Mg/Ca in the benthic foraminifera *Cibicidoides wuellerstorfi* and *Cibicidoides mundulus*: Temperature versus carbonate ion saturation

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ABSTRACT

Magnesium/calcium (Mg/Ca) ratios in two widely used benthic foraminiferal species, *Cibicidoides wuellerstorfi* and *Cibicidoides mundulus* (*Cibicidoides kullenbergi*), picked from global ocean core-tops and from six cores in the North Atlantic Ocean have been measured to investigate Mg/Ca variability, cleaning effect, and influences from bottom water temperature (BWT) and deep water carbonate ion saturation ($\Delta[\text{CO}_3^{2-}]$). Replicate measurements of the two species reveal Mg/Ca variability of 0.07 ± 0.07 mmol/mol. Compared with Mg/Ca in samples cleaned by oxidative cleaning, Mg/Ca ratios are significantly lowered, by 0.10 ± 0.09 mmol/mol, in samples cleaned by reductive cleaning, likely due to preferential leaching during the reductive cleaning step. The cleaning influence is large relative to glacial–interglacial Mg/Ca changes (0.05 – 0.31 mmol/mol by this study). Regression of core-top data from a wide range of locations show that *C. wuellerstorfi* Mg/Ca is strongly affected by deep water $\Delta[\text{CO}_3^{2-}]$ with a sensitivity of ~ 0.009 mmol/mol per $\mu\text{mol/kg}$. When BWT is included in regressions, the correlation is slightly more significant with a weak BWT sensitivity on Mg/Ca of between 0.03 ± 0.01 and 0.07 ± 0.02 mmol/mol per $^\circ\text{C}$. Because $\Delta[\text{CO}_3^{2-}]$ and BWT co-vary for most core-top samples, an alternate method of separating the two effects was made by comparing glacial to interglacial changes in Mg/Ca from a depth transect of North Atlantic cores where the BWT and carbonate ion histories since the last glacial period have been well constrained. Results from this transect suggest that the BWT effect is <0.03 mmol/mol per $^\circ\text{C}$, weaker than inferred from the core-top study. Therefore, core-top and down core data suggest that *C. wuellerstorfi* Mg/Ca is insensitive to BWT changes. The weak BWT effect, when compared with natural variability, complicates the use of Mg/Ca in this species to reconstruct past BWT. Taking all measured samples from various environments into account, *C. mundulus* Mg/Ca ratios show no correlation with BWT or deep water $\Delta[\text{CO}_3^{2-}]$.

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1. Introduction

The use of foraminiferal magnesium/calcium (Mg/Ca) ratios to estimate calcification temperatures from marine archives is now common. The exponential relationship between planktonic foraminiferal Mg/Ca and temperature has been well demonstrated by foraminifera culturing, sediment trap, and core-top studies (e.g., Mashiotto et al., 1999; Elderfield and Ganssen, 2000; Lea et al., 2000; Anand et al., 2003; Russell et al., 2004; McConnell and Thunell, 2005; Skinner and Elderfield, 2005). By comparison, variation of benthic foraminiferal Mg/Ca with bottom water temperature (BWT), largely investigated using core-top samples, is relatively poorly constrained. Benthic foraminiferal Mg/Ca, in general, shows positive correlations with BWT over large temperature ranges (-1 to 19 $^\circ\text{C}$) (Rosenthal et al., 1997; Lear et al., 2002; Martin et al., 2002), except in the Norwegian

Sea where BWT is sub-zero but much elevated benthic Mg/Ca values are observed (Martin et al., 2002; Elderfield et al., 2006). These data from the Norwegian Sea together with observations of core-top Mg/Ca values higher than predicted from calibrations have led to suggestions that bottom water carbonate ion saturation ($\Delta[\text{CO}_3^{2-}]$) is an additional influence on benthic foraminiferal Mg/Ca (Elderfield et al., 2006; Rosenthal et al., 2006).

A $\Delta[\text{CO}_3^{2-}]$ effect on benthic foraminiferal Mg/Ca significantly complicates the use of benthic Mg/Ca for BWT reconstructions. In order to extract the BWT signature from benthic foraminiferal Mg/Ca, sensitivities on benthic Mg/Ca from BWT and $\Delta[\text{CO}_3^{2-}]$ should be well quantified. However, some complications may be associated with literature benthic Mg/Ca studies. Many published calibrations are regional, apart from a few studies (e.g., Lear et al., 2002; Martin et al., 2002; Elderfield et al., 2006). Because changes in benthic Mg/Ca with temperature are small at low temperatures, effects of different cleaning methods (e.g., Rosenthal et al., 2004; Yu et al., 2007) and perhaps from inter-laboratory offsets of analytical standards (e.g., Lear et al., 2002; Martin et al., 2002) need to be evaluated. Inter-

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species differences in Mg/Ca also complicate calibrations based on mixed benthic species (Elderfield et al., 2006; Rosenthal et al., 1997). Therefore, controlling factors on benthic Mg/Ca warrant further evaluation.

In this study, we have expanded the dataset from the previous work (Elderfield et al., 2006) and present global core-top Mg/Ca data in two widely used benthic foraminifera, *Cibicides wuellerstorfi* and *Cibicides mundulus*. Additionally, we show down core benthic Mg/Ca ratios back to the last 40 kyr for a suite of cores located at water depths of 1–4 km in the North Atlantic. Past deep water $\Delta[\text{CO}_3^{2-}]$ for these down cores have evolved distinctly and been quantitatively estimated using an independent proxy boron/calcium (B/Ca) (Yu et al., 2008), facilitating evaluation of $\Delta[\text{CO}_3^{2-}]$ effects on benthic Mg/Ca. We have assessed influences on Mg/Ca in these two species from Mg/Ca variability, different cleaning methods, and changes in BWT and $\Delta[\text{CO}_3^{2-}]$. Our core-top and down core data suggest a very weak temperature effect on Mg/Ca in *C. wuellerstorfi* and no temperature influence on Mg/Ca in *C. mundulus*, restricting the use of their Mg/Ca for past BWT reconstructions.

2. Samples, methods, and data sources

2.1. Samples

We have measured Mg/Ca ratios in two widely distributed benthic foraminiferal species, *C. wuellerstorfi* and *C. mundulus* (also called *C. kullenbergi*), in core-top sediments from the global oceans (Appendix, Table A1). Sediments were verified to be Holocene in age using published benthic and planktonic foraminiferal $\delta^{18}\text{O}$ and radiocarbon dates (for details, refer to Yu and Elderfield, 2007). Down core Mg/Ca ratios were measured in *C. mundulus* from BOFS 17K and in *C. wuellerstorfi* from BOFS 11K, NEAP 8K, BOFS 10K, BOFS 5K, and BOFS 8K (see Table 1 for locations). Chronologies are from Barker et al. (2004) and Manighetti et al. (1995). The six cores span a water depth range of 1–4 km in the North Atlantic Ocean and have experienced distinct carbonate ion histories since the last glacial period, well constrained from previous studies (Crowley, 1983; Marchitto et al., 2002; Barker et al., 2004; Yu et al., 2008). Therefore, these six cores provide excellent examples to investigate possible $\Delta[\text{CO}_3^{2-}]$ effects on benthic foraminiferal Mg/Ca.

2.2. Analytical methods

Because results have been presented in the literature based on different foraminiferal cleaning methods, we have made an assessment of what differences exist between their uses. We have applied three different cleaning methods to clean core-top and down core samples: “Mg-cleaning” (Barker et al., 2003), “Cd-cleaning” (Boyle and Keigwin, 1985/86), and “citrate-cleaning” methods (Yu et al., 2007). The three cleaning methods are detailed in Yu et al. (2007). In brief, “Mg-cleaning” cleaning (also termed as oxidative cleaning,

noted by “O” in Table A1) does not include a reductive cleaning step, while “Cd-cleaning” (also termed as reductive cleaning, noted by “R” in Table A1) does. The “citrate-cleaning” method represents a modified “Cd-cleaning” procedure in which the reducing reagent hydrous hydrazine (N_2H_4) was not added into the cleaning solution (i.e., only contains NH_3 and citrate).

Benthic foraminiferal shells were picked from the 250–500 μm size fraction. When sample sizes were sufficiently large, shells were used for different cleanings and replicate measurements. At some depths in cores BOFS 17K and BOFS 11K where benthic shells were abundant, the “citrate-cleaning” method was also used. For NEAP 8K, BOFS 5K, and BOFS 8K, only the “Cd-cleaning” method (Boyle and Keigwin, 1985/86) was used to clean shells due to limited availability of material. For most cases, shells for each sample were gently crushed and mixed to homogenize them as much as possible before splitting into sub-samples which were respectively subject to different cleaning methods. In general, the starting material for each cleaning is ~300–500 μg , equivalent to ~10–15 tests.

Mg/Ca, B/Ca, and other element/Ca ratios were analyzed by inductively coupled plasma mass spectrometer (ICP-MS) according to the method described in Yu et al. (2005). Mg/Ca shows no correlation with Mn/Ca or Al/Ca, indicating that Mg/Ca is insignificantly biased by contamination from diagenetic coatings or silicates. Based on replicate analyses of standards and samples over about 3 yr, the long-term relative precision for Mg/Ca measurements is about 1.24%, corresponding to an absolute error of 0.02 mmol/mol.

2.3. Hydrographic data

Following the method described in Yu and Elderfield (2007), parameters including BWT, salinity, and pre-industrial calcite $\Delta[\text{CO}_3^{2-}]$ for core-top samples were estimated from nearby Global Ocean Data Analysis Project (GLODAP) sites (Key et al., 2004). The equilibrium constants K_1 and K_2 for carbonic acid are those from Mehrbach et al. (1973) refit by Dickson and Millero (1987), and K_B for boric acid and K_{SO_4} for the bisulfate ion are from Dickson (1990). The effects of pressure on K_1 , K_2 , and K_{SO_4} are from Millero (1995) and those on K_B are from Millero (1979). The value of the apparent solubility products for calcite (K_{sp}) is from Mucci (1983), taking account of pressure effects according to the formulations of Ingle (1975). Calcite saturation concentration, $[\text{CO}_3^{2-}]_{\text{sat}}$, is calculated by $[\text{CO}_3^{2-}]_{\text{sat}} = [\text{CO}_3^{2-}]/\Omega$, where Ω is the solubility ratio of calcite. Carbonate saturation state is defined as $\Delta[\text{CO}_3^{2-}] = [\text{CO}_3^{2-}] - [\text{CO}_3^{2-}]_{\text{sat}}$. $\text{CO}_2\text{sys.xls}$ (Ver. 12) (Pelletier et al., 2005) was used for seawater CO_2 system calculations.

2.4. Data sources

All data are given in the Appendix, Tables A1 and A2. In total, 164 core-top Mg/Ca measurements were obtained for *C. wuellerstorfi* from the Norwegian Sea, Atlantic, Indian, and Pacific Oceans. Among 57 Mg/Ca measurements for core-top *C. mundulus*, most data are for

Table 1
Holocene and LGM average Mg/Ca (mmol/mol) and B/Ca ($\mu\text{mol/mol}$) ratios for the six cores from the North Atlantic Ocean^a

Core	Location (latitude, longitude, water depth)	Holocene (0–5 kyr)			LGM (18–21 kyr)			LGM–Holocene	
		Mg/Ca	B/Ca	n^b	Mg/Ca	B/Ca	n^b	Mg/Ca	B/Ca
BOFS 17K	58.0°N, 16.5°W, 1150 m	1.11±0.04	166±2	8	1.28±0.08	187±8	4	0.17±0.09	21±8
BOFS 11K	55.2°N, 20.4°W, 2004 m	1.24±0.06	229±9	5	1.34±0.07	250±5	2	0.10±0.09	21±10
NEAP 8K	59.8°N, 23.8°W, 2360 m	1.10±0.08	213±6	12	1.40±0.13	241±10	6	0.31±0.15	28±12
BOFS 10K	54.7°N, 20.7°W, 2777 m	1.18±0.05	210±5	13	1.12±0.06	215±4	6	−0.05±0.08	5±7
BOFS 5K	50.7°N, 21.9°W, 3547 m	1.28±0.06	207±5	10	1.11±0.07	187±7	3	−0.17±0.09	−20±9
BOFS 8K ^c	52.5°N, 22.1°W, 4045 m	1.06±0.07	200±9	5	0.97±0.08	178±4	5	−0.09±0.11	−22±10

^a Mg/Ca and B/Ca are measured in *C. mundulus* from BOFS 17K and in *C. wuellerstorfi* from the rest cores.

^b n stands for number of samples.

^c Holocene is for 6–8 kyr.

samples from the Atlantic Ocean and a few samples from Indian and Pacific Oceans. Approximately half of the core-top dataset presented here has been previously published (Elderfield et al., 2006). We have expanded the dataset by adding new measurements for samples along depth transects in the Caribbean Basin and at the Ceara Rise as well as replicate measurements for samples used in Elderfield et al. (2006) using different cleaning methods (Table A1). To avoid any possible inter-

laboratory Mg/Ca offsets caused by analytical standards (Lear et al., 2002; Martin et al., 2002), we have solely focused on the dataset obtained from our own laboratory. Mg/Ca ratios in *C. mundulus* from BOFS 17K cleaned by different cleaning methods are from Yu et al. (2007). Benthic B/Ca shown in Fig. 4 are from Yu et al. (2008). Down core Mg/Ca and B/Ca ratios were measured in the same solutions. Benthic $\delta^{18}\text{O}$ data are from Yu et al. (2008) and references therein.

Fig. 1. Benthic Mg/Ca variability and cleaning effects. (A) Standard deviation (SD) of Mg/Ca for replicate measurements; (B) Comparison of Mg/Ca by different cleaning methods; (C, D) Differences in Mg/Ca of *C. mundulus* (C) and *C. wuellerstorfi* (D) cleaned by oxidative and reductive cleaning methods; (E–G) Comparison of Mg/Ca ratios by three different cleaning methods in down core samples. Some negative values in (C, D) are possibly due to benthic foraminiferal Mg/Ca variability.

Fig. 2. Core-top *C. wuellerstorfi* Mg/Ca versus (A, B) BWT and (C, D) deep water $\Delta[CO_3^{2-}]$; Mg/Ca from which $\Delta[CO_3^{2-}]$ effect removed based on multi-linear regression (Table 2III) versus BWT (E, F). Samples cleaned by the "Mg-cleaning" method (Barker et al., 2003) (A, C, E) and by the "Cd-cleaning" method (Boyle and Keigwin, 1985/86) (B, D, F) are separated. Also shown in (A, B, E, F) are exponential curves $Mg/Ca = 0.9 * e^{0.11 * T}$ for *C. pachyderma* living in warm waters (Elderfield et al., 2006) and $\lambda Mg = 0.009 * e^{0.031 * T}$ for inorganically precipitated carbonates (Oomori et al., 1987). Both curves are extrapolated to low temperatures and changes in Mg/Ca and λMg are scaled (6-fold changes) over the temperature range of -1.5 to 6.5 °C. The juxtapositions of the two ordinates are arbitrary. Foraminiferal Mg/Ca ratios are about an order of magnitude lower than expected from inorganic precipitation (Mucci, 1987; Oomori et al., 1987). Deep water $\Delta[CO_3^{2-}]$ in (C, D) are estimated using the GLODAP dataset (Key et al., 2004). One *C. wuellerstorfi* Mg/Ca is not included due to its too high ratio, indicative of contamination (Table A1).

3. Mg/Ca variability and cleaning effect

Replicate measurements of Mg/Ca ratios in *C. wuellerstorfi* and *C. mundulus* picked from the same core-top sediments (subject to the same cleaning method), based on 2–4 Mg/Ca replicates and starting shell weights of ~400 µg, show a standard deviation (SD) range of 0–0.3 mmol/mol, with the average of 0.07 ± 0.07 mmol/mol (Fig. 1A). This is significantly larger than the analytical error of 0.02 mmol/mol, suggestive of heterogeneous distributions of Mg in and/or between benthic foraminiferal shells. Using smaller samples could result in larger Mg/Ca variability. Large Mg/Ca inter- and intra-individual variability has been previously documented for benthic shells from culturing and core-top sediments (Curry and Marchitto, 2008; Hintz et al., 2006a,b; Lear et al., 2002; Marchitto et al., 2007; Raitzsch et al., 2008; Rathmann et al., 2004; Rosenthal et al., 1997). For example, Marchitto et al. (2007) observed an average reproducibility of core-top sample splits of 0.097 mmol/mol for Mg/Ca in *Cibicides pachyderma* from the Florida Straits. Laser ablation measurements show that Mg/Ca in core-top *Oridorsalis umbonatus* from a depth transect off Namibia varies 0.07–3.72 mmol/mol within single shells and 0.35–1.12 mmol/mol (SD) among shells from the same sample (Rathmann et al., 2004). Such large Mg/Ca variability within and between shells cannot be caused by seasonality or bioturbation mixing, but possibly implies vital effects due to variations of the microenvironments of the shells (Bentov and Erez, 2006). A vital effect is also suggested by Mg/Ca offsets between different benthic foraminiferal species (Elderfield et al., 2006; Lear et al., 2002; Rosenthal et al., 1997). Mg/Ca variability may also be affected by shell size effect (Elderfield et al., 2002), but this has not been investigated for benthic foraminifera due to limited shell availability.

Consistent with previous studies principally on planktonic foraminifera (e.g., Barker et al., 2003; Elderfield et al., 2006; Rosenthal et al., 2004; Yu et al., 2007), Mg/Ca ratios in shells cleaned by “Cd-cleaning” (Boyle and Keigwin, 1985/86) are significantly lowered compared with those cleaned by “Mg-cleaning” (Barker et al., 2003) (Fig. 1B–G). The difference between values from these cleaning methods is up to 0.3 mmol/mol, showing an average difference of 0.10 ± 0.09 mmol/mol (Fig. 1C, D). Fig. 1E–G shows the Mg/Ca differences in the down core records. Yu et al. (2007) argued that the decrease in Mg/Ca is caused by citrate-induced preferential dissolution of Mg-enriched carbonates during the reductive cleaning step and this is further supported by lower Mg/Ca in benthic shells cleaned by the “citrate-cleaning” method (Fig. 1E, F). The degree of preferential dissolution and hence the magnitude of decreases in benthic Mg/Ca during the reductive cleaning step would be affected by cleaning time, solution/sample ratio, shell particle size, and citrate concentration. Because it is difficult to control these factors and the effect on Mg/Ca is significantly large compared with glacial–interglacial ratio changes (0.05–0.31 mmol/mol) (Table 1), we favor the “Mg-cleaning” method (Barker et al., 2003) for foraminiferal carbonate cleaning (Yu et al., 2007). Due to inter-species offsets and significant cleaning effects, we have considered Mg/Ca in *C. wuellerstorfi* and *C. mundulus* cleaned by “Mg-cleaning” and “Cd-cleaning” methods separately.

4. Mg/Ca in *C. wuellerstorfi*

4.1. BWT effect

Fig. 2A, B shows Mg/Ca in *C. wuellerstorfi*, cleaned using two different methods, from global oceans spanning a BWT range of ~–1–4.5 °C. At 0.5–4.0 °C, core-top *C. wuellerstorfi* Mg/Ca increases with BWT, displaying a much higher temperature sensitivity than observed for *C. pachyderma* living in warm conditions (Elderfield et al., 2006; Lear et al., 2002; Martin et al., 2002) and for inorganically precipitated

carbonates (Oomori et al., 1987). As previously documented (Elderfield et al., 2006; Martin et al., 2002), *C. wuellerstorfi* from very cold waters (~–1 °C) in the Norwegian Sea show much higher ratios than would be expected by extrapolation of the Mg/Ca–BWT trend observed at warm conditions. Sourced from intermediate depths (Boyle and Keigwin, 1987), deep waters within the Caribbean Basin have roughly invariant and warm temperatures compared with the typical decrease in BWT with water depth seen in the North Atlantic (Fig. 3A). Mg/Ca in *C. wuellerstorfi* from a depth transect in the Caribbean Basin decreases with increasing water depth (Fig. 3A) and *C. wuellerstorfi* from M35024–6 (4.7 km) plots below the Mg/Ca–BWT trend defined by samples from 0.5–4 °C in Fig. 2A. Considering global core-top data together, there is no single relationship between *C. wuellerstorfi* Mg/Ca and BWT (Fig. 2A, B). Therefore, our core-top data argue against BWT as the leading control on Mg/Ca in *C. wuellerstorfi*, in line with previous studies (Elderfield et al., 2006; Rosenthal et al., 2006).

Fig. 3. Comparison of core-top *C. wuellerstorfi* Mg/Ca with (A) BWT and (B) deep water $\Delta[\text{CO}_3^{2-}]$ from the Caribbean Basin. Mg/Ca data were obtained using the “Mg-cleaning” method (Table A1). Hydrographic data are from the GLODAP dataset (Key et al., 2004). Upper and lower abscissas are not scaled by any relationship.

The response of *C. wuellerstorfi* Mg/Ca to BWT changes can be evaluated using down core data. Benthic foraminiferal $\delta^{18}\text{O}$ (Fig. 4) and pore fluid studies (Adkins et al., 2002; Schrag et al., 2002) indicate

Fig. 4. Down core benthic Mg/Ca ratios for six cores located at 1 to 4 km water depth in the North Atlantic Ocean together with benthic $\delta^{18}\text{O}$ and B/Ca ratios. Benthic Mg/Ca and B/Ca ratios were measured in the same samples cleaned by the “Cd-cleaning” method. The shaded band indicates the Last Glacial Maximum (LGM). Data are reported in Table A2.

colder BWT during the last glacial maximum (LGM) in the North Atlantic. *C. wuellerstorfi* from the two deepest cores BOFS 5K (3.5 km) and BOFS 8K (4.0 km) show lower Mg/Ca ratios during the last glacial relative to the Holocene (Table 1; Fig. 4E, F), seemingly responding to BWT decreases. However, Mg/Ca in *C. wuellerstorfi* remains roughly unchanged in BOFS 10K (2.8 km) and displays higher glacial ratios in BOFS 11K (2.0 km) and NEAP 8K (2.4 km) (Fig. 4B–D), inconsistent with benthic $\delta^{18}\text{O}$ data and pore water BWT results (Adkins et al., 2002; Schrag et al., 2002). Therefore, our down core Mg/Ca data provide strong evidence that BWT is not the sole control on *C. wuellerstorfi* Mg/Ca. Converting *C. wuellerstorfi* Mg/Ca directly to BWT would result in erroneous temperature estimations.

4.2. $\Delta[\text{CO}_3^{2-}]$ effect

As recognized by recent studies (Elderfield et al., 2006; Rosenthal et al., 2006), one important complication associated with benthic Mg/Ca is a $\Delta[\text{CO}_3^{2-}]$ effect. To distinguish $\Delta[\text{CO}_3^{2-}]$ from temperature effects, it is necessary to use samples from regions and periods where changes in BWT and $\Delta[\text{CO}_3^{2-}]$ are decoupled. In modern oceans, BWT and $\Delta[\text{CO}_3^{2-}]$ largely change in unison except for a limited number of regions such as the Norwegian Sea and the Caribbean Basin. These two regions therefore provide important locations to distinguish BWT and $\Delta[\text{CO}_3^{2-}]$ effects on benthic foraminiferal Mg/Ca measured in core-top sediments. Being one of the major starting points of the ocean circulation conveyor belt, the Norwegian Sea has very low BWT and high bottom water $\Delta[\text{CO}_3^{2-}]$ (Key et al., 2004). Irrespective of sub-zero BWT, *C. wuellerstorfi* from this region show high Mg/Ca ratios (Fig. 2A, B), consistent with a $\Delta[\text{CO}_3^{2-}]$ effect as previously suggested by Elderfield et al. (2006). In the Caribbean Basin, core-top *C. wuellerstorfi* Mg/Ca decreases with water depth unlike temperature but as does $\Delta[\text{CO}_3^{2-}]$, arguing for a $\Delta[\text{CO}_3^{2-}]$ effect (Fig. 3). Using depth transects from the Atlantic and Pacific Oceans, Rosenthal et al. (2006) found that Mg/Ca in *Hoeglundina elegans* is significantly affected by bottom water $\Delta[\text{CO}_3^{2-}]$. When our global core-top data are considered, *C. wuellerstorfi* Mg/Ca and deep water $\Delta[\text{CO}_3^{2-}]$ show a strong positive correlation ($R^2 = 0.70\text{--}0.71$; $n = 65\text{--}68$) (Fig. 2C, D; Table 2I). The correlation is not caused by dissolution. Comparison of Mg/Ca ratios in unstained and Rose Bengal stained benthic shells show similar values (Table A1), suggesting negligible dissolution effects on benthic Mg/Ca (Elderfield et al., 2006; Lear et al., 2002). The positive Mg/Ca– $\Delta[\text{CO}_3^{2-}]$ correlations suggest that bottom water $\Delta[\text{CO}_3^{2-}]$ imposes significant influences on *C. wuellerstorfi* Mg/Ca, consistent with Elderfield et al. (2006). Our core-top data define the $\Delta[\text{CO}_3^{2-}]$ sensitivities on *C. wuellerstorfi* Mg/Ca of 0.0108 ± 0.0008 and 0.0093 ± 0.0008 mmol/mol per $\mu\text{mol/kg}$ for samples cleaned by “Mg-cleaning” and “Cd-cleaning” methods, respectively (Table 2I).

An effective approach to test a $\Delta[\text{CO}_3^{2-}]$ effect is to investigate past benthic Mg/Ca variations at different depths in the North Atlantic Ocean. Previous studies suggest that deep waters at different depths have experienced distinct changes in carbonate ion chemistry due to hydrographic reorganizations. In brief, waters below ~ 3.5 km had lower $\Delta[\text{CO}_3^{2-}]$ during the glacial period (Barker et al., 2004; Broecker and Clark, 2001; Crowley, 1983; Fehrenbacher et al., 2006; Marchitto et al., 2002; Yu et al., 2008). By contrast, waters shallower than ~ 2.4 km had elevated glacial $\Delta[\text{CO}_3^{2-}]$, possibly due to lower atmospheric CO_2 and lower nutrient during the last glacial period (Barker and Elderfield, 2002; Bertram et al., 1995; Curry and Oppo, 2005; Petit et al., 1999; Yu et al., 2008). Variations of $\Delta[\text{CO}_3^{2-}]$ in the studied cores have been quantified using *C. wuellerstorfi* B/Ca measured in the same samples used for Mg/Ca (Yu et al., 2008). *Cibicides wuellerstorfi* Mg/Ca and B/Ca are remarkably correlated during the past 40 kyr in all five cores from the 2–4 km water depth (Fig. 4B–F). It is noted that benthic Mg/Ca data from shallow cores are particularly important to distinguish BWT and $\Delta[\text{CO}_3^{2-}]$ effects because their past BWT and $\Delta[\text{CO}_3^{2-}]$ changed in a decoupled manner since the last glacial (Fig. 4B–D). Only with data for cores from abyssal depths

Table 2

Regression analyses of Mg/Ca in core-top *C. wuellerstorfi* from the BWT range of ~ -1 – 4.5 °C and bottom water $\Delta[\text{CO}_3^{2-}]$ range of ~ 30 – 70 $\mu\text{mol kg}^{-1}$

Cleaning methods	b_0^a	b_1^a	b_2^a	N^b	R^2
I. Mg/Ca = $b_0 + b_1 \cdot \Delta[\text{CO}_3^{2-}]$					
Oxidative	0.99 ± 0.02	0.0108 ± 0.0008	–	68	0.71
Reductive	0.91 ± 0.02	0.0093 ± 0.0008	–	65	0.70
II. Mg/Ca = $b_0 + b_1 \cdot \Delta[\text{CO}_3^{2-}]$ (samples from $\Delta[\text{CO}_3^{2-}] \leq 25$ $\mu\text{mol kg}^{-1}$)					
Oxidative	1.00 ± 0.02	0.0167 ± 0.0013	–	41	0.80
Reductive	0.90 ± 0.01	0.0161 ± 0.0008	–	36	0.91
III. Mg/Ca = $b_0 + b_1 \cdot \Delta[\text{CO}_3^{2-}] + b_2 \cdot \text{BWT}$					
Oxidative	0.86 ± 0.04	0.0090 ± 0.0009	0.073 ± 0.02	68	0.76
Reductive	0.85 ± 0.03	0.0092 ± 0.0007	0.033 ± 0.01	65	0.72
Reductive ^c	0.82	0.0087	0.056		

^a Units for b_0 , b_1 , and b_2 are mmol/mol, mmol/mol per $\mu\text{mol/kg}$, and mmol/mol per °C, respectively.

^b Number of samples for regression analyses.

^c From Elderfield et al. (2006).

could variations in benthic Mg/Ca be equally attributed to BWT changes (Fig. 4E, F). Using $\Delta[\text{CO}_3^{2-}]$ calculated from *C. wuellerstorfi* B/Ca, down core samples plot along the trends defined by core-top samples on the Mg/Ca– $\Delta[\text{CO}_3^{2-}]$ diagrams (Fig. 5). Therefore, our down core data reinforce a strong $\Delta[\text{CO}_3^{2-}]$ influence, showing similar sensitivities on *C. wuellerstorfi* Mg/Ca suggested by core-top samples (Fig. 5; Table 2I). In a previous study (Martin et al., 2002), core M16772 (1°21'S, 11°58'W, 3912 m) from the eastern tropical Atlantic shows that *C. wuellerstorfi* Mg/Ca was lower at the LGM than the Holocene by ~ 0.4 mmol/mol and was attributed to lower LGM temperature. Using a $\Delta[\text{CO}_3^{2-}]$ sensitivity of 0.009 mmol/mol per $\mu\text{mol/kg}$, this change in Mg/Ca corresponds to a decrease in $\Delta[\text{CO}_3^{2-}]$ by ~ 44 $\mu\text{mol/kg}$, consistent with previous estimates and ocean circulation reorganization in the Atlantic Ocean (Broecker and Clark, 2001; Curry and Oppo, 2005; Fehrenbacher et al., 2006).

Core-top data show that there might exist a $\Delta[\text{CO}_3^{2-}]$ threshold for changes in *C. wuellerstorfi* Mg/Ca (Fig. 2C, D; Table 2II). When $\Delta[\text{CO}_3^{2-}]$ is < 25 $\mu\text{mol/kg}$, *C. wuellerstorfi* Mg/Ca seems to be more sensitive to $\Delta[\text{CO}_3^{2-}]$ changes (Fig. 2C, D). A threshold of $\Delta[\text{CO}_3^{2-}]$ at 25 $\mu\text{mol/kg}$ was documented for the partition coefficient of Zn into *C. wuellerstorfi* (Marchitto et al., 2000). Rosenthal et al. (2006) found that the carbonate ion effect on Mg/Ca in *H. elegans* (aragonitic) is only limited to $\Delta[\text{CO}_3^{2-}]$ (aragonite saturation) below 15 $\mu\text{mol/kg}$. However, a stronger sensitivity is not supported by Mg/Ca data from cores BOFS 5K and BOFS 8K (Fig. 5C). The sensitivity change observed for core-top samples may be an artefact caused by sample limitation and Mg variability (Section 3). With more core-top data added to the calibration, the sensitivity threshold may disappear. Further studies are required to investigate sensitivity changes as well as other possible controlling factors by measuring Mg/Ca in samples from broad environments.

4.3. Sensitivity test

To extract BWT signatures from benthic Mg/Ca, relative sensitivities of $\Delta[\text{CO}_3^{2-}]$ and BWT on *C. wuellerstorfi* Mg/Ca must be precisely quantified. For our core-top samples, Table 2III shows that the correlation becomes slightly more significant, with R^2 values increasing from 0.70–0.71 to 0.72–0.76, when the BWT component is included in multi-linear regressions. The sensitivity of $\Delta[\text{CO}_3^{2-}]$ remains roughly at 0.009 mmol/mol per $\mu\text{mol/kg}$ (Table 2I, III), irrespective of the cleaning procedure employed and whether or not BWT is included in the sensitivity equation. Our obtained sensitivity of $\Delta[\text{CO}_3^{2-}]$ on *C. wuellerstorfi* Mg/Ca is similar to those (0.0083–0.010) from previous works (Elderfield et al., 2006; Healey et al., 2008; Raitzsch et al., 2008). By contrast, the temperature sensitivity ranges from ~ 0.03 to 0.07 mmol/mol per °C, depending on different cleaning methods used for Mg/Ca measurements (Table 2III). After removing the $\Delta[\text{CO}_3^{2-}]$ component using $\Delta[\text{CO}_3^{2-}]$

sensitivities from multi-linear regression analyses, core-top *C. wuellerstorfi* Mg/Ca show a very weak dependence on BWT (oxidative cleaning: $\text{Mg/Ca}_{\Delta[\text{CO}_3^{2-}] \text{ removed}} = 0.86 \pm 0.04 + (0.073 \pm 0.017) \cdot \text{BWT}$, $R^2 = 0.23$, $n = 68$;

Fig. 5. Comparison of core-top and down core *C. wuellerstorfi* Mg/Ca versus deep water $\Delta[\text{CO}_3^{2-}]$. Deep water $\Delta[\text{CO}_3^{2-}]$ for core-top samples and down core samples are estimated using the GLODAP dataset (Key et al., 2004) and *C. wuellerstorfi* B/Ca (upper abscissas) (Yu and Elderfield, 2007), respectively. The lower and upper abscissas are linearly linked by $\text{B/Ca} (\mu\text{mol/mol}) = 1.14 \cdot \Delta[\text{CO}_3^{2-}] (\mu\text{mol/kg}) + 177.1$ (Yu and Elderfield, 2007). Ratios obtained using “Mg-cleaning” (A) and “Cd-cleaning” (B, C) methods are separately plotted. For clarity, sites from water depth shallower than 2.8 km and deeper cores are plotted in (B) and (C), respectively. Data are reported in Table A2.

Fig. 6. Sensitivity test of (A) $\Delta[\text{CO}_3^{2-}]$ and (B) BWT effects on *C. wuellerstorfi* Mg/Ca. The observed LGM–Holocene changes are indicated by circles with error bars indicating one standard deviation. In (A), changes in *C. wuellerstorfi* Mg/Ca caused by $\Delta[\text{CO}_3^{2-}]$ variations at different depths are calculated by: $\Delta\text{Mg/Ca}_{\Delta[\text{CO}_3^{2-}]} = b_1 * (\Delta\text{B/Ca}) / 1.14$, where b_1 (mmol/mol per $\mu\text{mol/kg}$) and 1.14 ($\mu\text{mol/mol}$ per $\mu\text{mol/kg}$) are sensitivities of $\Delta[\text{CO}_3^{2-}]$ on *C. wuellerstorfi* Mg/Ca and B/Ca, respectively. In (B), changes in *C. wuellerstorfi* Mg/Ca are calculated assuming a LGM–Holocene BWT change of 3 °C at various of BWT sensitivities, b_2 (mmol/mol per °C), on Mg/Ca. Refer to Table 1 for LGM–Holocene Mg/Ca and B/Ca changes. See text for details.

reductive cleaning: $\text{Mg/Ca}_{\Delta[\text{CO}_3^{2-}]_{\text{removed}}} = 0.85 \pm 0.03 + (0.033 \pm 0.014) * \text{BWT}$, $R^2 = 0.09$, $n = 65$), insignificantly different from inorganic precipitation experiment estimates (Fig. 2E, F) (Katz, 1973; Mucci, 1987; Oomori et al., 1987).

Because $\Delta[\text{CO}_3^{2-}]$ and BWT for most core-top samples co-vary, we have tested their sensitivities and the feasibility of extracting BWT signatures from *C. wuellerstorfi* Mg/Ca using Holocene and LGM data for the five cores from the North Atlantic (Fig. 6; Table 1). Two approaches were carried out to test relative sensitivities of BWT and $\Delta[\text{CO}_3^{2-}]$ on *C. wuellerstorfi* Mg/Ca, assuming that these are the only controls on Mg/Ca. In the first approach, we take the advantage of LGM–Holocene $\Delta[\text{CO}_3^{2-}]$ changes estimated from *C. wuellerstorfi* B/Ca (Table 1) (Yu et al., 2008). We predict the LGM–Holocene changes in Mg/Ca ($\Delta\text{Mg/Ca}_{\Delta[\text{CO}_3^{2-}]}$) that would arise from such changes in $\Delta[\text{CO}_3^{2-}]$ given a range in sensitivities of $\Delta[\text{CO}_3^{2-}]$ on *C. wuellerstorfi* Mg/Ca and assuming no BWT influence. Thus, the influence of BWT on Mg/Ca can be estimated by

comparing the calculated $\Delta\text{Mg/Ca}_{\Delta[\text{CO}_3^{2-}]}$ with the observed LGM–Holocene Mg/Ca changes ($\Delta\text{Mg/Ca}_{\text{LGM-HOLOCENE}}$). The observed $\Delta\text{Mg/Ca}_{\text{LGM-HOLOCENE}}$ are consistent, within error, with a dominant $\Delta[\text{CO}_3^{2-}]$ effect on Mg/Ca at a sensitivity of ~ 0.009 mmol/mol per $\mu\text{mol/kg}$ (Fig. 6A), similar to that obtained from core-top data (Table 2I, III). Fig. 7 shows that the calculated Mg/Ca are indistinguishable from the measured ratios at this sensitivity, considering the natural Mg/Ca variability (Section 3). Were significant portions of the observed $\Delta\text{Mg/Ca}_{\text{LGM-HOLOCENE}}$ to be attributed to LGM–

Fig. 7. Comparison of measured Mg/Ca in *C. wuellerstorfi* with those predicted using changes in $\Delta[\text{CO}_3^{2-}]$. The Mg/Ca variations caused by $\Delta[\text{CO}_3^{2-}]$ changes are calculated by: $\text{Mg/Ca}_{\text{predicted}} = \text{Mg/Ca}_{\text{HOL}} + (\text{B/Ca} - \text{B/Ca}_{\text{HOL}}) / 1.14 * 0.009$, where 1.14 ($\mu\text{mol/mol}$ per $\mu\text{mol/kg}$) is the sensitivity of $\Delta[\text{CO}_3^{2-}]$ on *C. wuellerstorfi* B/Ca (Yu and Elderfield, 2007) and 0.009 (mmol/mol per $\mu\text{mol/kg}$) is the sensitivity of $\Delta[\text{CO}_3^{2-}]$ on *C. wuellerstorfi* Mg/Ca (Table 2), respectively. The average $\text{Mg/Ca}_{\text{HOL}}$ and B/Ca_{HOL} ratios are given in Table 1. Also shown are differences between predicted and measured ratios. n: total number samples for each core.

Holocene BWT changes (which decrease Mg/Ca at all water depths), it would require the $\Delta[\text{CO}_3^{2-}]$ effect on *C. wuellerstorfi* Mg/Ca to be nonlinear and show a stronger sensitivity at high $\Delta[\text{CO}_3^{2-}]$ than at low concentrations (Fig. 6A). This is not supported by core-top data (Fig. 2C, D). Therefore, down core Mg/Ca and B/Ca data indicate that *C. wuellerstorfi* Mg/Ca is only weakly affected by BWT and significantly influenced by deep water $\Delta[\text{CO}_3^{2-}]$. This can be well demonstrated by roughly unchanged *C. wuellerstorfi* Mg/Ca in BOFS 10K (2.8 km) (Fig. 4D). LGM bottom waters at the depth of this site had lower temperatures but similar $\Delta[\text{CO}_3^{2-}]$ than Holocene values, suggestive of a dominant $\Delta[\text{CO}_3^{2-}]$ effect on *C. wuellerstorfi* Mg/Ca.

In the second approach, decreases in *C. wuellerstorfi* Mg/Ca were calculated at a range of temperature sensitivities on Mg/Ca (Table 2III) and assuming no $\Delta[\text{CO}_3^{2-}]$ influence (Fig. 6B). A 3 °C change in BWT between Holocene and LGM was assumed at all water depths. Pore fluid studies show that LGM–Holocene BWT changes are 4.0–4.4 °C at ODP 981 (55.5°N, 14.7°W, 2184 m) located at Feni Drift and ODP 1063 (33.7°N, 57.6°W, 4584 m) on Bermuda Rise (Adkins et al., 2002; Schrag et al., 2002). A 3 °C change in BWT may be a conservative estimate. Because glacial bottom water $\Delta[\text{CO}_3^{2-}]$ was lower than today in abyssal North Atlantic (Crowley, 1983; Broecker and Clark, 2001; Marchitto et al., 2002; Barker et al., 2004; Fehrenbacher et al., 2006; Yu et al., 2008), the observed $\Delta\text{Mg/Ca}_{\text{LGM-HOLOCENE}}$ (−0.09 to −0.17 mmol/mol) at BOFS 5K and BOFS 8K constrain the BWT sensitivity to be weaker

than 0.03 mmol/mol per °C (Table 1; Fig. 6B). Although a BWT effect cannot be entirely excluded, both sensitivity exercises suggest that *C. wuellerstorfi* Mg/Ca is affected only weakly by BWT and significantly by bottom water $\Delta[\text{CO}_3^{2-}]$, preventing successful extraction of temperature signatures from *C. wuellerstorfi* Mg/Ca.

5. Mg/Ca in *C. mundulus*

Considering the entire core-top and down core dataset obtained in this study, *C. mundulus* Mg/Ca shows no correlation with BWT or bottom water $\Delta[\text{CO}_3^{2-}]$ (Fig. 8), in contrast with early studies (Elderfield et al., 2006; Healey et al., 2008). The higher glacial *C. mundulus* Mg/Ca in BOFS 17K than Holocene provide strong evidence arguing against BWT as the sole control on *C. mundulus* Mg/Ca (Figs. 1E and 4A). If only samples (except for one data from T90 15B; see Table A1.2) from <~50 $\mu\text{mol/kg}$ are considered, core-top *C. mundulus* Mg/Ca appears to increase with deep water $\Delta[\text{CO}_3^{2-}]$ (Fig. 8C,D), which has been previously documented for this species from the Southern Atlantic (Raitzsch et al., 2008). Above ~50 $\mu\text{mol/kg}$, core-top and down core *C. mundulus* Mg/Ca shows no significant relationship with bottom water $\Delta[\text{CO}_3^{2-}]$ (Fig. 8C, D). This may suggest a sensitivity threshold for *C. mundulus* Mg/Ca to deep water $\Delta[\text{CO}_3^{2-}]$, but further study is required to investigate this possibility. In BOFS 17K, *C. mundulus* Mg/Ca and B/Ca (hence $\Delta[\text{CO}_3^{2-}]$) are positively correlated for reductively

Fig. 8. *C. mundulus* Mg/Ca versus (A, B) BWT and (C, D) deep water $\Delta[\text{CO}_3^{2-}]$. Ratios obtained using “Mg-cleaning” (A, C) and “Cd-cleaning” (B, D) methods are separately plotted. Two curves in (A, B) are as explained in Fig. 2. In (C, D), deep water $\Delta[\text{CO}_3^{2-}]$ for core-top samples are estimated using the GLODAP dataset (Key et al., 2004). Superimposed on (C, D) are down core *C. mundulus* Mg/Ca versus B/Ca ratios (the upper abscissas) from BOFS 17K. The lower and upper abscissas are linearly linked by $\text{B/Ca} (\mu\text{mol/mol}) = 0.69 * \Delta[\text{CO}_3^{2-}] (\mu\text{mol/kg}) + 119.1$ (Yu and Elderfield, 2007). One *C. mundulus* Mg/Ca is not included due to its too high, possibly contaminated, ratio (Table A1). Data are reported in Tables A1 and A2.

cleaned samples ($\text{Mg}/\text{Ca}=0.0045 \cdot \text{B}/\text{Ca}+0.397$, $n=47$, $R^2=0.32$) (Figs. 4A and 8D). However, no correlation is observed for samples cleaned by the “Mg-cleaning” procedure ($\text{Mg}/\text{Ca}=0.0009 \cdot \text{B}/\text{Ca}+1.097$, $n=35$, $R^2=0.02$) (Fig. 8C), demonstrating possible artifacts caused by different cleaning methods.

It is noteworthy that *C. mundulus* and *C. wuellerstorfi* from the same genus behave differently to deep water $\Delta[\text{CO}_3^{2-}]$ changes. Compared with *C. wuellerstorfi* which is epifaunal and therefore whose shell chemistry reflects the composition of bottom waters, *C. mundulus* appears mostly to have an epifaunal habitat but can also occasionally exist as a shallow infaunal species (Rathburn and Corliss, 1994; Hodell et al., 2001). This might complicate its shell chemistry because pore waters tend to equilibration with CaCO_3 at subsurface depths (Martin and Sayles, 1996; Martin and Sayles, 2006). Bottom water $\Delta[\text{CO}_3^{2-}]$ has been used to compare with benthic Mg/Ca and this comparison might be affected by variations in the habitat depth for *C. mundulus*. However, our previous study shows that *C. mundulus* B/Ca is strongly correlated with deep water $\Delta[\text{CO}_3^{2-}]$ (Yu and Elderfield, 2007), indicating insignificant pore water influences. This may suggest that 1) *C. mundulus* we analyzed mainly have epifaunal habitat depths, and/or 2) pore water $\Delta[\text{CO}_3^{2-}]$ largely reflects bottom water $\Delta[\text{CO}_3^{2-}]$ variations at shallow sediment depths where processes such as regeneration, carbonate dissolution, and water exchange at sediment boundary do not affect fluid chemistry to a significant degree. An alternative reason for distinct responses between benthic species may be vital effects, warranting further study in the future. Different responses of different benthic species even within the same genus to $\Delta[\text{CO}_3^{2-}]$ highlights the necessity to use single species for Mg/Ca measurements.

6. Conclusions

In this study, we have investigated the influences of Mg/Ca variability, cleaning effects, BWT, and $\Delta[\text{CO}_3^{2-}]$ on Mg/Ca in two widely used benthic foraminiferal species, *C. wuellerstorfi* and *C. mundulus*, using core-top samples from the global oceans and down core samples from six down cores at 1–4 km water depths from the North Atlantic Ocean. Mg/Ca in the two species shows sizable variability (0.07 ± 0.07 mmol/mol) and is significantly affected by different cleaning procedures (0.10 ± 0.09 mmol/mol) in comparison with glacial–interglacial Mg/Ca changes (0.05 – 0.31 mmol/mol). Core-top and down core data show that Mg/Ca in *C. wuellerstorfi* is significantly affected by bottom water $\Delta[\text{CO}_3^{2-}]$ at a sensitivity of ~ 0.009 mmol/mol per $\mu\text{mol}/\text{kg}$. Different temperature sensitivities are obtained for core-top and down core samples. Taking all data into account, our study suggests a very weak temperature sensitivity, probably <0.03 mmol/mol per $^\circ\text{C}$, on *C. wuellerstorfi* Mg/Ca . Within the context of the modern deep-sea variability of ~ 5 $^\circ\text{C}$ in BWT and ~ 100 $\mu\text{mol}/\text{kg}$ in $\Delta[\text{CO}_3^{2-}]$ (Fig. 2), *C. wuellerstorfi* Mg/Ca changes are 0.15 mmol/mol (a maximum estimate) and 0.9 mmol/mol, respectively. The natural Mg/Ca variability is equivalent to ~ 2 $^\circ\text{C}$ in BWT (40% of the 5 $^\circ\text{C}$ range, a minimum estimate) and ~ 8 $\mu\text{mol}/\text{kg}$ in $\Delta[\text{CO}_3^{2-}]$ (8% of the ~ 100 $\mu\text{mol}/\text{kg}$ range). This weak BWT effect complicates the use of Mg/Ca in *C. wuellerstorfi* to reconstruct past BWT. Given the dominance of the $\Delta[\text{CO}_3^{2-}]$ effect, extraction of a BWT effect from *C. wuellerstorfi* Mg/Ca seems extremely challenging. Surprisingly, Mg/Ca in *C. mundulus* shows no correlation with BWT or $\Delta[\text{CO}_3^{2-}]$ over the entire environmental range investigated, maybe a consequence of vital effects.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2008.09.015.

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