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Controls on Sr/Ca in benthic foraminifera and implications for seawater Sr/Ca during the late Pleistocene

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ABSTRACT

Changes in the Sr to Ca ratio of sea water have important implications for the interpretation of past climate. It has proven difficult to interpret Sr/Ca of foraminiferal calcite as a measure of seawater Sr/Ca or as reflecting the influence of deep water carbonate ion saturation ($\Delta[CO_3^{2-}]$) on the incorporation of Sr into benthic foraminiferal carbonate. Here, we address this issue by measurements of paired benthic foraminiferal Sr/Ca and B/Ca (a proxy for deep water $\Delta[CO_3^{2-}]$) for core-tops from the global ocean and three down cores at different settings during the Last Glacial–interglacial cycle. These new data suggest a significant control of deep water $\Delta[CO_3^{2-}]$ on benthic foraminiferal Sr/Ca, and that down-core shell Sr/Ca variations can be largely accounted for by past deep water $\Delta[CO_3^{2-}]$ changes. We conclude that seawater Sr/Ca has likely remained near-constant on glacial–interglacial timescales during the late Pleistocene, in agreement with model results. With due caution, benthic Sr/Ca may be used as an auxiliary proxy for deep water $\Delta[CO_3^{2-}]$ if seawater Sr/Ca is constant.

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1. Introduction

The purpose of this study is to determine whether past changes have occurred in the Sr to Ca ratio of sea water. Most estimates of the evolution of seawater Sr/Ca come from analyses of foraminiferal carbonate. For example, benthic foraminiferal Sr/Ca data suggest that late Cretaceous (75–65 Ma) seawater Sr/Ca was ~50% higher than today (Lear et al., 2003). On glacial–interglacial timescales, changes in the locus of carbonate deposition between the shelves and deep sea (shelf-basin fractionation) predict variations in both deep water carbonate ion concentration ($[CO_3^{2-}]$) and in seawater Sr/Ca (Stoll and Schrag, 1998; Hodell et al., 2001). It has been calculated that a 1–2% enrichment of seawater Sr/Ca could occur shortly after sea-level low stands (Stoll and Schrag, 1998; Stoll et al., 1999). However, a stack of foraminiferal Sr/Ca data (Martin et al., 1999), which shows a high correlation with deep South Atlantic % $CaCO_3$ (Hodell et al., 2001), suggests a ≥3% variation in seawater Sr/Ca between glacials and interglacials during the late Pleistocene. Some other studies have shown that foraminiferal shells record Sr/Ca variations of up to 12% on glacial–interglacial timescales (Stoll et al., 1999; Elderfield et al., 2000).

Several explanations have been proposed to reconcile the discrepancy in seawater Sr/Ca estimates based on foraminifera data and modelling. For example, some of the Sr/Ca variability may be caused by secondary influences on foraminiferal Sr/Ca, such as temperature, salinity, pH, dissolution, and shell size (Cronblad and Malmgren, 1981; McCorkle et al., 1995; Brown and Elderfield, 1996; Rathburn and DeDeckker, 1997; Lea et al., 1999; Martin et al., 1999; Elderfield et al., 2000, 2002; Russell et al., 2004). Strikingly, most explanations involve a role for seawater carbonate ion saturation ($\Delta[CO_3^{2-}]$). Previous experiments have shown a strong influence of the degree of seawater carbonate saturation on the incorporation of Sr into inorganic carbonates (Lorens, 1981; Morse and Bender, 1990; Tang et al., 2008). In order to test the influence of seawater $\Delta[CO_3^{2-}]$ on shell Sr/Ca, it is necessary to compare Sr/Ca data from foraminifera with a measure of $\Delta[CO_3^{2-}]$ on the same samples. This is now possible through the application of foraminiferal B/Ca to estimate seawater $\Delta[CO_3^{2-}]$ (Yu and Elderfield, 2007).

In this study, we carried out a systematic investigation into paired Sr/Ca and B/Ca in benthic foraminifera, presenting Sr/Ca and B/Ca for core-tops from the global ocean and for three glacial–interglacial records from the Atlantic and Indian Oceans.

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2. Samples and methods

We analysed Sr/Ca in three calcitic (*Cibicidoides wuellerstorfi*, *Cibicidoides mundulus*, *and Uvigerina* spp.) and one aragonitic (*Hoeglundina elegans*) benthic foraminiferal species from 156 core-top samples from the global ocean (Tables S1–4). These core-tops are verified to be late Holocene (0–5 ka) in age (Yu and Elderfield, 2007). For down-core work, we measured Sr/Ca in *C. mundulus* from core BOFS 17K (58°N, 16.5°W, 1150 m) in the polar North Atlantic, and in *C. wuellerstorfi* from core VM28-122 (12°N, 79°W, 3623 m) in the Caribbean Basin and core WIND 28K (10.2°S, 151.8°E, 4147 m) in the southwestern Indian Ocean. These core sites experienced contrasting deep water $\Delta[CO_3^{2-}]$ histories (Yu et al., 2008, 2010a, 2010b), making them useful for investigation of the effects of deep water $\Delta[CO_3^{2-}]$ on shell Sr/Ca.

For each measurement, approximately 10–15 shells (corresponding to ~500 μg) were picked from the 250–500 μm size fraction, to minimize complications from any shell size influence (Elderfield et al., 2002). Tests were cleaned following two procedures: "Mg-cleaning" (Barker et al., 2003) and "Cd-cleaning" (Boyle and Keigwin, 1985/86). No significant Sr/Ca offset is observed between the two cleaning methods (Fig. S1) (Yu et al., 2007). Shell Sr/Ca and B/Ca were simultaneously measured by ICP-MS (Yu et al., 2005). Based on repeated analyses of a consistency standard (Sr/Ca = 1.407 mmol/mol), the long-term precision in Sr/Ca is about ±1% or ±0.014 mmol/mol (1 σ). Whenever possible, duplicate analyses were made. In total, we obtained 244 Sr/Ca measurements for 156 core-tops, and 366 Sr/Ca measurements for 267 down-core samples (Supplementary Table S1–7). The data presented in Figs. 1–3 are the averages of duplicate measurements. Considering possible analytical Sr/Ca offsets between laboratories (Hathorne et al., 2013) and the large dataset we generated, we do not include core-top Sr/Ca data from the literature. Deep water $\Delta[CO_3^{2-}]$ was estimated for core-top samples using the GLODAP dataset (Key et al., 2004), following the procedure of Yu and Elderfield (2007). Benthic B/Ca data are from Yu and Elderfield (2007) and Yu et al. (2010a, 2010b, 2008).

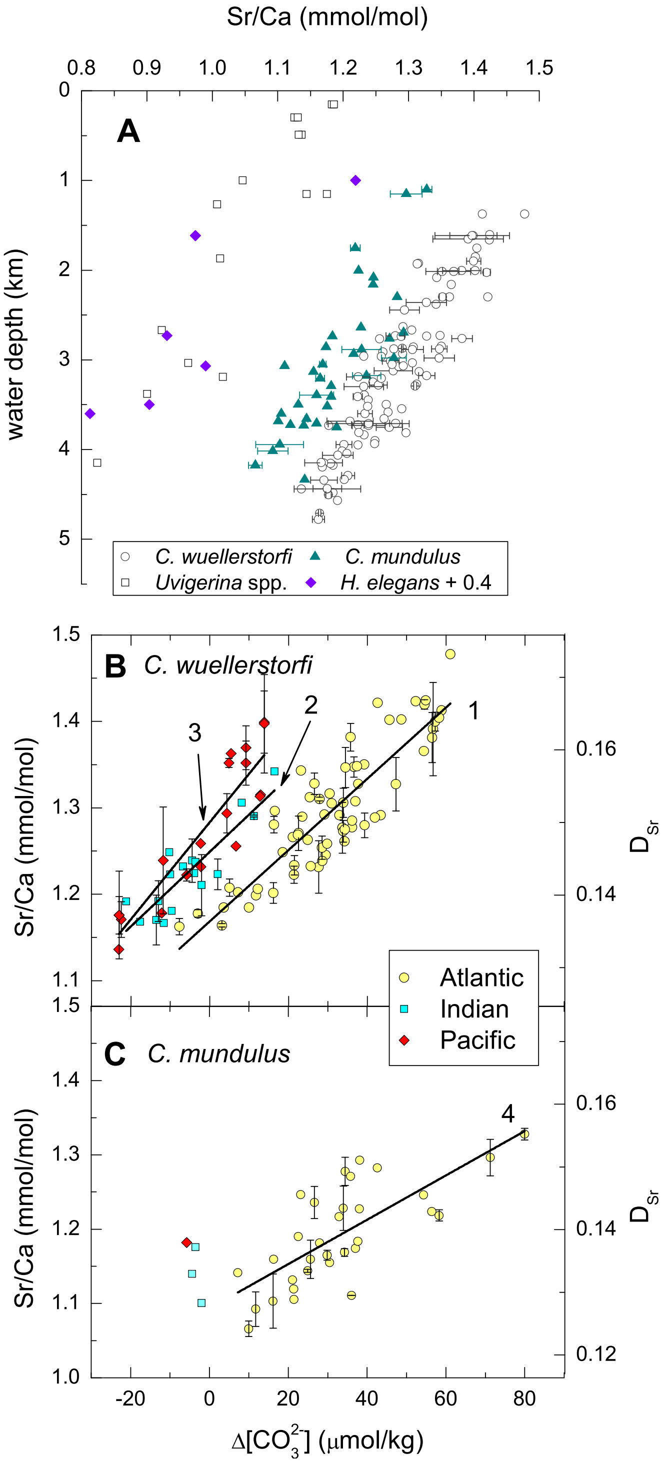

Fig. 1. Core-top benthic foraminiferal Sr/Ca. (**A**) Benthic foraminiferal Sr/Ca vs. water depth; (**B**) *C. wuellerstorfi* Sr/Ca vs. deep water $\Delta[CO_3^{2-}]$; (**C**) *C. mundulus* Sr/Ca vs. deep water $\Delta[CO_3^{2-}]$. Error bars represent $\pm 1\sigma$ of replicates. $D_{Sr} = (Sr/Ca)_{shell}/(Sr/Ca)_{seawater}$, where $(Sr/Ca)_{seawater} = 8.529$ mmol/mol. Solid lines in **B** and **C** represent the best linear fits: 1: $Sr/Ca = 1.168 \pm 0.010 + 0.0041 \pm 0.0003 \times \Delta[CO_3^{2-}]$, $n = 65$, $r^2 = 0.78$, $P < 0.0001$, Atlantic; 2: $Sr/Ca = 1.249 \pm 0.007 + 0.0043 \pm 0.0006 \times \Delta[CO_3^{2-}]$, $n = 17$, $r^2 = 0.76$, $P < 0.0001$, Indian; 3: $Sr/Ca = 1.283 \pm 0.008 + 0.0056 \pm 0.0006 \times \Delta[CO_3^{2-}]$, $n = 19$, $r^2 = 0.82$, $P < 0.0001$, Pacific; 4: $Sr/Ca = 1.093 \pm 0.019 + 0.0030 \pm 0.0005 \times \Delta[CO_3^{2-}]$, $n = 32$, $r^2 = 0.52$, $P < 0.0001$, Atlantic.

3. Results and discussion

3.1. Core-top Sr/Ca

Our core-top Sr/Ca data for four benthic foraminiferal species from the global ocean (Fig. 1) are consistent with previously published results (Figs. S2, S3) (McCorkle et al., 1995; Elderfield et al., 1996; Lear et al., 2003), but we present a larger data set with broader geographic coverage. Our results reveal clear interspecies offsets, with Sr/Ca ratios from high to low in the order of: *C. wuellerstorfi* (1.15–1.45 mmol/mol) > *C. mundulus* (1.08–1.32 mmol/mol) > *Uvigerina* spp. (0.82–1.19 mmol/mol) > *H. elegans* (0.41–1.92 mmol/mol) (Fig. 1A). These interspecies offsets strengthen the previous suggestion of significant biological (reflected by different Sr/Ca between *Cibicidoides* genera) and mineralogical (deduced from Sr/Ca offsets between calcitic and aragonitic species) effects on the incorporation of Sr into benthic foraminiferal species (Rosenthal et al., 1997).

Sr/Ca in each of the four studied species declines roughly linearly with increasing water depth (Fig. 1A). From 1 to 4.5 km, Sr/Ca decreases by ~18%, ~18%, ~27%, and ~41% in *C. wuellerstorfi*, *C. mundulus*, *Uvigerina* spp., and *H. elegans*, respectively. In contrast to previous studies (Cronblad and Malmgren, 1981; Rathburn and DeDeckker, 1997; Elderfield et al., 2000; Reichart et al., 2003; Dissard et al., 2010), these changes show no correlation with deep water temperature or salinity (Fig. S4), suggesting that these parameters have little influence on benthic foraminiferal Sr/Ca

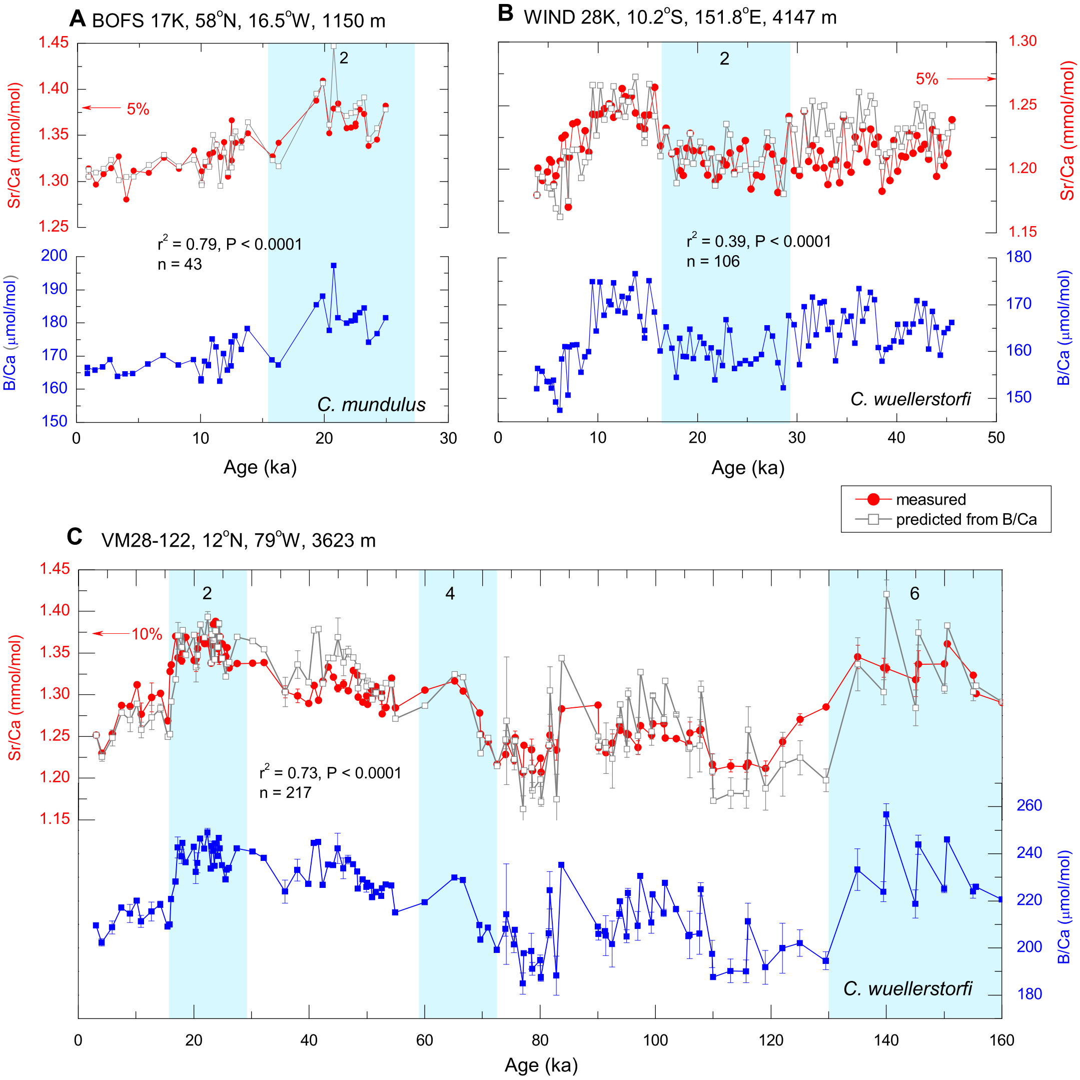

Fig. 2. Down-core benthic foraminiferal Sr/Ca and B/Ca. (**A**) BOFS 17K, (**B**) WIND 28K, and (**C**) VM28-122. Grey empty squares represent predicted Sr/Ca using benthic B/Ca (Yu et al., 2008; Yu et al., 2010a; Yu et al., 2010b) (see text for details). Shaded regions indicate even-numbered MIS. Arrows along the *y*-axes show 5% (A, B) and 10% (C) increases in Sr/Ca relative to the core-top values. Also shown are the correlation between benthic foraminiferal Sr/Ca and B/Ca (r^2 and *P*-value) and number of samples (*n*) in each core. In all three cores, changes in Sr/Ca can be effectively accounted for by changes in the incorporation of Sr into foraminiferal shells associated with past deep water $\Delta[CO_3^{2-}]$ variations. Hence, there is no need to invoke seawater Sr/Ca changes in the past. Errors in **C** represent ±1σ of replicates. Age models are from Yu et al. (2008, 2010a, 2010b).

(Katz et al., 1972; Rosenthal et al., 1997). The production and remineralization of celestite skeletons ($SrSO_4$) by acantharia in the upper ocean may cause small variations in seawater Sr/Ca and lead to more enriched seawater Sr/Ca in the deep ocean (de Villiers, 1999), but this effect would produce a trend opposite to the declining shell Sr/Ca with increasing water depth shown by our core-top samples (Fig. 1A). We observe no correlation between benthic Sr/Ca and deep water pH or $[CO_3^{2-}]$ (Fig. S5).

Our data argue against post-mortal dissolution (McCorkle et al., 1995; Brown and Elderfield, 1996) as a feasible explanation for the decline in benthic foraminiferal Sr/Ca with increasing water depth shown in Fig. 1A, for four reasons: (i) Rose Bengal dyed (recently alive) and non-Rose Bengal dyed (already dead and exposed to deep waters for certain amount of time) shells show similar Sr/Ca (Fig. S1); (ii) Sr/Ca starts to decrease well above the carbonate saturation horizon ($\Delta[CO_3^{2-}] = 0$ μmol/kg) where dissolution is expected to be minimal (Fig. 1B, C); (iii) *C. wuellerstorfi* Sr/Ca show insignificant inter-ocean differences despite generally more corrosive (lower $\Delta[CO_3^{2-}]$) deep waters in the Indo-Pacific Oceans than in the Atlantic Ocean at the same water depth (Fig. 1A, B); and (iv) on the Sr/Ca-$\Delta[CO_3^{2-}]$ plot (Fig. 1B), data from each ocean basin show no notable change in slope at $\Delta[CO_3^{2-}] = 0$ μmol/kg, which separates supersaturated (minimal dissolution) from undersaturated (strong dissolution) waters.

3.2. Down-core Sr/Ca

Our down-core benthic Sr/Ca records show different amplitudes and patterns at three locations in the Atlantic and Indian Oceans (Fig. 2). In the North Atlantic, *C. mundulus* Sr/Ca in core BOFS 17K show ~5% higher values during the Last Glacial period (18–24 ka) than the late Holocene (Fig. 2A). In the southwestern Indian Ocean, *C. wuellerstorfi* Sr/Ca in core WIND 28K display an obvious peak with an amplitude of ~4% during the last deglacial, and are otherwise similar to modern (Fig. 2B). The long record in VM28-122 from the Caribbean Basin shows high Sr/Ca during Marine Isotope Stages (MIS) 2, 4 and 6, and low Sr/Ca during MIS 1, 3, and 5, and exhibits a large variability of ~10% during the last 160 ka (Fig. 2C).

The linear decrease of core-top Sr/Ca with water depth (Fig. 1A) has been attributed to a pressure effect on the partitioning of Sr into

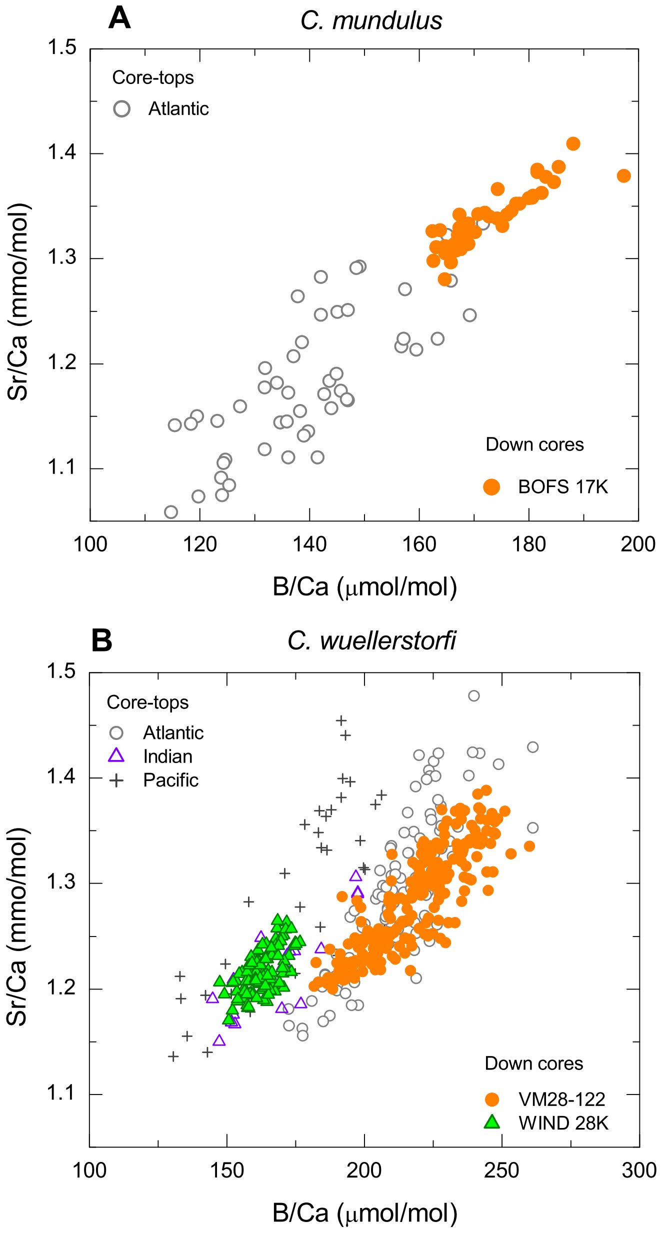

Fig. 3. Benthic Sr/Ca vs. B/Ca for core-top and down core samples. (**A**) *C. mundulus*, (**B**) *C. wuellerstorfi*. In each ocean basin, core-top and down-core samples show similar trends and distributions for both species, but samples from different basins are clearly separated.

benthic foraminiferal carbonate, and down-core benthic Sr/Ca variations after a pressure effect correction have been treated to reflect past seawater Sr/Ca oscillations (Lear et al., 2003). If correct, and because of limited sea-level fluctuations (<~150 m) on glacial–interglacial timescales over the period considered here (Fairbanks, 1989; Grant et al., 2012), our down-core benthic Sr/Ca records (Fig. 2) would then suggest contrasting seawater Sr/Ca histories, in both amplitude and pattern, at the three locations. This would contradict the homogenous seawater Sr/Ca in the global ocean at any given time that is expected based on the long residence times of Sr (~5 Ma) and Ca (~1 Ma) and the consequently well-mixed nature of the two elements in the ocean. Therefore, despite the tight correlations between core-top benthic Sr/Ca and water depth (Fig. 1A), we dismiss the argument for a direct link between variations in water depth (or pressure) and in benthic foraminiferal Sr/Ca. Instead, it implies that some (partially) pressure-related variable, such as carbonate saturation state, may be responsible for the large changes in core-top and down-core benthic Sr/Ca.

3.3. *A $\Delta[CO_3^{2-}]$ effect*

In the modern deep ocean (>~2 km water depth), seawater $[CO_3^{2-}]$ decreases slightly (Atlantic) or remains roughly stable (Pacific) with increasing water depth, due to remineralization of biogenic matter (Yu et al., 2014b). By comparison, the carbonate saturation concentration ($[CO_3^{2-}]_{sat}$) increases with increasing water depth due to a pressure effect on the solubility of $CaCO_3$ (Ingle, 1975). Consequently, deep water $\Delta[CO_3^{2-}]$ ($= [CO_3^{2-}] - [CO_3^{2-}]_{sat}$) generally decreases with increasing water depth. Additionally, inorganic precipitation experiments show that seawater carbonate saturation state influences carbonate Sr/Ca (Lorens, 1981; Morse and Bender, 1990; Tang et al., 2008). This effect is also seen for cultured planktonic foraminifera (Lea et al., 1999; Russell et al., 2004; Dueñas-Bohórquez et al., 2009) and cultured benthic foraminifera (Dissard et al., 2010; Raitzsch et al., 2010).

Our core-top benthic Sr/Ca data show strong positive correlations with deep water $\Delta[CO_3^{2-}]$ for *C. wuellerstorfi* and *C. mundulus* (Fig. 1B, C). For down-core samples, we can employ benthic B/Ca ratios, which were measured simultaneously in the same samples as Sr/Ca, as an independent proxy for deep water $\Delta[CO_3^{2-}]$ (Yu and Elderfield, 2007). Benthic foraminiferal Sr/Ca and B/Ca are significantly correlated ($r^2 = 0.39–0.79$, $P < 0.0001$) in all three cores (Figs. 2 and 3). We therefore suggest that Sr/Ca in *C. wuellerstorfi* and *C. mundulus* are significantly affected by deep water $\Delta[CO_3^{2-}]$. It is possible that deep water $\Delta[CO_3^{2-}]$ may affect the incorporation of Sr into these species by influencing foraminiferal growth rates (Lorens, 1981; Morse and Bender, 1990; Paquette and Reeder, 1995; Kisakurek et al., 2008; Tang et al., 2008). We have fewer core-top *H. elegans* and *Uvigerina* spp. with the calcification of the latter species being additionally affected by pore water chemistry due to its infaunal habitat. Although a robust test requires more measurements, *H. elegans* and *Uvigerina* spp. Sr/Ca for this limited data set also shows strong correlations with deep water $\Delta[CO_3^{2-}]$ (Fig. S6) (Rosenthal et al., 1997).

Because of the large number of measurements for core-top *C. wuellerstorfi* and *C. mundulus*, we have attempted to assess the sensitivity of benthic Sr/Ca to deep water $\Delta[CO_3^{2-}]$ changes for these two species. An inspection of the data reveals that core-top *C. wuellerstorfi* from different ocean basins appear to have distinct relationships between Sr/Ca and $\Delta[CO_3^{2-}]$ (Fig. 1B), a feature also evidenced in data from the literature (Fig. S3) (McCorkle et al., 1995; Elderfield et al., 1996; Lear et al., 2003). On the Sr/Ca–B/Ca plot (Fig. 3B), down-core samples from the Atlantic Ocean are obviously separated from those from the Indian Ocean. We therefore have carried out regression analyses separately for core-top samples from each ocean basin. Benthic Sr/Ca and deep water $\Delta[CO_3^{2-}]$ are significantly correlated for *C. wuellerstorfi* ($r^2 = 0.76–0.82$, $P < 0.0001$) and *C. mundulus* ($r^2 = 0.52$, $P < 0.0001$). The sensitivities of *C. wuellerstorfi* Sr/Ca to deep water $\Delta[CO_3^{2-}]$ are 0.0041, 0.0043, and 0.0056 mmol/mol per μmol/kg for the Atlantic, Indian and Pacific Oceans, respectively. The sensitivity of *C. mundulus* Sr/Ca to deep water $\Delta[CO_3^{2-}]$ for the Atlantic is lower at 0.0030 mmol/mol per μmol/kg (Fig. 1B, C).

Regressions for the complete core-top data from the global ocean would result in significantly poorer correlations (*C. wuellerstorfi*: $r^2 = 0.59$; *C. mundulus*: $r^2 = 0.46$) and, more critically, the derived sensitivities would lead to inconsistent reconstructions of seawater Sr/Ca variations downcore (Fig. S7). A previous study (Carpenter and Lohmann, 1992) suggested that lattice Mg may influence shell Sr/Ca, but this cannot explain the interocean contrast in benthic Sr/Ca, because core-top *C. wuellerstorfi* from the Atlantic and Pacific show similar Mg/Ca at a given deep water $\Delta[CO_3^{2-}]$ (Fig. S8). The inter-ocean differences in benthic Sr/Ca- deep water $\Delta[CO_3^{2-}]$ may imply secondary factors affecting benthic Sr/Ca, and more data are required to understand reasons causing such differences. We suggest that, with due caution, *C. wuellerstorfi* and *C. mundulus* Sr/Ca may be used as an auxiliary proxy for deep water $\Delta[CO_3^{2-}]$ if seawater Sr/Ca is stable.

3.4. Glacial–interglacial seawater Sr/Ca variations

To evaluate the effect of changes in past deep water $\Delta[CO_3^{2-}]$ on down-core benthic Sr/Ca, we employ benthic B/Ca to independently quantify $\Delta[CO_3^{2-}]$ changes and apply basin-specific Sr/Ca-$\Delta[CO_3^{2-}]$ sensitivities derived from core-tops to the three down-core data sets (Fig. 2). Assuming a constant seawater Sr/Ca ratio over the last 160 ka, changes in shell Sr/Ca are calculated by:

$$(\mathrm{Sr/Ca})_{\mathrm{down-core}} = (\mathrm{Sr/Ca})_{\mathrm{core-top}} + \left\{ \left[(\mathrm{B/Ca})_{\mathrm{down-core}} - (\mathrm{B/Ca})_{\mathrm{core-top}} \right] \Big/ S1 \right\} \times S2 \quad (1)$$

where S1 is the sensitivity of B/Ca to deep water $\Delta[CO_3^{2-}]$ (0.69 and 1.14 μmol/mol per μmol/kg for *C. mundulus* and *C. wuellerstorfi*, respectively) (Yu and Elderfield, 2007) and S2 is the ocean-specific sensitivity of benthic Sr/Ca to deep water $\Delta[CO_3^{2-}]$ shown in Fig. 1 (0.0030, 0.0043, and 0.0041 mmol/mol per μmol/kg for BOFS 17K, WIND 28K, and VM28-122, respectively). In all three cores, the shell Sr/Ca predicted solely from deep water $\Delta[CO_3^{2-}]$ variations closely match the measured shell Sr/Ca. This suggests that down-core shell Sr/Ca variability is dominated by the partitioning of Sr into foraminiferal tests associated with past seawater $\Delta[CO_3^{2-}]$ changes, and it appears unnecessary to invoke a change in seawater Sr/Ca to explain benthic Sr/Ca changes in the past 160 ka.

As an alternative way to investigate reasons for down-core benthic Sr/Ca changes, we have compared the distributions of down-core and core-top samples on the Sr/Ca–B/Ca plot (Fig. 3). Benthic Sr/Ca and B/Ca are significantly correlated in all three cores. *C. mundulus* data in BOFS 17K fall along the trend defined by the core-top samples (Fig. 3A). *C. wuellerstorfi* from VM28-122 and WIND 28K are plotted in two groups, overlapping the arrays defined by core-tops from the Atlantic and Indian Oceans, respectively (Fig. 3B). Because seawater Sr/Ca is constant in the modern ocean, the large core-top shell Sr/Ca variability must be caused by the incorporation of Sr into benthic foraminiferal carbonates, which is attributed to deep water $\Delta[CO_3^{2-}]$ changes (see above). The similar distribution of down-core and core-top samples shown in Fig. 3, therefore, supports the view that down-core benthic Sr/Ca variations do not necessarily reflect seawater Sr/Ca changes in the past. Instead, the strong Sr/Ca–B/Ca correlations for both core-top and down-core samples (Figs. 1 and 3) provide convincing evidence that down-core benthic Sr/Ca is likely caused by past deep water $\Delta[CO_3^{2-}]$ changes.

3.5. Implications

Our inferred near-stable seawater Sr/Ca on glacial–interglacial timescales contrasts with the ≥3% oscillations deduced from stacking of foraminiferal Sr/Ca (Martin et al., 1999). We note that the stacked Sr/Ca curve bears strong similarities to %$CaCO_3$ (which is significantly affected by deep water $\Delta[CO_3^{2-}]$) in ODP 1089 from the South Atlantic (Hodell et al., 2001; Yu et al., 2014a), suggesting an influence of deep water $\Delta[CO_3^{2-}]$ on the stacked Sr/Ca. However, the interpretation of stacked Sr/Ca (Martin et al., 1999) is complicated because it incorporates planktonic Sr/Ca in various species into which Sr uptake remains largely uncertain (Elderfield et al., 2000, 2002). Additionally, individual benthic Sr/Ca record likely has been affected by varying degrees of deep water $\Delta[CO_3^{2-}]$ changes at different sites (Fig. 2). Our conclusion of roughly constant seawater Sr/Ca during the late Pleistocene is consistent with previous modelling (Stoll and Schrag, 1998; Stoll et al., 1999), and supports minimal change in the balance of Sr and Ca fluxes between river inputs and carbonate burial in the ocean during Quaternary glacial cycles (Henderson et al., 1994; Stoll et al., 1999).

Our findings may have implications for longer term seawater Sr/Ca changes. Lear et al. (2003) showed that benthic Sr/Ca during the late Cretaceous (75–65 Ma) was ~1.5 times the modern value. The shallower carbonate compensation depth combined with elevated Ca^{2+} possibly reflects a lower deep water $\Delta[CO_3^{2-}]$ during the Cretaceous (Tyrrell and Zeebe, 2004). If deepwater $\Delta[CO_3^{2-}]$ affects Sr incorporation into the species used by Lear et al. (2003), taking account of a $\Delta[CO_3^{2-}]$ effect would lead to a higher estimate of Cretaceous seawater Sr/Ca (>1.5× of modern value). This would cause seawater Sr/Ca reconstructions based on benthic foraminifera to deviate even more from those based on mid-ocean ridge carbonate veins, which suggest lower seawater Sr/Ca during Jurassic to Paleogene than today (Coggon et al., 2010). We note that uncertainties are associated with both methods (Broecker and Yu, 2011), warranting further work to reconcile inter-proxy discrepancies for ancient materials.

4. Conclusion

Previously published benthic foraminiferal Sr/Ca data have led to conflicting seawater Sr/Ca reconstructions on various timescales. We systematically investigated reasons responsible for Sr/Ca variations in four benthic foraminiferal species using core-top and down-core samples from diverse geographic settings. We show that benthic Sr/Ca is not meaningfully affected by temperature, salinity, post-depositional dissolution, pH, $[CO_3^{2-}]$, or water depth (pressure). Our paired Sr/Ca and B/Ca data provide convincing evidence for a deep water $\Delta[CO_3^{2-}]$ effect on the partitioning of Sr into benthic foraminifera. As a result, changes in benthic foraminiferal Sr/Ca cannot be directly interpreted to reflect seawater Sr/Ca variations. Using benthic B/Ca as an independent proxy for deep water $\Delta[CO_3^{2-}]$, we demonstrate that down-core benthic foraminiferal Sr/Ca oscillations can be largely accounted for by past deep water $\Delta[CO_3^{2-}]$ changes. We conclude that seawater Sr/Ca has likely remained near-constant on glacial–interglacial timescales during the late Pleistocene. Future work should aim to better understand inter-ocean differences in benthic Sr/Ca-deep water $\Delta[CO_3^{2-}]$ relationships. With due caution, *C. wuellerstorfi* and *C. mundulus* Sr/Ca may be employed as an auxiliary proxy for deep water $\Delta[CO_3^{2-}]$ when seawater Sr/Ca remains constant.

Author contributions

JY picked shells, generated and interpreted data, and wrote the paper; HE's lab was used to generate a portion of the data presented here; ZJ picked a portion of shells for this study; PT assisted to generate data in the lab; All authors commented on the manuscript.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.quascirev.2014.05.018.

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