3^{2-}]$, or other hydrographic variables. Application of the previous U/Ca-$\Delta[CO_3^{2-}]$ relationships to downcore benthic U/Ca results in inconsistent deep-water $[CO_3^{2-}]$ reconstructions inferred from other proxies and past ocean circulation changes. Our downcore benthic (representing lattice-bound and coating compositions) U/Mn records reveal enhanced stratification in the polar North Atlantic during the LGM. A comparison of benthic U/Mn and U/Ca with aU in TNO57-21 from the South Atlantic demonstrates a strong postdepositional diagenetic effect on changes in these ratios, suggesting that U/Mn and U/Ca variations likely indicate past sedimentary redox conditions. U/Mn in TNO57-21 shows systematic changes linked to atmospheric CO_2 variations on millennial timescales, indicating tight coupling of the deep South Atlantic redox-conditions to carbon cycle during the last ~100 ka. Furthermore, our U/Mn record at TNO57-21 indicates poorer ventilation of the deep South Atlantic during MIS 4 than during the LGM.

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