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The B/Ca proxy for past seawater carbonate chemistry reconstructions-laser ablation based calibrations for *C. mundulus*, *C. wuellerstorfi* and its morphotype *C. cf. wuellerstorfi*

F. Kersten[1], R. Tiedemann[1], J. Fietzke[2], and M. Frische[2]

[1]Alfred-Wegener-Institut Helmholtz-Zentrum für Polar-und Meeresforschung, 27570 Bremerhaven, Germany
[2]GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany

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Correspondence to: F. Kersten (franziska.kersten@awi.de)

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Abstract

B/Ca ratios in *Cibicides mundulus* and *Cibicides wuellerstorfi* have been shown to correlate with the degree of calcite saturation in seawater ($\Delta[CO_3^{2-}]$). In the South Pacific, a region of high importance in the global carbon cycle, these species are not continuously present in down-core records. Small numbers of epibenthic foraminifera in samples present an additional challenge, which can be overcome by using laser ablation-inductively coupled-mass spectrometry (LA-ICP-MS). We present a laser ablation based core-top calibration for *Cibicides cf. wuellerstorfi*, a *C. wuellerstorfi* morphotype that is abundant in the South Pacific and extend the existing global core top calibration for *C. mundulus* and *C. wuellerstorfi* to this region. B/Ca in *C. cf. wuellerstorfi* are linearly correlated with $\Delta[CO_3^{2-}]$ and possibly display a higher sensitivity to calcite saturation changes than *C. wuellerstorfi*. Trace element profiles through *C. wuellerstorfi* and *C. mundulus* reveal an intra-shell B/Ca variation of ±36 % around the mean shell value. Mg/Ca and B/Ca display opposite trends along the shell. Both phenomena likely result from ontogenetic effects. Intra-shell variability equals intra-sample variability, mean sample B/Ca values can thus be reliably calculated from averaged spot results of single specimen. In the global B/Ca–$\Delta[CO_3^{2-}]$ range, we observe an inverse relationship between water mass age and $\Delta[CO_3^{2-}]$.

1 Introduction

Carbon exchange between the ocean and the atmosphere occurs primarily via CO_2 gas exchange and is mediated by the biological and solubility pumps. The ocean is the largest carbon reservoir in this system and changes in its carbon inventory are thus considered to be potential primary drivers of past glacial to interglacial atmospheric CO_2 fluctuations (Broecker and Peng, 1987). Means to reconstruct oceanic inorganic carbon system parameters for the past are essential in order to better understand the ocean's role in carbon cycling on glacial to interglacial timescales. A close link be-

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tween atmospheric CO_2 and Antarctic temperature that has been observed for the past 800 000 yr (Wolff et al., 2005; Lüthi et al., 2008), furthermore highlights the significance of Southern Ocean processes in this context (e.g. Sigman and Boyle, 2000; Stephens and Keeling, 2000; Köhler et al., 2005; Fischer et al., 2010).

It has been demonstrated that benthic foraminiferal B/Ca ratios can be used to reconstruct past seawater carbonate ion concentrations (Yu and Elderfield, 2007). The calibration is most robust for *Cibicides wuellerstorfi* and *Cibicides mundulus*, two species that are widely used to reconstruct changes in bottom water chemistry due to their epibenthic habitat (Lutze and Thiel, 1989) and wide geographic distribution. Yet, recent work on South Pacific samples has shown that these species are not continuously present in down-core material in this area, and that *Cibicides cf. wuellerstorfi*, a *C. wuellerstorfi* morphotype is more common than other *Cibicides* species (personal communication: Hayward, Ronge). Proxy calibrations are not available for *C. cf. wuellerstorfi* at this point, presenting a challenge to reliable down-core reconstructions of past seawater chemistry properties in this region. Moreover, samples from the South Pacific often do not yield enough monospecific *Cibicides* individuals for conventional wet-chemical mass spectrometric trace element proxy analyses. We present here, new laser ablation-inductively coupled plasma-mass spectrometer (LA-ICP-MS) measured B/Ca core-top data from the South Pacific, that enable us to calibrate the B/Ca proxy for *C. cf. wuellerstorfi*, and to extend the existing calibration for *C. wuellerstorfi* and *C. mundulus* from Yu and Elderfield (2007) to this region.

1.1 Basis of the B/Ca proxy

CO_2, when dissolved in water reacts to form (primarily) bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and hydrogen (H^+) ions. The proportion of these species controls the seawater pH (Fig. 1). Within the observed oceanic pH range, borate $B(OH)_4^-$ and boric acid $B(OH)_3$, form the second most important acid base pair contributing to the seawater pH buffering system (Fig. 1). Next to HCO_3^- and CO_3^{2-}, foraminifera incorporate $B(OH)_4^-$

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into their shells during calcification (Hemming and Hanson, 1992). Based on this, B/Ca ratios as well as the boron isotopic composition in foraminiferal shells have the potential to serve as proxies for past ocean carbonate system parameters (Sanyal et al., 1995; Lemarchand et al., 2000; Henderson, 2002; Pagani et al., 2005; Yu and Elderfield, 2007). Yu and Elderfield (2007) demonstrated a species-specific linear relationship between benthic foraminiferal B/Ca ratios and the degree of calcite saturation ($\Delta[CO_3^{2-}]$) in seawater, thus providing a powerful tool for past ocean carbonate ion concentration reconstructions.

1.2 Potential complications

Several studies demonstrated pronounced interspecies variability in B/Ca, hence individual core top calibrations are necessary (Yu and Elderfield, 2007; Brown et al., 2011; Rae et al., 2011). It has moreover recently been recognized that trace element concentrations are offset between different morphotypes of the same species (Rae et al., 2011). Morphotype-specific calibrations are thus essential, when working in areas where *C. wuellerstorfi* and *C. mundulus* sensu stricto are not continuously present.

Raitzsch et al. (2011) documented a heterogeneous distribution of Boron in *C. wuellerstorfi* with increasing B/Ca ratios from the oldest towards the youngest chambers. Seeing that *C. wuellerstorfi* is exposed to relatively constant environmental conditions during its lifetime, intra-shell B/Ca variability is likely indicative of physiological trends (Raitzsch et al., 2011).

In order to mimimize the influence of possible ontogenetic effects, we have focused laser ablation spot measurements on the three oldest chambers. In addition, we analysed intra-shell variability in *C. mundulus* in comparison to *C. wuellerstorfi*.

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2 Materials and methods

2.1 Samples

This study is based on sediment surface samples, which were recovered with a multicorer from the Pacific Sector of the Southern Ocean between 669 and 3938 m water depth, during marine expeditions ANT XXVI-2 and SO213 (Gersonde, 2011; Tiedemann, 2012) (Fig. 2; Table 1). Core top calibrations are predominantly based on the upper cm of multicorer sediments. Cores where the upper three cm were sampled, stem from close to New Zealand, a region where relatively high sedimentation rates have been documented (~6 cm/1000 yr; Pahnke et al., 2003). To allow comparison of relative offsets between co-occurring *C. wuellerstorfi* and *C. cf. wuellerstorfi,* we analysed down-core material from cores PS75/100-4 and 103-1 in addition (Fig. 5, Table 1).

Foraminifer species *C. wuellerstorfi*, *C. cf. wuellerstorfi* and *C. mundulus* were picked from 19 multicorer samples. Analysed specimen were between 315 and 500 µm in size and did not show signs of alteration or secondary mineral fillings. Both *C. mundulus* and *C. wuellerstorfi* live above the sediment–water interface and we assume a similar living environment for *C. cf. wuellerstorfi*. *C. cf. wuellerstorfi* were identified based on the definition of Hayward et al. (2010), who refer to the genus as *C. dispars*, which is a summary of variable recent planoconvex *Cibicides* morphologies. We use the name *C. cf. wuellerstorfi* in order to specify the morphotype that was chosen for this study, which resembles *C. wuellerstorfi*. Selected specimens have a heavily perforated, flat spiral side that is highly similar to *C. wuellerstorfi*, hence the nomenclature. The convex umbilical side shows no pores under the REM, sutures are slightly depressed and curved back towards the acute periphery (Fig. 3).

2.2 Analytical techniques

B/Ca ratios were analysed at the Geomar Helmholtz Centre for Ocean Research Kiel, using a 193 nm Excimer laser ablation system (Coherent, GeoLasPro) coupled to

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a high resolution-ICP-MS (Nu Instruments, AttoM). For each sample 3–6 shells were used and trace elemental composition was analysed on four spots with 90 µm diameter each, in the three oldest chambers on the umbilical side. The NIST 615 standard (Jochum et al., 2011) was measured before and after sets of five foraminifer shells and used for signal calibration. Given standard deviations depend on the number of shells in each sample and include measurement uncertainty of the standard. In order to exclude contamination effects, foraminifer shells as well as the NIST 615 standard were pre-ablated before analysis begun, and samples with Mn/Ca above 0.2 $mmol\,mol^{-1}$ and Al/Ca higher than 0.4 $mmol\,mol^{-1}$ were discarded from the dataset.

2.3 Core top calibration with modern hydrography

For the core top calibration, mean sample B/Ca was calculated from averaged spot measurements per shell and compared to modern ocean $\Delta[CO_3^{2-}]$ (Table 1). Modern ocean $\Delta[CO_3^{2-}]$ was calculated with CO_2sys (Pierrot and Wallace, 2006). Required input parameters (TA, DIC, [Si], [P], temperature, salinity and pressure) were taken from ANT XXVI-2 and SO213 cruise data (Gersonde, 2011; Tiedemann, 2012) and nearby GLODAP sites (Key et al., 2004). Following this approach, the carbonate ion concentration in seawater can be reconstructed with:

$$\left[CO_3^{2-}\right] = \Delta\left[CO_3^{2-}\right] + \left[CO_3^{2-}\right]_{sat}. \quad (1)$$

3 Results

3.1 Relationship between B/Ca and modern oceanographic parameters

Our core top data cover a range of 669 to 3938 m water depth, associated with a temperature and salinity span of 1.4–6.8 °C and 34.29–34.73 psu, respectively. Plots of foraminiferal B/Ca vs. temperature and salinity might indicate a minor temperature influence in *C. wuellerstorfi* and *C. mundulus*, but show no significant relationship for

C. cf. wuellerstorfi (Fig. 4a, b). Seawater $\Delta[CO_3^{2-}]$ and temperature co-vary with water depth in our study area (Fig. 4d), making it impossible to untangle the individual effect these parameters exert on B/Ca. However, Yu and Elderfield (2007) demonstrated that the close correlation between B/Ca ratios and the degree of carbonate saturation is globally robust and more significant than a possible temperature effect. In order to check for the influence of carbonate system components other than $\Delta[CO_3^{2-}]$, we plotted B/Ca as a function of DIC, a term that contains all three inorganic carbon species abundant in seawater ($DIC = [CO_2]_{aq} + [HCO_3^-] + [CO_3^{2-}]$) (Fig. 4c). We find no significant correlation between DIC and foraminiferal B/Ca in either of the studied species.

3.2 Comparison of B/Ca ratios in *C. cf. wuellerstorfi* and *C. wuellerstorfi*

Comparative B/Ca measurements in co-occuring *C. wuellerstorfi* and *C. cf. wuellerstorfi* reveal a non-constant offset that ranges between 1.9 and 71 $\mu mol\,mol^{-1}$ in our samples (Fig. 5). Applying the *C. wuellerstorfi* B/Ca-calibration from Yu and Elderfield (2007) to both morphotypes, would yield a maximum difference of ∼62 $\mu mol\,kg^{-1}$ $\Delta[CO_3^{2-}]$ within the same sample. This discrepancy between the two morphotypes equals almost the entire observed range in the ocean, highlighting the necessity of an individual B/Ca–$\Delta[CO_3^{2-}]$ calibration for *C. cf. wuellerstorfi*.

3.3 Intra-shell B/Ca variability

In order to estimate intra-shell variability, we measured trace element concentrations at 12 spots that were evenly placed throughout the shells of two randomly chosen *C. wuellerstorfi* and *C. mundulus* specimen (Fig. 6, samples PS75/105-1_2cm and 101-2_0cm). Trace element profiles in both *C. wuellerstorfi* and *C. mundulus* reveal a variation of up to ±36 % around mean shell B/Ca. Analogue to Raitzsch et al. (2011), we find increasing B/Ca from the oldest to the youngest chambers in *C. wuellerstorfi*, while Mg/Ca initially decreases and then sharply increases from the third youngest to the penultimate chamber (Fig. 6, bottom). In *C. mundulus*, a clear anti-correlation between B/Ca and Mg/Ca can be observed, with the former mainly increasing throughout most of the shell until dropping again in the youngest two chambers, opposing the trend of the latter (Fig. 6, top panel). The observed within-shell variability is similar to the within-sample B/Ca range. Due to technical problems, we were unfortunately not able to measure trace element profiles on *C. cf. wuellerstorfi*.

3.4 B/Ca–$\Delta[CO_3^{2-}]$ calibration

3.4.1 *C. cf. wuellerstorfi*

Analysed B/Ca ratios in *C. cf. wuellerstorfi* range from 126 to 327 $\mu mol\,mol^{-1}$ (Table 1). We find that mean sample B/Ca is linearly correlated with the degree of calcite saturation in modern seawater, despite the observed intra-sample variability (Fig. 7a). Analogue to *C. wuellerstorfi*, a linear regression function provides the best fit, hence the correlation between B/Ca ratios in *C. cf. wuellerstorfi* and modern ocean $\Delta[CO_3^{2-}]$ is expressed in:

$$B/Ca = 2.27\left(\Delta\left[CO_3^{2-}\right]\right) + 152.5 \quad \left(R^2 = 0.76\right). \tag{2}$$

The *C. cf. wuellerstorfi* calibration curve shows a steeper slope than the one for *C. wuellerstorfi* (Fig. 7), resulting from a higher B/Ca range in the analysed *C. cf. wuellerstorfi* samples compared to *C. wuellerstorfi*.

3.4.2 *C. wuellerstorfi*

B/Ca ratios in *C. wuellerstorfi* vary between 183 and 254 $\mu mol\,mol^{-1}$ in our samples (Table 1). Yu and Elderfield (2007) report a whole ocean B/Ca range of 130–260 $\mu mol\,mol^{-1}$ for this species. Our data plot within the existing global B/Ca–$\Delta[CO_3^{2-}]$ array, however a slight regional adaptation for Pacific core tops appears to be useful (Fig. 7b). Our samples, from the South Pacific show overall higher B/Ca values and a larger range than *C. wuellerstorfi* samples from Yu and Elderfield (2007) from the equatorial Pacific. Hence, we suggest a revised B/Ca–$\Delta[CO_3^{2-}]$ calibration for the Pacific, based on this study and including the data from Yu and Elderfield (2007):

$$B/Ca = 1.39\left(\Delta\left[CO_3^{2-}\right]\right) + 175.5 \quad \left(R^2 = 0.87\right). \tag{3}$$

As a result, we obtain a correlation with a slightly more moderate slope that covers a wider range in $\Delta[CO_3^{2-}]$ than the one based solely on data from Yu and Elderfield (2007) (Fig. 7b, inset).

3.4.3 *C. mundulus*

B/Ca ratios in our core top *C. mundulus* samples range between 99 and 133 µmol mol^{-1} (Table 1). The *C. mundulus* dataset from Yu and Elderfield (2007), containing mostly Atlantic Ocean as well as two Indian Ocean samples, covers a B/Ca range of 120 to 170 µmol mol^{-1} (Fig. 7c). Adding our samples to the Yu and Elderfield (2007) data, results in a calibration with a slightly higher R^2 and a steeper slope for the regression curve (Fig. 7c):

$$B/Ca = 0.80\left(\Delta\left[CO_3^{2-}\right]\right) + 114.5 \quad \left(R^2 = 0.79\right). \tag{4}$$

4 Discussion

4.1 Inter-species, -morphotype and intra-shell trace element variability

Trace element variability within shells of the same species as well as offsets between species or morphotypes of the same species have been documented in a number of studies (e.g. Yu and Elderfield, 2007; Allen et al., 2011; Rae et al., 2011; Raitzsch et al., 2011; this study). These features appear to be common in benthic as well as planktic foraminifera, the underlying processes are however not fully constrained.

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Raitzsch et al. (2011) suggested that the inverse distribution of Mg/Ca and B/Ca throughout *C. wuellerstorfi* shells, a characteristic that we also observe in *C. mundulus*, might result from ontogenetic effects. An in-depth analysis of possible underlying mechanisms is beyond the scope of this study. We can however exclude changes in physical or chemical parameters in the ambient seawater as the cause of intra-shell as well as interspecies B/Ca variability (within the same sample), based on the similar habitat of *C. mundulus, C. wuellerstorfi* and presumably *C. cf. wuellerstorfi*. Specifically, we can rule out that intra-shell Mg/Ca variability (Fig. 6) is controlled by fluctuations in the ambient temperature. The two specimen chosen for trace element profile analyses stem from water depths of 669 and 1773 m, respectively. The observed within-shell Mg/Ca fluctuation would correspond to a temperature change of ∼5 °C, which is highly unlikely to occur at these depths throughout the short lifecycle of *Cibicides spp.* (∼3 yr; Groß, 1998).

Despite intra-shell trace element variations, we find that averaged laser ablation spot measurements give a reliable mean shell B/Ca, analogue to Raitzsch et al. (2011).

Rae et al. (2011) present a possible explanation for inter-species differences in B/Ca. They suggest that during calcification, small quantities of $B(OH)_4^-$ are transported to an internal reservoir together with HCO_3^-, and that even small changes in this flux can produce significant offsets in foraminiferal B/Ca. Following this, we hypothesize that the offset between *C. cf. wuellerstorfi* and *C. wuellerstorfi* might also result from biomineralization effects. Hence, we suggest that the steeper slope in *C. cf. wuellerstorfi* B/Ca vs. $\Delta[CO_3^{2-}]$ when compared to its morphotype, could indicate a higher sensitivity to calcite saturation changes in *C. cf. wuellerstorfi*, making this a species with high potential for past seawater carbonate ion reconstruction.

4.2 The B/Ca–$\Delta[CO_3^{2-}]$ range

In the global B/Ca–$\Delta[CO_3^{2-}]$ range, samples from the Atlantic Ocean and Norwegian Sea tend towards relatively high B/Ca and $\Delta[CO_3^{2-}]$ in *C. wuellerstorfi* and *C. mundu-*

lus, respectively. In contrast, core tops from Indo-Pacific waters show overall lower B/Ca corresponding with lower $\Delta[CO_3^{2-}]$ for the most part (Yu and Elderfield, 2007; this study) (Fig. 7b, c). This might suggest, that high in situ $[CO_3^{2-}]$ and $\Delta[CO_3^{2-}]$ are primarily a characteristic of young and thus well ventilated waters (as are typically found in the Atlantic Ocean and Norwegian Sea), while low $\Delta[CO_3^{2-}]$ are associated with more corrosive and less well ventilated waters (typical for the Indo-Pacific). However, our South Pacific intermediate- to deep-water transect of *C. cf. wuellerstorfi* and *C. wuellerstorfi* core top samples, shows a large range in B/Ca values (Fig. 7b), apparently challenging this observation. Two of our *C. wuellerstorfi* core top samples are marked by high B/Ca and $\Delta[CO_3^{2-}]$ values, that are similar to Norwegian Sea samples from Yu and Elderfield (2007) (Fig. 7b). The two South Pacific samples were recovered from water depths of 669 and 835 m, within the realm of Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW), respectively. SAMW and AAIW are both young water masses that are formed at the surface in the Subantarctic and Polar Front Zone, respectively. Due to their low density, they subduct only to intermediate depths and spread north- and eastwards in the Pacific. Norwegian Sea samples in the Yu and Elderfield (2007) dataset, stem from water depths between 1375 and 3299 m, which were flooded by young Norwegian Sea Deep Water (NSDW). A comparison of in situ data between NSDW and AAIW/SAMW (CARINA and GLODAP databases) shows that $\delta^{13}C$ and carbonate ion concentrations in these water masses are quite similar (~100–110 µmol kg^{-1} and ~1–1.1 ‰; Key et al., 2004). The observed high $\delta^{13}C$ values, indicative of well ventilated water masses, support the above mentioned assumption. In contrast to this, two *C. wuellerstorfi* samples as well as all of the *C. mundulus* core top samples from our South Pacific transect display low "Pacific-type" B/Ca values (Fig. 7b, c). They were recovered from water depths between 1773 and 3410 m. Relatively low in situ $[CO_3^{2-}]$ and $\delta^{13}C$ values (~75 µmol kg^{-1}; ~0.38–0.6 ‰; Key et al., 2004) are found in this depth range, reflective of less well ventilated, aged Circumpolar Deep Water (CDW) (Fig. 2). The large B/Ca–$\Delta[CO_3^{2-}]$ span in *C. cf. wuellerstorfi* is associated with a depth range of 669–3938 m, and a $\delta^{13}C$ decline from ~1.41 to

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−0.9 ‰ (Key et al., 2004), yet again arguing for a close link between water mass age and $\Delta[CO_3^{2-}]$.

4.3 Potential of the laser ablation method in the Southern Ocean

The importance of the Southern Ocean with respect to the carbon cycle is evident in the past and today. Currently, the Southern Ocean acts as a sink for CO_2, which is transported to intermediate and deep waters and consequently alters the inorganic carbon chemistry there (Sabine et al., 2004; Sandrini et al., 2007). In the past, the source-sink behaviour of the Southern Ocean has varied simultaneously with glacial to interglacial climate change (Fischer et al., 2010; Sigman et al., 2010). The majority of paleoceanographic studies linked large parts of the atmospheric CO_2 rise during the last deglaciation to enhanced overturning in the Southern Ocean, which released CO_2 to the atmosphere (Anderson et al., 2009; Meckler et al., 2013). This should have left an imprint on the carbonate ion concentration within the water column of the Southern Ocean, a theory that can be tested with the B/Ca proxy. However carbonate-rich sediments are scarcely abundant in the South Pacific, due to the fact that large areas of the ocean floor lie below the lysocline (4000–4300 m; Milliman et al., 1999). In addition to that, carbonate preservation is generally reduced during Glacials in the Southern Ocean (Diekmann, 2007). Hence, limited sample availability as well as reduced time resolution of sediment records along glacial terminations has hampered down-core studies in the past. In addition to that, low boron concentrations in foraminifers (∼10 ppm; Rae et al., 2011) make it impossible to measure B/Ca on samples with small numbers of specimen from the same species with the conventional wet-chemical approach, which requires a minimum of 10 individuals per sample. This study as well as work by Raitzsch et al. (2011) demonstrate that the laser ablation technique can be successfully used to overcome this problem. With the new laser ablation core top B/Ca measurements that we present for *C. wuellerstorfi* and *C. mundulus*, we are able to expand the B/Ca–$\Delta[CO_3^{2-}]$ relationship to the Pacific sector of the Southern Ocean.

5 Conclusions

B/Ca ratios display distinct trends in *C. wuellerstorfi* and *C. cf. wuellerstorfi*, an individual core top calibration for *C. cf. wuellerstorfi* is thus essential. Our data suggest a linear correlation between core top sample B/Ca in *C. cf. wuellerstorfi* and the degree of seawater calcite saturation. The observed relationship is robust for temperature-, $\Delta[CO_3^{2-}]$- and water depth-ranges of ~1.5–7 °C, −16–67 µmol kg^{-1} and 669–3938 m, respectively. We are thus confident that this calibration can be applied successfully to down-core B/Ca studies in the Pacific sector of the Southern Ocean.

Roughly inverse Mg/Ca and B/Ca trace element profiles in *C. wuellerstorfi* and *C. mundulus* are likely not due to changes in physical and chemical properties in ambient seawater.

Intra-shell variability equals intra-sample variability, hence mean B/Ca can be reliably calculated from individual laser ablation spot measurements.

In the global B/Ca–$\Delta[CO_3^{2-}]$ range, high values appear to be associated with well ventilated water masses, while low values mirror aged, less well ventilated water masses.

The laser ablation technique provides an opportunity to measure trace element compositions on samples with little measurable material that could not be analysed with the conventional wet-chemical approach.

Supplementary material related to this article is available online at: http://www.clim-past-discuss.net/9/4425/2013/cpd-9-4425-2013-supplement.pdf.

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References

Allen, K. A., Hönisch, B., Eggins, S. M., Yu, J., Spero, H. J., and Elderfield, H.: Controls on boron incorporation in cultured tests of the planktic foraminifer Orbulina universa, Earth Planet. Sc. Lett., 309, 291–301, doi:10.1016/j.epsl.2011.07.010, 2011.

Anderson, R. F., Ali, S., Bradtmiller, L. I., Nielsen, S. H. H., Fleisher, M. Q., Anderson, B. E., and Burckle, L. H.: Wind-driven upwelling in the Southern Ocean and the deglacial rise in atmospheric CO_2, Science, 323, 1443–1448, doi:10.1126/science.1167441, 2009.

Broecker, W. S. and Peng, T.-H.: The role of $CaCO_3$ compensation in the glacial to interglacial atmospheric CO_2 change, Global Biogeochem. Cy., 1, 15–29, doi:10.1029/GB001i001p00015, 1987.

Brown, R. E., Anderson, L. D., Thomas, E., and Zachos, J. C.: A core-top calibration of B/Ca in the benthic foraminifers Nuttallides umbonifera and Oridorsalis umbonatus: a proxy for Cenozoic bottom water carbonate saturation, Earth Planet. Sc. Lett., 310, 360–368, doi:10.1016/j.epsl.2011.08.023, 2011.

Diekmann, B.: Sedimentary patterns in the late Quaternary Southern Ocean, Deep-Sea Res. Pt. II, 54, 2350–2366, 2007.

Emerson, S. and Hedges, J.: Chemical Oceanography and the Marine Carbon Cycle, Cambridge University Press, New York, 2008.

Fischer, H., Schmitt, J., Lüthi, D., Stocker, T., Tschumi, T., Parekh, R., Joos, F., Köhler, P., Völker, C., Gersonde, R., Babante, C., Floch, M. L., and Wolff, D. R. E.: The role of Southern Ocean processes in orbital and millennial CO_2 variations – A synthesis, Quaternary Sci. Rev., 29, 193–205, 2010.

Gersonde, R.: The expedition of the research vessel "Polarstern" to the polar South Pacific in 2009/2010 (ANT-XXVI/2-BIPOMAC), in: Berichte zur Polar-und Meeresforschung, vol. 632, Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, p. 330, 2011.

Groß, O.: Investigations on autecology, migration and bioturbation of living benthic deep-sea Foraminifera (Protozoa), Ph. D. thesis, Institut für Hydrobiologie und Fischereiwissenschaft, Hamburg, 1998.

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Hayward, B., Grenfell, H., Sabaa, A., and Buzas, M.: Recent New Zealand Deep Water-Benthic Foraminifera: Taxonomy, Ecologic Distribution, Biogeography, and Use in Paleoenvironmental Assessment, GNS Science, New Zealand, 2010.
Hemming, N. and Hanson, G.: Boron isotopic composition and concentration in modern marine carbonates, Geochim. Cosmochim. Acta, 56, 537–543, doi:10.1016/0016-7037(92)90151-8, 1992.
Henderson, G. M.: New oceanic proxies for paleoclimate, Earth Planet. Sc. Lett., 203, 1–13, doi:10.1016/S0012-821X(02)00809-9, 2002.
Jochum, K., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D., Stracke, A., Birbaum, K., Frick, D., Günther, D., and Enzweiler, J.: Determination of reference values for NIST SRM 610-617 glasses following ISO guidelines, Geostand. Geoanal. Res., 35, 397–429, doi:10.1111/j.1751-908X.2011.00120.x, 2011.
Key, R., Kozyr, A., Sabine, C., Lee, K., Wanninkhof, R., Bullister, J., Feely, R., Millero, F., Mordy, C., and Peng, T.-H.: A global ocean carbon climatology: results from Global Data Analysis Project (GLODAP), Global Biogeochem. Cy., 18, GB4031, doi:10.1029/2004GB002247, 2004.
Köhler, P., Fischer, H., Munhoven, G., and Zeebe, R. E.: Quantitative interpretation of atmospheric carbon records over the last glacial termination, Global Biogeochem. Cy., 19, GB4020, doi:10.1029/2004GB002345, 2005.
Lemarchand, D., Gaillardet, J., Lewin, E., and Allegre, C. J.: The influence of rivers on marine boron isotopes and implications for reconstructing past ocean pH, Nature, 408, 951–954, 2000.
Lüthi, D., Floch, M. L., Bereiter, B., Blunier, T., Barnola, J.-M., Siegenthaler, U., Raynaud, D., Jouzel, J., Fischer, H., Kawamura, K., and Stocker, T.: High-resolution carbon dioxide concentration record 650,000–800,000 yr before present, Nature, 453, 379–382, 2008.
Lutze, G. and Thiel, H.: Epibenthic foraminifera from elevated microhabitats: *Cibicidoides wuellerstorfi* and *Planulina ariminensis*, J. Foramin. Res., 19, 153–158, 1989.
Meckler, A. N., Sigman, D. M., Gibson, K. A., Francois, R., Martinez-Garcia, A., Jaccard, S. L., Rohl, U., Peterson, L. C., Tiedemann, R., and Haug, G. H.: Deglacial pulses of deep-ocean silicate into the subtropical North Atlantic Ocean, Nature, 495, 495–498, 2013.
Milliman, J., Troy, P., Balch, W., Adams, A., Li, Y.-H., and Mackenzie, F.: Biologically mediated dissolution of calcium carbonate above the chemical lysocline?, Deep-Sea Res. Pt. I, 46, 1653–1669, 1999.

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Pahnke, K., Zahn, R., Elderfield, H., and Schulz, M.: 340,000 yr centennial-scale marine record of Southern Hemisphere climatic oscillation, Science, 301, 948–952, 2003.
Pagani, M., Lemarchand, D., Spivack, A., and Gaillardet, J.: A critical evaluation of the boron isotope-pH proxy: the accuracy of ancient pH estimates, Geochim. Cosmochim. Acta, 69, 953–961, 2005.
Pierrot, D. and Wallace, D.: MS Excel Program Developed for CO_2 System Calculations. ORNL/CDIAC-105a., Tech. rep., Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, doi:10.3334/CDIAC/otg.CO2SYS_XLS_CDIAC105a, 2006.
Rae, J. W., Foster, G. L., Schmidt, D. N., and Elliott, T.: Boron isotopes and B/Ca in benthic foraminifera: proxies for the deep ocean carbonate system, Earth Planet. Sc. Lett., 302, 403–413, doi:10.1016/j.epsl.2010.12.034, 2011.
Raitzsch, M., Hathorne, E., Kuhnert, H., Groeneveld, J., and Bickert, T.: Modern and late Pleistocene B/Ca ratios of the benthic foraminifer *Planulina wuellerstorfi* determined with laser ablation ICP-MS, Geology, 39, 1039–1042, 2011.
Sabine, C., Feely, R., Gruber, N., Key, R., Wong, C., Douglas, D., Tilbrook, B., Millero, F., Peng, T.-H., Kozyr, A., Ono, T., and Rios, A.: The oceanic sink for anthropogenic CO_2, Science, 305, 367–371, 2004.
Sandrini, S., Ait-Ameur, N., Rivaro, P., Massolo, S., Touratier, F., Tositti, L., and Goyet, C.: Anthropogenic CO_2 distribution in the Ross Sea, Antarctica, Antarct. Sci., 19, 395–407, 2007.
Sanyal, A., Hemming, N., Hanson, G., and Broecker, W.: Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera, Nature, 373, 234–236, 1995.
Schlitzer, R.: Ocean Data View, available at: http://odv.awi.de (last access: 5 August 2013), 2012.
Sigman, D. M. and Boyle, E.: Glacial/interglacial variations in atmospheric carbon dioxide, Nature, 407, 859–869, 2000.
Sigman, D. M., Hain, M. P., and Haug, G. H.: The polar ocean and glacial cycles in atmospheric CO_2 concentration, Nature, 466, 47–55, 2010.
Stephens, B. and Keeling, R.: The influence of Antarctic sea ice on glacial-interglacial CO_2 variations, Nature, 404, 171–174, 2000.
Tiedemann, R. and cruise participants: Cruise Report SO213 SOPATRA “South Pacific Paleoceanographic Transects – Geodynamic and Climatic Variability in Space and Time”, unpublished, 2012.

Wolff, E., Kull, C., Chappellaz, J., Fischer, H., Miller, H., Stocker, T. F., Watson, A. J., Flower, B., Joos, F., Köhler, P., Matsumoto, K., Monnin, E., Mudelsee, M., Paillard, D., and Shackleton, N.: Modeling past atmospheric CO_2: results of a challenge, EOS T. Am. Geophys. Un., 86, 341–345, doi:10.1029/2005EO380003, 2005.

Yu, J. and Elderfield, H.: Benthic foraminiferal B/Ca ratios reflect deep water carbonate saturation state, Earth Planet. Sc. Lett., 258, 73–86, 2007.

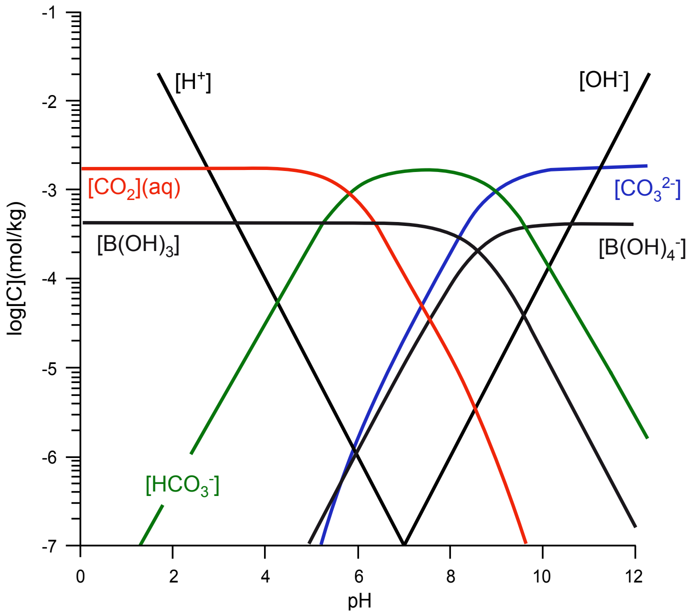

Fig. 1. Concentrations of carbonate, borate and water species in seawater vs. pH at average salinity (S = 35 psu) and temperature (T = 20 °C). Modified after Emerson and Hedges (2008).

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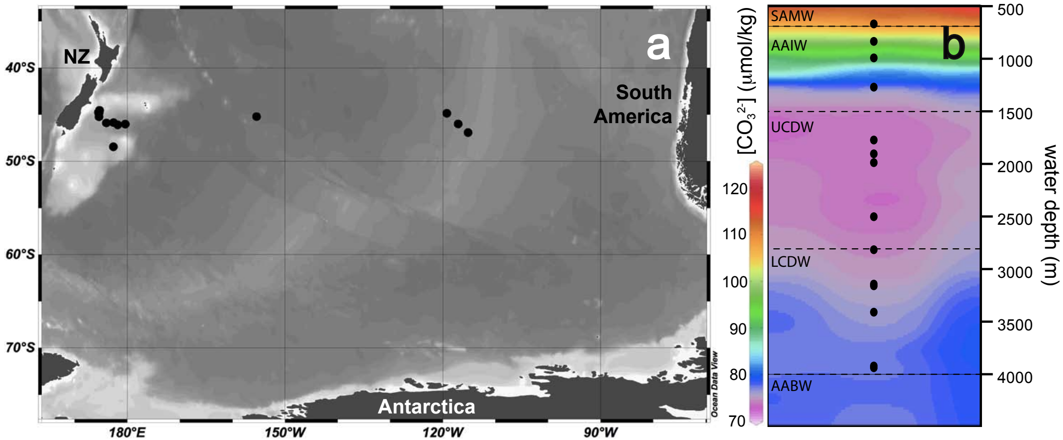

Fig. 2. Location of studied core tops. **(a)** Map view generated with Ocean Data View (Schlitzer, 2012), **(b)** water column profile at ~45° S with $[CO_3^{2-}]$ (Key et al., 2004) and important water masses in the study area. Abbreviations as follows: SAMW = Subantarctic Mode Water, AAIW = Antarctic Intermediate Water, U/LCDW = Upper and Lower Circumpolar Deep Water, AABW = Antarctic Bottom Water.

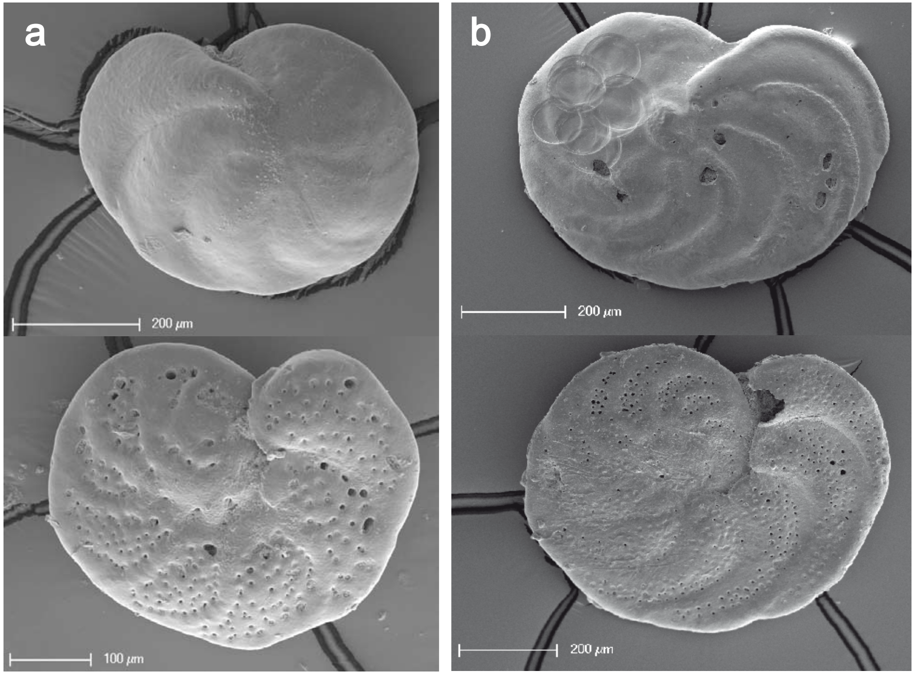

Fig. 3. Umbilical and spiral view of **(a)** *C. cf. wuellerstorfi* and **(b)** *C. wuellerstorfi* with laser ablation spots on the umbilical side (REM images, scale is given for size reference).

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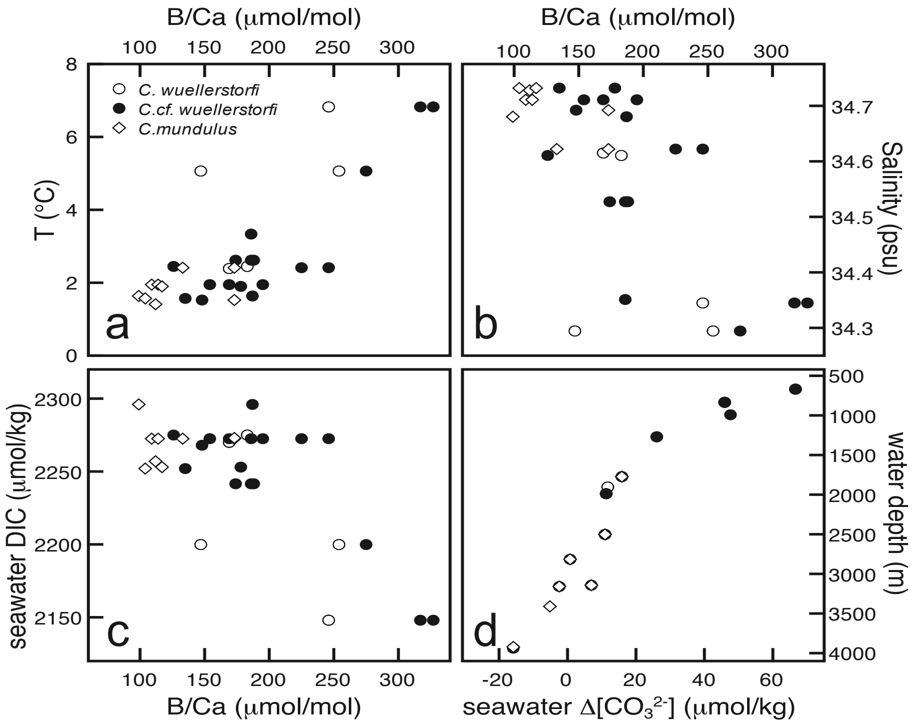

Fig. 4. Foraminiferal B/Ca vs. **(a)** temperature, **(b)** salinity, **(c)** seawater DIC and **(d)** seawater $\Delta[CO_3^{2-}]$ vs. water depth. Temperature and salinity data from Gersonde (2011) and Tiedemann (2012); DIC and seawater $\Delta[CO_3^{2-}]$ data from Key et al. (2004).

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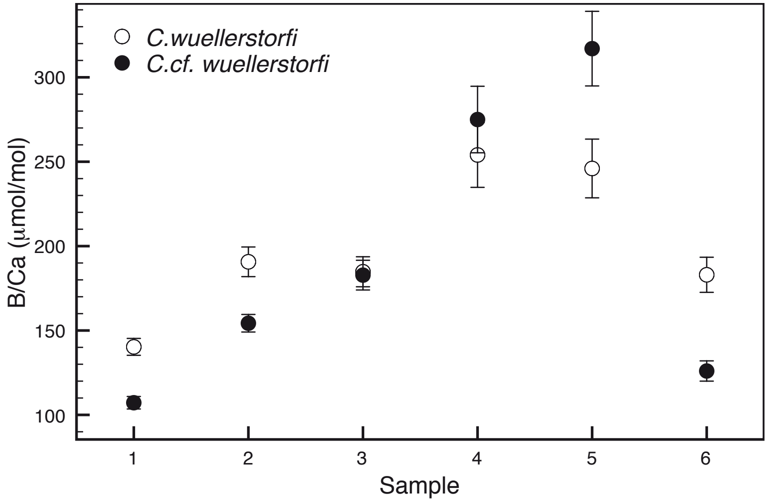

Fig. 5. Paired B/Ca analyses in *C. cf. wuellerstorfi* and *C. wuellerstorfi* for six samples (core top samples: PS75/104-2, 105-1, SO213 68-1, down core samples: PS75/100-4, 103-1). 2σ error bars display combined uncertainty of sample and standard measurements.

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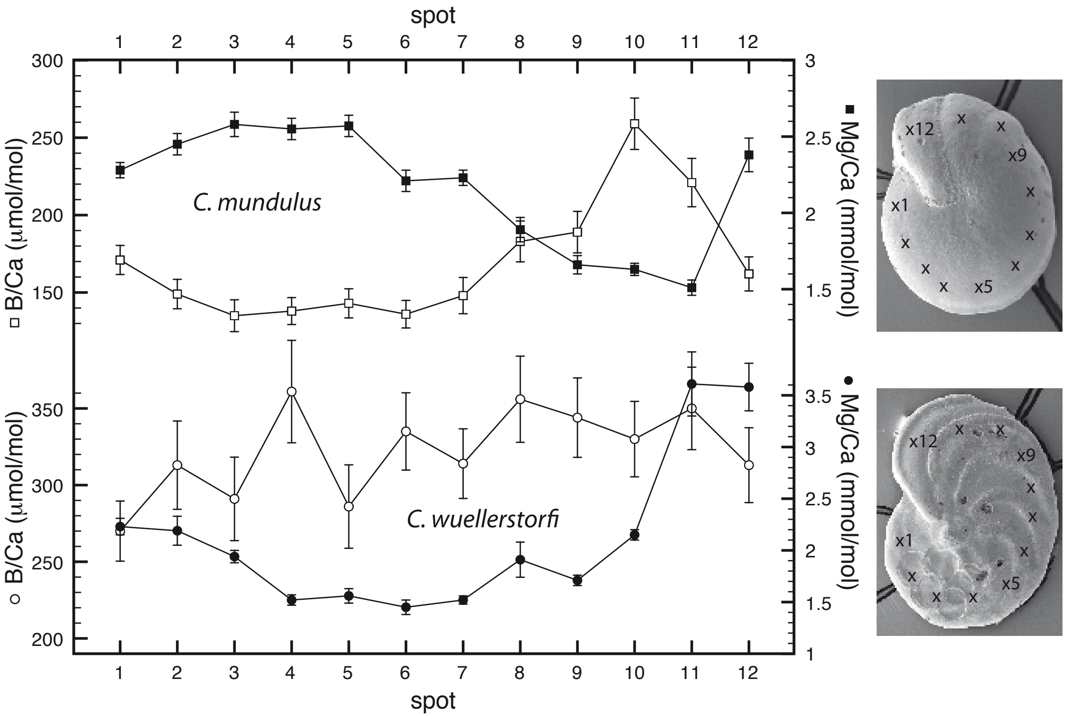

Fig. 6. B/Ca and Mg/Ca element profiles through *C. mundulus* (sample PS75/101-2_0cm, top panel) and *C. wuellerstorfi* (sample PS75/105-1_2cm, bottom panel); crosses indicate placement of laser ablation spots throughout the shells.

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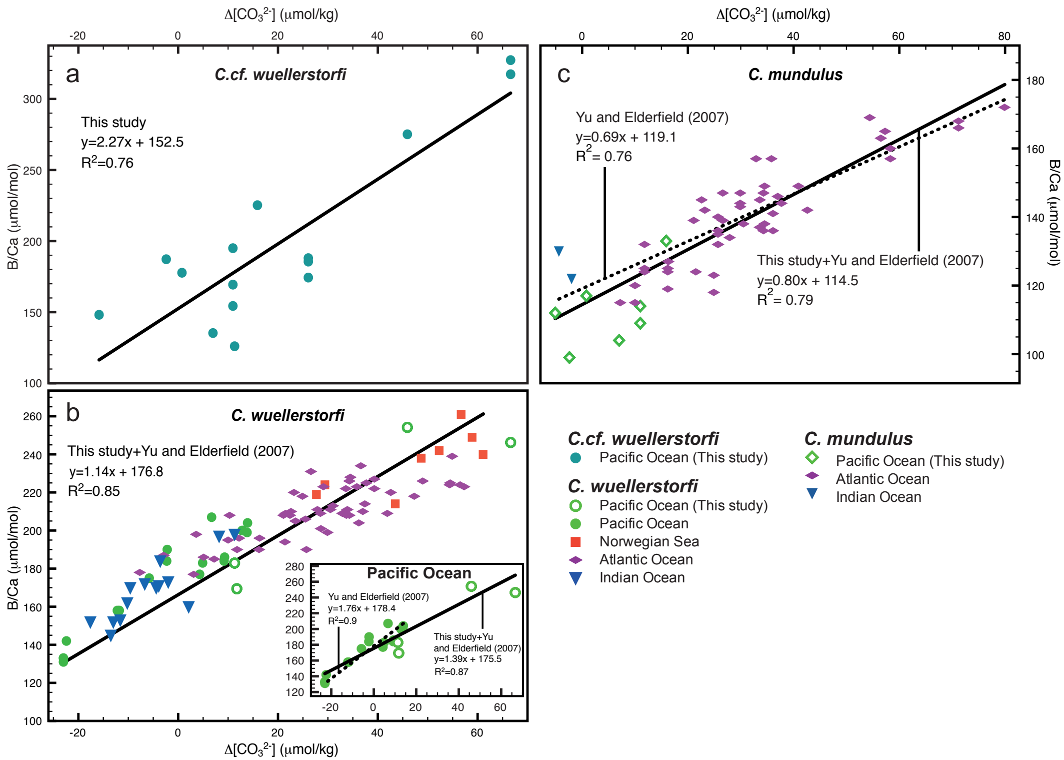

Fig. 7. Empirical relationship between foraminiferal B/Ca and the modern degree of calcite saturation in seawater (Δ[CO_3^{2-}]) for **(a)** *C. cf. wuellerstorfi*, **(b)** *C. wuellerstorfi* and **(c)** *C. mundulus*. The inset in **(b)** focuses on Pacific Ocean core tops. Data from Yu and Elderfield (2007) are given to allow comparison to calibrations from this study.

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