A core-top study of dissolution effect on B/Ca in *Globigerinoides sacculifer* from the tropical Atlantic: Potential bias for paleo-reconstruction of seawater carbonate chemistry

R. Coadic, F. Bassinot, E. Douville, and E. Michel
LSCE (CEA/CNRS/UVSQ), Domaine du CNRS, Gif-sur-Yvette, France
(bassinot@lsce.ipsl.fr)

D. Dissard
LOCEAN, Université Pierre et Marie Curie, Paris CEDEX 05, France

M. Greaves
Godwin Laboratory, Department of Earth Sciences, University of Cambridge, Cambridge, UK

[1] It has been recently shown that B/Ca in planktonic foraminiferal calcite can be used as a proxy for seawater pH. Based on the study of surface sediments (multi-cores) retrieved along a depth transect on the Sierra Leone Rise (Eastern Equatorial Atlantic), we document the decrease of B/Ca and Mg/Ca of *Globigerinoides sacculifer* shells with increasing water depth and dissolution. This effect of dissolution on B/Ca may potentially represent a severe bias for paleo-pH reconstructions using this species. Samples of *G. sacculifer* were analyzed independently at two laboratories for B/Ca and Mg/Ca. Both sets of results show a systematic decrease of B/Ca and Mg/Ca along the depth transect, with an overall loss of ~14 μmol/mol (~15%) for B/Ca and of ~0.7 mmol/mol (~21%) for Mg/Ca between the shallowest (2640 m) and the deepest (4950 m) sites. Because of this dissolution effect, surface water pH reconstructed from B/Ca of *G. sacculifer* decreases by ~0.11 units between the shallowest site and the deepest site, a magnitude similar to the expected glacial/interglacial surface water pH changes.

1. Introduction

[2] Boron isotopic composition of foraminifers has been used to reconstruct sea surface pH variations and estimate past atmospheric CO_2 changes for periods older than those covered by ice cores [e.g., *Spivack et al.*, 1993; *Sanyal et al.*, 1997; *Pearson and Palmer* 1999, 2000; *Palmer and Pearson*, 2003; *Hönisch and Hemming*, 2005]. However, the amount of material required to

perform accurate boron isotopic analyses makes it usually difficult to apply this method to mono-specific planktonic foraminifera samples, picked along marine sediment cores. Recently, it was demonstrated that planktonic foraminifera B/Ca ratio could be used as a proxy for surface seawater pH reconstruction [*Yu et al.*, 2007; *Ni et al.*, 2007; *Foster*, 2008; *Tripati et al.*, ; *Palmer et al.*, 2010].

[3] Both proxies, boron isotopic composition of marine carbonates and B/Ca ratio of foraminifera shells, are based on the speciation of boron in the ocean. In an aqueous solution, boron mainly exists as two species, boric acid $B(OH)_3$ and borate ion $B(OH)_4^-$, that have significantly different isotopic compositions. The relative proportion of these species is highly pH dependent. Boron is incorporated within the lattice of biogenic carbonates precipitated from the dissolved species present in seawater. Because the boron isotopic composition of these marine carbonates falls close to the isotopic composition of the dissolved borate ions, $B(OH)_4^-$ is thought to be the species chiefly incorporated in marine carbonates, following the mechanism proposed by *Hemming and Hanson* [1992]:

$$CaCO_3 + B(OH)_4^- = Ca(HBO_3) + HCO_3^- + H_2O \quad (1)$$

[4] It should be noted that recent studies have shown that boric acid could be also incorporated in marine carbonates. However, these studies were performed on inorganic calcite and deep-sea aragonite corals [*Klochko et al.*, 2009; *Rollion-Bard et al.*, 2011], not on foraminifera.

[5] The partition coefficient (K_D) of $B(OH)_4^-$ between sea water and the calcium carbonate is defined as

$$K_D = [B/Ca]_{CaCO3} / [B(OH)_{4-}HCO_{3-}]_{seawater} \quad (2)$$

[6] The use of B/Ca ratio of planktonic foraminifer shells as a pH proxy is based on the fact that the $[B(OH)_4^-/HCO_3^-]$ ratio of seawater is pH dependent [e.g., *Yu et al.*, 2007; *Allen et al.*, 2011]. Thus, if K_D is known, it is possible to estimate surface seawater pH from the measurement of B/Ca ratio in marine carbonates through the calculation of $[B(OH)_4^-/HCO_3^-]$:

$$\left[B(OH)_{4-}/HCO_{3-}\right]_{seawater} = [B/Ca]_{CaCO3}/K_D \quad (3)$$

[7] Modern calibration exercises based on core top material or derived from culture experiments have made it possible to study empirically the relationships between the B/Ca of several foraminifer shells and seawater $[B(OH)_4^-/HCO_3^-]$. Results suggest that K_D could be strongly species specific and temperature dependent [*Yu et al.*, 2007; *Foster*, 2008; *Allen et al.*, 2012a]. However, *Foster* [2008] and *Tripati et al.* [] found opposite temperature dependency for the same foraminifer species. When the temperature influence on K_D is confirmed and better estimated, measuring the foraminifera Mg/Ca (a temperature proxy) simultaneously with B/Ca will make it possible to correct for the potential temperature effect on paleo-pH reconstructions.

[8] Another key issue regarding the use of B/Ca ratio in foraminifer carbonate shells for paleoceanographic reconstructions is the possible bias associated with the partial dissolution of calcium carbonates at the seafloor. It is known that partial or selective dissolution has an impact on several geochemical paleo-environmental proxies, including $\delta^{11}B$ [e.g., *Spivack and You*, 1997; *Wara et al.*, 2003; *Hönisch and Hemming*, 2004], U/Ca ratio [*Russell et al.*, 1994, *Yu et al.*, 2008], Sr/Ca ratio [e.g., *Lohmann*, 1995; *Brown and Elderfield*, 1996], and Mg/Ca ratio [e.g., *Lohmann*, 1995; *Brown and Elderfield*, 1996; *Rosenthal et al.*, 2000; *Dekens et al.*, 2002; *Regenberg et al.*, 2006; *Nouet and Bassinot*, 2007]. A preliminary study performed by *Yu and Elderfield* [2007] concluded that B/Ca ratios of benthic foraminiferal calcite seem to be unaffected by dissolution at the seafloor. As far as planktonic foraminifera are concerned, this might not be the case. *Seki et al.* [2010], for instance, recently suggested that the B/Ca of *Globigerinoides sacculifer* might be affected by dissolution. However, their depth transect study is based on surface sediments obtained from the top of Ocean Drilling Program (ODP) sites. This does not constitute an optimal sedimentary material to perform calibration exercises on recently deposited shells since the sediment interface is not sampled properly through ODP coring. Conflicting apparently with *Seki et al.* results, Wara *et al.* (2003) found a negative correlation between their down-core B/Ca and size-normalized shell weight of *G. sacculifer*—a dissolution proxy—in ODP Site 806 (Ontong Java Plateau, Western Equatorial Pacific).

[9] In this study, we investigate the dissolution impact on planktonic foraminifera B/Ca ratio and its effect on surface water pH reconstructions. For that purpose, we analyzed B/Ca ratios of the planktonic species *G. sacculifer* picked from the upper 1 cm of short cores obtained with a multi-corer at seven sites along a depth transect on the Sierra Leone Rise (eastern equatorial Atlantic Ocean). Multi-corers are designed to sample surface sediments with minimal

disturbances, providing therefore an ideal sedimentary material for proxy calibration exercises and for studying the effect of early diagenesis and dissolution at the seafloor. Beside B/Ca, we also measured Mg/Ca, a ratio used for temperature reconstructions [e.g., *Elderfield and Ganssen*, 2000; *Cléroux et al.*, 2008; *Sadekov et al.*, 2009], which is also known to be sensitive to dissolution [e.g., *Brown and Elderfield*, 1996; *Rosenthal*, 2000; *Dekens et al.*, 2002]. B/Ca and Mg/Ca measured on *G. sacculifer* were compared to several qualitative dissolution proxies measured from the same samples.

2. Material and Methods

2.1. Site Locations and Hydrographic Settings

[10] During the 1998 winter cruise of the R/V *Knorr*, surface sediment samples were collected using a multi-corer at seven sites located along the Sierra Leone Rise (eastern equatorial Atlantic),

between ~2640 m and ~4950 m of water depth. Core locations are shown in Figure 1 and listed in Table 1. Because of the close vicinity of the seven sites, there are no significant differences in sea surface temperature (SST, $\leq 0.7\,°C$ difference between stations A and G), salinity (SSS, ≤ 0.3‰, difference between stations A and G) [World Ocean Atlas; *Boyer et al.*, 2009] or sea surface $[CO_3^{2-}]$ (289 ± 4 mol/k) obtained from the Global Ocean Data Analysis Project database (GLODAP) [*Key et al.*, 2004; *Sabine et al.*, 2005] (Figure 2).

[11] Dissolved carbon system speciation along the water column in the vicinity of the Sierra Leone Rise was estimated with the CO2calc software [*Robbins et al.*, 2010]. We run CO2calc with total alkalinity (ALK), temperature (T), salinity (S), nutrient levels, and pre-industrial total dissolved inorganic carbon (DIC) obtained from nearest GLODAP sites [*Key et al.*, 2004; *Sabine et al.*, 2005]. We used equilibrium constants K_1 and K_2 from *Mehrbach et al.* [1973], refit by *Dickson and*
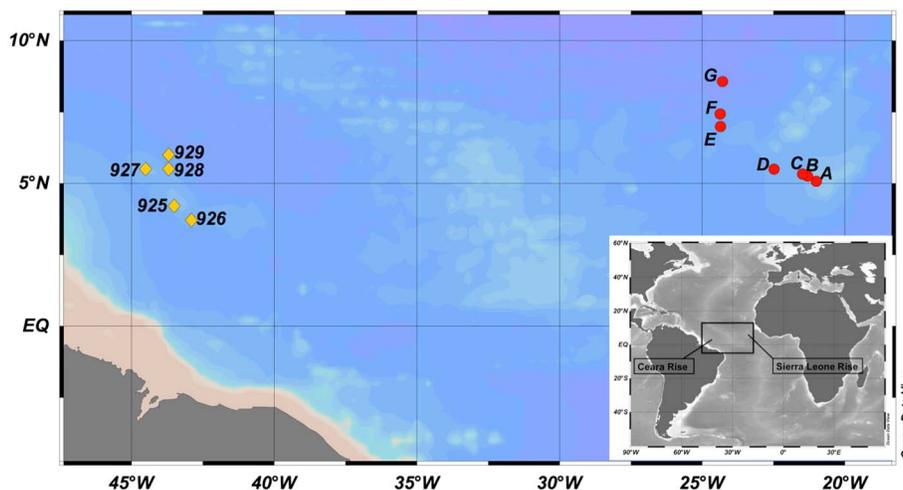

Figure 1. Location of sites on the Sierra Leone Rise (this study) and ODP sites from the Ceara Rise [*Seki et al.*, 2010].

Table 1. Location and Depth (m) of Sampling Sites

Station	Latitude	Longitude	Water depth (m)	Deepwater $\Delta[CO_3^{2-}]$ ($\mu mol \cdot kg_{sw}^{-1}$)	Cibicidoides Oxygen Isotopic Composition (‰ vs. VPDB)
A	5°07 N	21°01 W	2637	34	2.5 ± 0.06
B	5°25 N	21°31 W	3147	24	2.75 ± 0.16
C	5°32 N	21°48 W	3593	15	2.68 ± 0.12
D	5°50 N	22°48 W	4013	7	2.68 ± 0.17
E	7°00 N	24°36 W	4202	3	2.63
F	7°43 N	24°37 W	4750	−7	2.57 ± 0.04
G	8°57 N	24°29 W	4930	−11	2.75 ± 0.11

The carbonate ion composition of bottom waters ($\mu mol \cdot kg_{sw}^{-1}$) is estimated using the GLODAP data base (see section 2.4: Hydrographic data). *C. wullerstörfi* and *C. kullenbergi* oxygen isotopic analysis is expressed in ‰ versus VPDB. The reproducibility is given from 2 to 5 replicates.

Millero [1987], and K_{HSO4} from *Dickson* [1990]. To establish the relationship between pH and the $[B(OH)_4^-/HCO_3^-]$ of seawater, we calculated separately the concentrations of carbonate and borate ions for fixed DIC and salinity and at given temperatures and pH. Then, we expressed the $[B(OH)_4^-/HCO_3^-]$ ratio of seawater as a function of pH. Carbonate ion saturation at depth, ΔCO_3^{2-}, is defined as the difference between in situ carbonate ion concentration $[CO_3^{2-}]$ and the saturation $[CO_3^{2-}]_{sat}$, calculated using the solubility ratio of calcite Ω_C. For Sierra Leone Rise, we used data from nearby GLODAP sites (cruises 21, 23, and 46).

[12] Deep waters at the depths of the multi-corer sites show a large range of carbonate ion saturation relative to calcite, with ΔCO_3^{2-} dropping from $+34\,\mu mol \cdot kg^{-1}$ at the shallowest site (A) to -11 mol·kg^{-1} at the deepest one (G; Figure 3). Several studies have shown that carbonate dissolution in surface sediments starts well above the saturation level in the water column [e.g., *Emerson and*

Bender, 1981; *Regenberg et al.*, 2006] owing to the decay of organic matter during early diagenesis processes. *Regenberg et al.* [2006] recently showed that a noticeable increase in the dissolution of pelagic carbonates at the seafloor is observed when the ΔCO_3^{2-} of bottom water drops below ~ 15–$20\,\mu mol/kg$. Our set of multi-core tops provides, therefore, a promising material to study dissolution effects on both B/Ca and Mg/Ca ratios of planktonic foraminifer shells deposited on the Sierra Leone Rise.

2.2. Age Control and Foraminifer Selection

[13] Taking advantage of the depth transect, a number of studies have used gravity cores retrieved along the Sierra Leone Rise, either for paleoceanographic reconstructions [*Curry and Lohmann* 1986; 1990] or to analyze the dissolution effects on geochemical proxies such as Mg/Ca [*Rosenthal et al.*, 2000, *Dekens et al.*, 2002]. Oxygen isotope stratigraphy of these gravity cores indicated
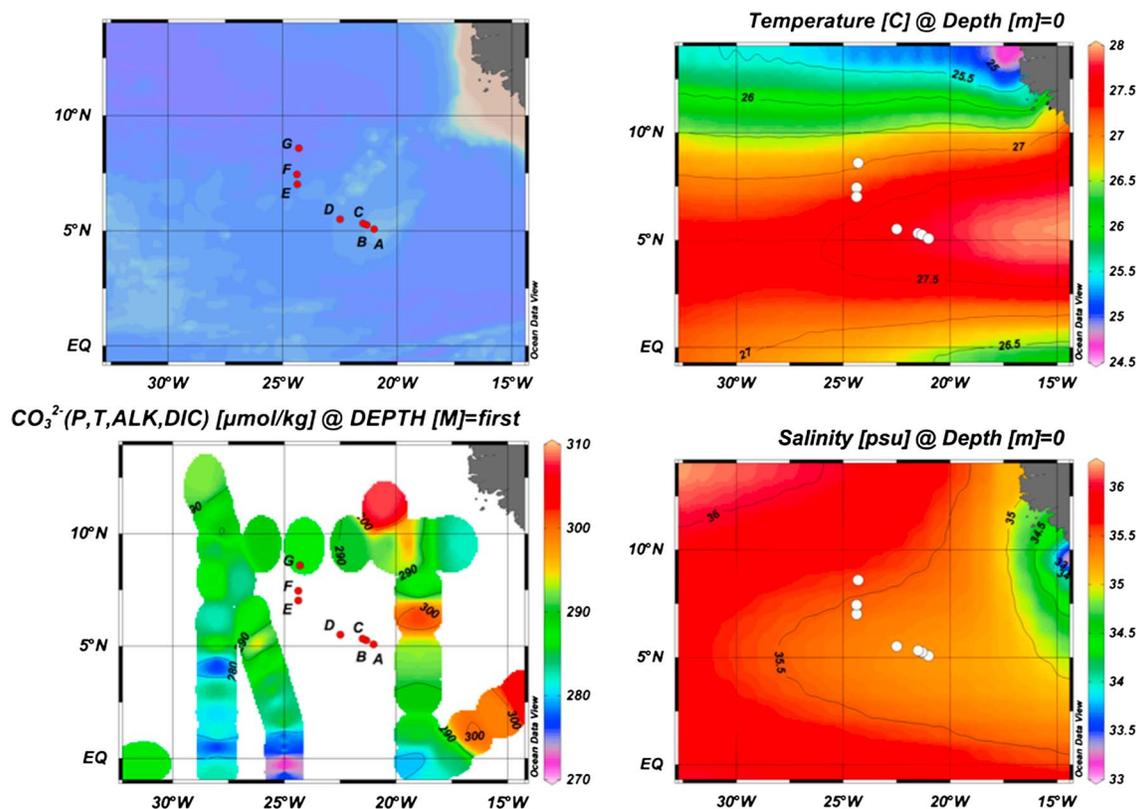

Figure 2. Surface water mean annual temperature and salinity over the Sierra Leone Rise obtained with the World Ocean Atlas 2009 [*Boyer et al.*, 2009] and surface water carbonate ion concentration calculated from the GLODAP data set [*Key et al.*, 2004]. Temperatures and salinities are from the World Ocean Atlas and represent a climatic average over past decades. Carbonate ion concentrations are calculated from the GLODAP data set following equilibrium constants preconized by *Dickson et al.* [2007]. As shown in the figure, only few, discrete data points are available. A mean value calculated for the Sierra Leone Rise area (18°W to 27°W, 3°N to 11°N) gives a $[CO_3^{2-}]$ of $289 \pm 4\,\mu mol/kg$ (1σ).
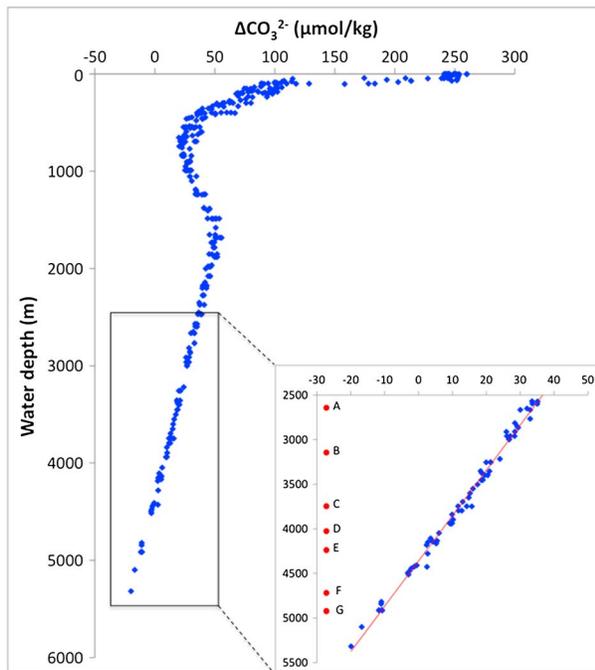
Figure 3. Water depth (m) versus ΔCO_3^{2-} ($\mu mol \cdot kg_{sw}^{-1}$) in the vicinity of the Sierra Leone Rise estimated from the GLODAP data set [*Sabine et al.*, 2005]. Figure inset represents the ΔCO_3^{2-} trend change between 2500 and 5000 m of water depth; red circles represent the station depths.

that Holocene values of benthic foraminifers *Cibicidoides wuellerstörfi* or *Cibicidoides spp* are in the range 2.5–2.8‰ [*Curry and Lohmann* 1986; 1990]. The small variability of benthic $\delta^{18}O$ along the transect is explained by the fact that sediments are bathed by North Atlantic Deep Water. Temperature along the depth transect decreases by no more than 0.5°C [World Ocean Atlas; *Boyer et al.*, 2009] corresponding to a 0.12‰ increase in calcite isotopic composition [*Shackleton et al.*, 1974]. Deep-water oxygen isotopic composition along the transect is also stable with 0.1‰ variation (GEOSECS) [*Östlund et al.*, 1987]. The sedimentation rates over the Sierra Leone Rise are rather low, with thickness of the Holocene section in the order of ~20 cm. To sample recent sedimentary material, we retrieved cores with a multi-corer and worked on the first centimeter of sediments, which is usually not well preserved through conventional coring. The upper first centimeter of each core was sampled and wet-sieved on a 150 μm mesh sieve. The coarse fraction was dried 12 h at 50°C and stored for analysis. *C. wuellerstörfi* and *C. kullenbergi* isotopic compositions were obtained at LSCE on an ISOPRIME mass-spectrometer. Four to five replicate analyses were performed at sites A, B, C, D, and G and two at sites E and F.

VPDB is defined with respect to the NBS19 calcite standard. The mean external reproducibility (1σ) of our carbonate standards is ±0.06‰ for $\delta^{18}O$ (measured NBS18 $\delta^{18}O$ value is -23.2 ± 0.2‰ VPDB). The *Cibicidoides* $\delta^{18}O$ values we obtained at stations A to G are remarkably homogeneous, falling all within the narrow range 2.5 to 2.75‰ (Table 1) and are similar to the Holocene values previously found in this area [*Curry and Lohmann*, 1986, 1990]. The homogeneity of our $\delta^{18}O$ data clearly indicates that bioturbation does not result in a noticeable upward mixing of glacial shells at any of our Sierra Leone Rise sites.

[14] The planktonic species *G. ruber* (sensu stricto) is frequently used in paleoeanographic studies because it is a shallow dwelling species, limited to the first 30 m of the water column. However, because *G. ruber* is very sensitive to dissolution, the deep sites of the Serra Leone Rise transect contain almost no intact shells of this species. In order to cover the full range of water depths and ΔCO_3^{2-} along the Sierra Leone Rise transect, we focused our study on *G. sacculifer*, a surface dwelling planktonic species, whose shells could still be found easily at the two deepest sites (F and G). We selected *G. sacculifer* specimens without the final sac-like chamber in order to avoid any potential bias linked to changing depth habitat during reproduction and/or to the development of gametogenic calcite.

[15] The *post mortem* precipitation of diagenetic calcite on foraminifer shells may potentially affect their trace element composition [e.g., *Boyle*, 1983]. Because dissolved Mg is 8 times more abundant than Ca in seawater, this diagenetic calcite is characterized by high Mg/Ca, as was clearly evidenced from recent studies conducted on foraminifer shells from the eastern Mediterranean Sea [*Boussetta et al.*, 2011; *Sabbatini et al.*, 2011]. In foraminifer shells from the Sierra Leone Rise, we could not detect diagenetic calcite overgrowth, neither through direct SEM observations [*Gehlen et al.*, 2004] nor through X-Ray diffractometry analyses [*Gehlen et al.*, 2005 *Nouet and Bassinot*, 2007]. Anomalously high Mg/Ca values were never detected during ICP-AES analyses performed on shells of different planktonic foraminifer species [e.g., *Nouet and Bassinot*, 2007; *Mathien-Blard and Bassinot*, 2009] or through trace element cartography of foraminifer shells using particle-induced X-ray emission [PIXE; *Gehlen et al.*, 2004]. We are confident, therefore, that there is no early diagenetic calcification of foraminifer shells in surface sediments from the Sierra Leone Rise.

2.3. Cleaning Method

[16] Two sets of samples were prepared for B/Ca and Mg/Ca measurements. The first was cleaned and analyzed at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE, Domaine du CNRS, Gif-sur-Yvette, France) and the second at the Godwin Laboratory for Palaeoclimate Research (University of Cambridge, United Kingdom). This comparative study was not performed as part of an inter-laboratory calibration exercise (which would have required more replicate analyses of carefully selected carbonate standards) but to make it possible to double check any potential change of B/Ca and Mg/Ca with increasing water depth of deposition along the Sierra Leone Rise. We used the same cleaning protocol for analyses conducted in the two laboratories [*Barker et al.* 2003] developed for Mg/Ca analyses.

[17] Approximately 25 to 35 individuals (typically ~500 µg of calcium carbonate) of *G. sacculifer* (without final sac-like chamber) were handpicked from the 300–355 µm size fraction and weighed using a precision microbalance. Samples were gently crushed in order to open the chambers and allow any chamber fill to be removed during the following cleaning steps. After crushing, clays were removed by successive Milli-Q water and ethanol or methanol ultrasonic washes, and an oxidative step (H_2O_2, 100 °C) was applied in order to remove organic matter. Subsequently, a dilute acid leach (0.001 M HNO_3) was performed in order to remove any contaminants that may have been adsorbed onto the shells. Finally, samples were dissolved in 300 µl (Godwin Laboratory) or 350 µl (LSCE) of 0.1 M HNO_3.

2.4. B/Ca and Mg/Ca Analyses

[18] In the following paragraphs, we provide key aspects of the protocol used both at the Godwin Laboratory and at LSCE for the determination of B/Ca and Mg/Ca in foraminiferal calcite by ICP-QMS. For further information, the reader is referred to the paper of *Yu et al.* [2005] in which the analytical protocol is described thoroughly.

[19] It is well known that a calcium matrix effect complicates achieving high levels of accuracy in the analysis of trace elements in foraminiferal calcite, either through Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) [*de Villiers et al.*, 2002] or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) [*Rosenthal et al.*, 1999; *Yu et al.*, 2005; *Harding et al.*, 2006;

Bourdin et al., 2011]. In order to overcome this Ca matrix effect, B/Ca and Mg/Ca ratios were determined directly from drift-corrected intensity ratios using external, matrix-matched, standards with a constant calcium concentration (100 ppm [Ca]), and known, variable B/Ca and Mg/Ca values. In this procedure, instead of regressing element intensity counts against elemental concentrations in calibration solutions, then obtaining elemental ratios from the calculated concentrations, the raw intensity ratios for B/Ca and Mg/Ca (corrected for blank intensity) are regressed directly against the B/Ca (µmol/mol) and Mg/Ca (mmol/mol) of the standard solutions. This "intensity ratio calibration" procedure is similar to that described by *Rosenthal et al.* [1999] and *de Villiers et al.* [2002]. For such a calibration method, multi-element stock standard solutions (with B and Mg, but including also Li, Al, Mn, Z, Sr, Cd, and U) were prepared gravimetrically by spiking a 10,000 µg/ml Ca standard with appropriate amounts of mono-elemental 1000 µg/ml certified ICP-MS grade stock solutions. The stock standards, prepared in large quantities, are stored carefully. Calibration solutions needed for analytical sessions are diluted to Ca 100 ppm on demand.

[20] In order to achieve this matrix-matched, intensity ratio calibration procedure, an aliquot (~50 µl) of each sample solution was diluted and its calcium concentration determined using an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). Based on these measurements, the calcium concentration of the remainder of each sample was adjusted to 100 ppm. These samples, adjusted to 100 ppm [Ca], were then run on an Inductively Coupled Plasma-Quadrupole Mass Spectrometer (ICP-QMS) for the determination of B/Ca and Mg/Ca. At LSCE, the ICP-QMS in use is an Xseries II from Thermo-Scientific, and at the Godwin Laboratory, it is an Elan DRC II from Perkin Elmer.

[21] Because boron is leached from glassware under acidic conditions, a mini cyclonic quartz spray chamber was used both at the LSCE and the Godwin Laboratory in order to reduce the boron background level. The tests performed by *Yu et al.* [2005] showed that the boron blank is substantially decreased, to ~5%, compared with ~30% when using a glass spray chamber. In order to minimize the memory effect, acid (0.1 M HNO_3) washout time between samples was set to at least 60 s. Given the limited foraminiferal sample size, small diameter tubing was used in conjunction with micro-concentric nebulizers. The nebulizer used at the Godwin Laboratory is an ESI MicroFlow

PFA-50 and that used at LSCE is an EPOND, PFA No-Break nebulizer (EP 2050–4250), both systems having an uptake rate of ~50 μl/min. Prior to each daily session of analyses, in order to avoid decreasing sensitivity along the session caused by Ca deposition on sampling cones, we performed a cone pre-conditioning procedure by injecting pure Ca solution (100 ppm) for 1–2 h [*Yu et al.*, 2005].

[22] Blank correction was ensured by measuring in each run aliquots of the same acid as used for sample dissolution and dilution. In both laboratories, one of the standard solutions (with B/Ca and Mg/Ca close to values found in foraminifers) is used as a drift-correction standard and analyzed every five samples. Drift along a typical analytical session (~6 h) is less than 5% for boron and 1% for magnesium. In the LSCE analytical protocol, we also measured, every 10 samples, the B/Ca ratio of a giant clam powder reference material (JCt-1), whose published B/Ca ratio of 184 μmol/mol [*Okai et al.*, 2004] is close to B/Ca values measured in foraminifers. A recent inter-calibration exercise was performed for minor and trace elements including the B/Ca ratio (Hathorne et al., manuscript in preparation, 2013) and LSCE mean value for standard JCt-1 was 189 μmol/mol, close to the resulting average value of 191 μmol/mol (from only three replying laboratories). After correction for any potential drift during the run, a final correction was applied to all the samples in order to match the average B/Ca of JCt to the value of 189 μmol/mol. At LSCE, based on ~100 replicate measurements of the giant clam powder reference material JCt-1,

the reproducibility is 3.5% for B/Ca measurements and is 1.5% for replicate Mg/Ca measurements of a reference standard solution. The long-term standard reproducibility at the Godwin Laboratory, monitored over 5 years, is 2.1% (r.s.d) for B/Ca and 0.9% for Mg/Ca, consistent with precisions of 4.2% and 1.4% measured over a 3 month period by *Yu et al.* [2005].

3. Results

[23] *G. sacculifer* Mg/Ca and B/Ca data obtained on the Sierra Leone Rise core tops are plotted versus water depth in Figures 4 and 5, respectively, and presented in Table 2. Values in the figures and in the table represent a mean of 5 to 6 replicates for analyses performed at LSCE and 2 to 3 replicates for analyses performed at the Godwin Laboratory. At the deepest station (G, 4950 m of water depth), dissolution had already removed the most fragile planktonic species (i.e., *G. ruber*) and weakened the remaining foraminifer tests. As a result, we could pick less *G. sacculifer* than for shallower stations, and station G results are a mean of only 2 replicates analyzed at each laboratory.

3.1. Profile of Mg/Ca Versus Water Depth

[24] Mg/Ca data obtained at LSCE and at the Godwin Laboratory are plotted in Figure 4. Mg/Ca values range between 3.5 and 2.7 mmol/mol. We cannot distinguish the two datasets from one another within the limit of the error bars. Such a good
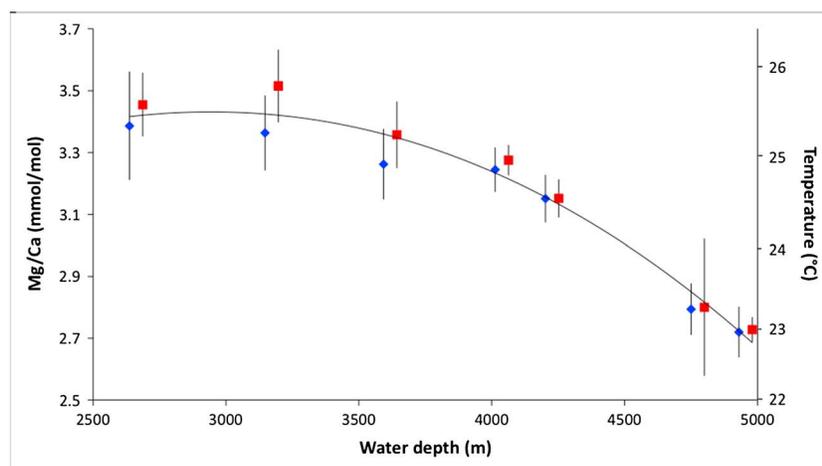
Figure 4. Profiles of *G. sacculifer* Mg/Ca (mmol·mol^{-1}) versus water depth (m). Mg/Ca values were obtained at the Godwin laboratory (red squares) and at LSCE (blue diamonds). Error bars represent the larger of the standard deviation of the replicates and standard reproducibility (1.5%). For more readability, Godwin's stations have been deepened by 50 m. Lines represent two possible trends for the data sets. The right axis shows temperature calculated from Mg/Ca *G. sacculifer* values.
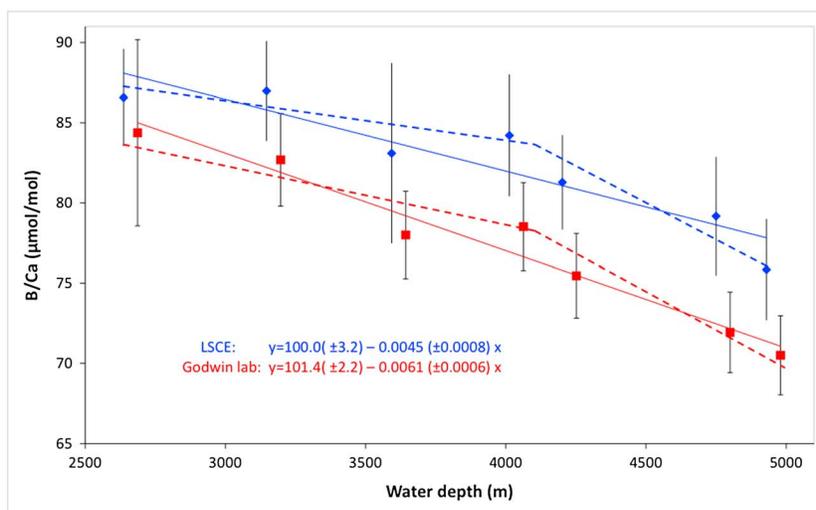
Figure 5. Profiles of *G. sacculifer* B/Ca (μmol·mol^{-1}) versus water depth (m). B/Ca values were obtained at the Godwin laboratory (red squares) and at LSCE (blue diamonds). Error bars represent the maximum between the standard deviation of the replicates and the standard reproducibility (3.5%). For more readability, Godwin's stations have been deepened by 50 m. Blue and red lines represent the possible trends for each set of results. Linear regression equations are also shown in the figure.

Table 2. B/Ca (μmol·mol^{-1}) and Mg/Ca (mmol·mol^{-1}) data, measured per station at both LSCE and the Godwin laboratory. Errors are the maximum between standard reproducibility ($\pm3.5\%$ at 2σ) and replicates standard deviation (2 SD)

Station	Water Depth (m)	Deep Water Δ [CO_3^{2-}] (μmol/kg$_{sw}^{-1}$)	LSCE, Gif-sur-Yvette			Godwin Laboratory, Cambridge		
			B/Ca (μmol/mol)	Mg/Ca (mmol/mol)		B/Ca (μmol/mol)	Mg/Ca (mmol/mol)	
A	2637	34	86.6 ± 3.0	3.45 ± 0.05	$n=5$	84.4 ± 5.8	3.45 ± 0.10	$n=3$
B	3147	24	87.0 ± 3.1	3.36 ± 0.12	$n=6$	82.7 ± 2.9	3.52 ± 0.12	$n=3$
C	3593	15	83.1 ± 5.6	3.26 ± 0.11	$n=6$	78.0 ± 2.7	3.36 ± 0.11	$n=3$
D	4013	7	84.2 ± 3.8	3.24 ± 0.07	$n=6$	78.5 ± 2.7	3.28 ± 0.05	$n=3$
E	4202	3	81.3 ± 3.0	3.15 ± 0.08	$n=6$	75.5 ± 2.6	3.15 ± 0.06	$n=3$
F	4750	−7	79.2 ± 3.7	2.79 ± 0.08	$n=5$	71.9 ± 2.5	2.80 ± 0.22	$n=3$
G	4930	−11	75.8 ± 3.2	2.72 ± 0.08	$n=2$	70.5 ± 2.5	2.73 ± 0.04	$n=2$

concordance of results between the two laboratories confirms the robustness of inter-laboratory calibration exercises performed on carbonate reference materials [*Greaves et al.*, 2008] and foraminifera samples [*Rosenthal et al.*, 2004]. The stations B and C, which show the largest Mg/Ca differences between the LSCE and Godwin Laboratory results, are the stations where standard deviations estimated from the replicates are also high. This may be due to sample heterogeneities between the multi-corer sub-samples (see section 4.1).

[25] The datasets show a significant decrease of Mg/Ca along the depth transect. An initial slight decrease in Mg/Ca with increasing depth is noticeable in the uppermost part of the transect (between

stations A and D). Over this depth interval, Mg/Ca of *G. sacculifer* decreases from 3.45 to 3.25 mmol/mol at a rate of approximately −7%/km, a decrease rate similar to that observed on the Mg/Ca of *G. ruber* picked from the same core tops [*Levi*, 2003]. The two deepest stations, however, show significantly lower Mg/Ca values (averaging 2.7 mmol/mol) compared to the shallow part of the depth profile. This suggests an increase of dissolution effects at mid-transect, with a change in slope of the Mg/Ca profile occurring around the depth of Station D or E (~4000 m of water depth). Given the error bars associated with the data, there are two different ways of modeling the Mg/Ca decrease with depth. The first one calls for a small decrease in Mg/Ca until a

threshold depth around 4000 m at which dissolution increases, and the second one calls for a steady increase of dissolution intensity along the whole depth profile.

3.2. B/Ca Versus Water Depth Profile

[26] The trend of B/Ca data with water depth observed in the LSCE and the Godwin Laboratory data is comparable although the values show an offset; the Godwin Laboratory B/Ca being ~6 μmol/mol lower in average than the LSCE values (Figure 5). Cross-calibration of the standard solutions used at LSCE and the Godwin Laboratory showed that B/Ca standard solutions were approximately 2.5 μmol/mol lower at Cambridge than at LSCE. Offset of either profile by this amount would bring the two data sets within the limits of the error bars over the whole depth profile. Divergence of the linear trends with depth through the data from the two laboratories can be accounted for by the variability within the two sets of analytical data. Means and standard deviations plotted in Figure 5 (as well as linear regression equations and their uncertainties) were calculated using all of the B/Ca analyses obtained at LSCE and the Godwin Laboratory, with no analyses rejected for statistical reasons. Rejection of individual data points as outliers would be sufficient for the slopes of linear regression lines to be within error of each other. Recently, *Allen et al.* [2012b] reported a systematic offset between Rutgers University B/Ca data and those from Godwin laboratory, but the causes for such an offset were not discussed. An inter-laboratory exercise mainly dedicated to Sr/Ca and Mg/Ca ratios for JCt-1 (Hathone et al., in preparation) revealed three scattered values for B/Ca ratio from 184 to 206 μmol/mol. The question of inter-laboratory coherency clearly calls for a more advanced international calibration exercise dedicated to B/Ca, similar to that achieved for Mg/Ca analyses on foraminifers [*Rosenthal et al.*, 2004]. Such an exercise would also make it possible to identify and promote the use of standard carbonates with known B/Ca ratios (coherent with levels typically found in foraminifers), in order to improve inter-laboratory analytical consistency (a similar exercise was recently performed for Mg/Ca analyses in foraminifers [*Greaves et al.*, 2008]).

[27] Given the data available, it is beyond the scope of the present paper to investigate further the causes for the difference in foraminiferal B/Ca measurements between the two laboratories. As far as dissolution effects are concerned, and allowing for

the ~6 μ/mol offset between *G. sacculifer* data obtained at the LSCE and the Godwin Laboratory, it is crucial to note that both datasets clearly document a decrease in B/Ca with increasing water depth of deposition, with a similar amplitude of ~12 μ/mol (from 84.4 to 70.5 μ/mol and 87 to 75.8 μ/mol from stations A to G, for Godwin Laboratory and LSCE, respectively). Thus, similar to what is observed for the Mg/Ca profile (see above), the B/Ca values at the deepest stations significantly depart from the values measured at the shallower sites.

[28] The *G. sacculifer* B/Ca profile along the Sierra Leone Rise obtained at the Godwin Laboratory suggests a rather linear decrease of B/Ca with increasing water depth of deposition (Figure 5). Within the limit of the error bars, a linear regression could also be fitted to the LSCE data, although the particularly low values found at the deepest stations may suggest a more complex evolution in which B/Ca of *G. sacculifer* decreases only slightly from station A to station D and shows a more drastic drop below about 4000 m (Figure 5). Such a two-step evolution is similar to that shown by the *G. sacculifer* Mg/Ca profile along the Sierra Leone Rise (Figure 4). Given the error bars associated to B/Ca measurements, it is not possible to decipher confidently between the "linear scenario" and the "two-step scenario". But the important aspect as far as this study is concerned is that both the LSCE and the Godwin Laboratory data show that B/Ca of *G. sacculifer* decreases along the Sierra Leone Rise depth transect.

4. Discussion

4.1. Dissolution Along the Sierra Leone Rise Depth Transect

[29] Dissolution of foraminifer shells at the seafloor is a complex phenomenon that depends on the combination of various factors such as (i) the sensitivity of foraminifer species towards dissolution [e.g., *Berger*, 1968], (ii) the saturation state of bottom water relative to calcium carbonate [e.g., *Broecker et al.*, 2001; *Dekens et al.*, 2002; *Marchitto et al.*, 2005; *Regenberg et al.*, 2006], and (iii) the oxidation of organic matter within the first few millimeters to centimeters of the sediment and the resulting acidification of pore water [e.g., *Emerson and Bender*, 1981]. In order to investigate whether depth-related changes in Mg/Ca and B/Ca profiles can be assigned to a dissolution imprint, we compared our trace element data with three dissolution proxies analyzed on the same Sierra

Leone Rise samples [Figure 6; data from this study and from *Gehlen, et al.*, 2005]. (i) The first proxy is the relative amount (weight percentage) of the coarse, >150 μm size fraction [*Gehlen et al.*, 2005]. This coarse fraction is chiefly foraminifer dominated. The decreasing coarse fraction percent with depth results from the fragmentation of foraminifer shells with increasing dissolution [i.e., *Le and Shackleton*, 1992; *Bassinot et al.*, 1994; *Gehlen et al.*, 2005]. (ii) The second proxy is the weight of size-normalized *G. sacculifer* shells picked for this study in the 300–355 μm size fraction. As evidenced from other studies performed on surface sediments, the weight of size-normalized foraminifer shells decreases with the loss of carbonate through dissolution [e.g., *Broecker and Clark*, 2001; *Rosenthal and Lohmann*, 2002; *Bassinot et al.*, 2004]. (iii) The third proxy is based on the XRD determination of calcite crystallinity of the >150 μm coarse fraction [*Gehlen et al.*, 2005]. As dissolution proceeds, the poorly crystallized calcite is removed preferentially, resulting in the improvement of the crystallinity of the remaining material, estimated from the thinning of the main calcite peak (104) in powder X-ray diffractograms.

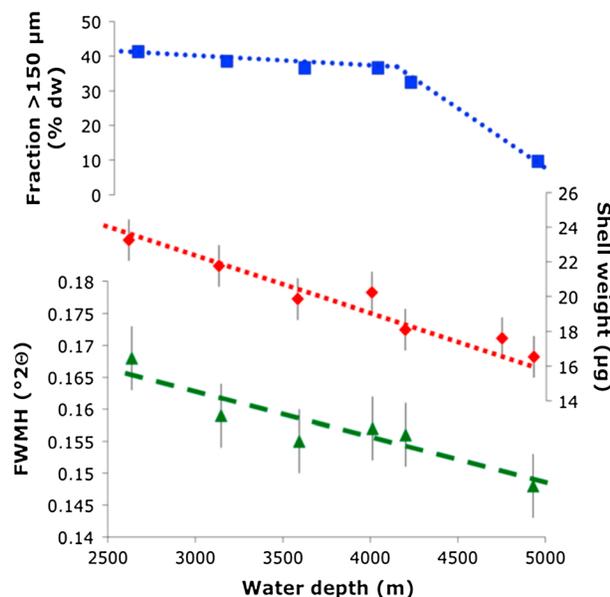[30] The depth profiles of these three dissolution proxies clearly confirm that increase in dissolution

plays a significant role in the evolution of pelagic carbonates retrieved from the tops of multi-cores along the Sierra Leone Rise slope (Figure 6). There are, however, differences between the profiles which may reflect either the various proxy responses or sediment heterogeneity. Such sediment heterogeneity could result, for instance, from the fact that supra-lysoclinal dissolution is likely associated to the decay of organic matter whose spatial distribution is patchy. The coarse fraction content suggests the existence of a significant change in the dissolution profile, with a knee at around ~4000 m of water depth, similar to what is observed on the Mg/Ca profile and possibly also in the B/Ca profile obtained at LSCE (see section 3.2). The two other proxies (crystallinity and shell weight) show a more constant evolution with increasing water depth (Figure 6).

[31] These three proxies (crystallinity, >150 μm and *G sacculifer* shell weight) are indicators of dissolution intensity, but they are also affected by other parameters such as, for instance, sea surface $[CO_3^=]$, which has been proposed as a control on the initial thickness and weight of planktonic foraminifer tests [*Barker and Elderfield*, 2002]. We performed a Principal Component Analysis (PCA) in order to extract the variance common to all three proxies, a component which should better represent the dissolution effect. The first principal component (PC1) explains 94% of the total variance. Among the three proxies, it is the normalized size weight of *G. sacculifer* which shows the strongest correlation to PC1 ($R^2 = 0.94$), with the percent coarse fraction (>150 μm) showing the lowest ($R^2 = 0.88$).

4.2. Effect of Dissolution on *G. sacculifer* B/Ca and Mg/Ca

[32] We performed Reduced Major Axis (RMA) regressions to test the correlation between our two sets of B/Ca data and (i) *G. sacculifer* size normalized shell weights and (ii) PC1. The correlations between B/Ca and shell weight or PC1 remain always high, with R^2 ranging from ~0.8 to 0.99, when the slopes and intercepts are allowed to vary $\pm 2.6\sigma$ around their mean value (95% confidence interval). These strong and robust correlations between B/Ca data and the dissolution proxies clearly confirm that B/Ca changes along the Sierra Leone Rise are chiefly explained by dissolution effects.

[33] Our results show a clear decrease of B/Ca along the depth transect. However, within the limits of the error bars, it is not possible to see whether the decrease is linear with increasing water depth or

Figure 6. Profiles of three dissolution proxies versus water depth (m): (i) Relative amount of fraction >150 μm (% dry weight) (top panel, blue squares), (ii) shell weight (μg) of *G. sacculifer* picked from our samples (middle panel, red diamonds), and (iii) full width at half maximum (FWMH, °2θ) of the calcite X-ray diffraction peak (bottom panel, green triangles).

whether there is a change in the slope at about ~4000 m (see above). The Mg/Ca profiles obtained at the LSCE and the Godwin Laboratory, on the other hand, unambiguously suggest an enhanced rate of Mg loss with water depth at ~4000 m. This water depth corresponds to the depth below which the saturation level of bottom water relative to calcite (ΔCO_3^{2-}) drops below ~10 µmol/kg along the Sierra Leone Rise (see Figure 3). This seems to be in good agreement, therefore, with previous studies which have shown that there exists a threshold for supralysoclinal dissolution of pelagic carbonates at around ~15–20 µmol/kg [*Regenberg et al.*, 2006].

[34] *Seki et al.* [2010] produced a planktonic foraminifer B/Ca profile along a depth transect on Ceara Rise (west equatorial Atlantic Ocean). They studied the evolution of $\delta^{11}B$ and B/Ca of *G. sacculifer* with water depth on the upper part of five ODP sites (sites 925 to 929, water depths ranging from 3050 to 4350 m). They found that $\delta^{11}B$ of *G. sacculifer* declines by ~0.7‰ and B/Ca declines by ~10 µmol/mol (from 86 to 76 µmol/mol) from the shallowest station to the deepest station (Figure 7). They associated these declines with the bottom water saturation relative to $CaCO_3$ and concluded that they were caused by partial dissolution of foraminifera tests in deep water and at low calcite saturation. In order to compare their data with ours, we plotted their B/Ca values as a function of ΔCO_3^{2-} calculated in nearby sites from the GLODAP database (Figure 8). Similar to what we observed for the B/Ca data sets from the Sierra Leone Rise, the plot of Ceara Rise B/Ca data versus ΔCO_3^{2-} clearly shows the decrease of B/Ca with decreasing ΔCO_3^{2-} (increasing water depth).

[35] In conclusion, the clear decrease of B/Ca of *G. sacculifer* with increasing water depth of

deposition along the Sierra Leone Rise corresponds to a relationship between the decreasing B/Ca and bottom water ΔCO_3^{2-}, similar to that observed also from a Ceara Rise depth transect [*Seki et al.*, 2010]. This clearly suggests that B/Ca of *G. sacculifer* is affected by dissolution. Analogous to what was observed for Mg [e.g., *Brown and Elderfield*, 1996; *Dekens et al.*, 2002; *Rosenthal and Lohmann*, 2002; *Nouet and Bassinot*, 2007], more concentrated B calcite appears to be preferentially removed as dissolution occurs, resulting in remaining shells with reduced B/Ca ratios.

4.3. Impact of Dissolution-induced Changes of B/Ca and Mg/Ca on pH Reconstruction Using *G. sacculifer*

[36] We have shown that both the B/Ca and Mg/Ca compositions of *G. sacculifer* are subject to dissolution. Since the partition coefficient of $B(OH)_4^-$ between sea water and calcium carbonate (K_D) seems to be affected by temperature [e.g., *Foster*, 2008; *Tripati et al.*, ; *Allen et al.*, 2011], the use of B/Ca and Mg/Ca for paleo-surface pH reconstructions can be biased both through the direct dissolution effect on B/Ca as well as through the K_D computation using the Mg/Ca thermometer (which can also be biased by dissolution). In this section, taking the deepest station G as an example, we evaluate such a bias on pH evaluation in relation (i) to the Mg/Ca-based estimation of K_D and (ii) to the B/Ca ratio.

[37] Lacking plankton tow or sediment trap material in the studied area, we assumed that station A (the shallowest site of the transect) has not suffered significantly from dissolution and could represent
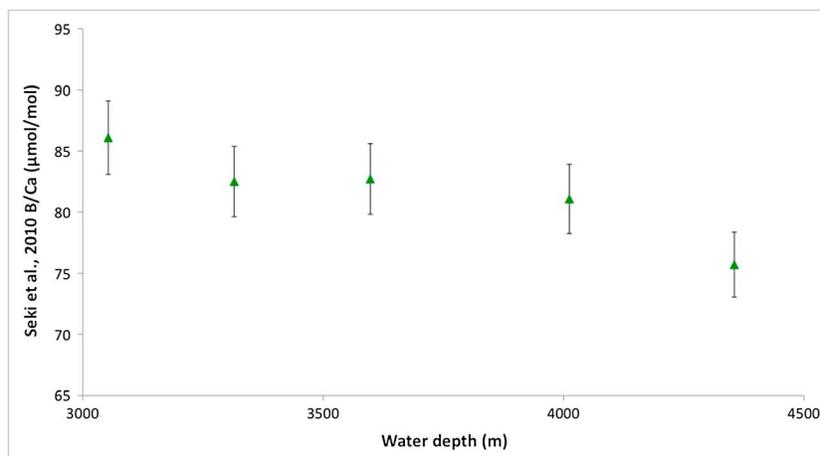

Figure 7. *G. sacculifer* B/Ca versus water depth obtained on a depth transect along Ceara Rise (west equatorial Atlantic ocean) based on core tops from five ODP sites [*Seki et al.*, 2010]. Errors bars are ±4 µmol/mol.
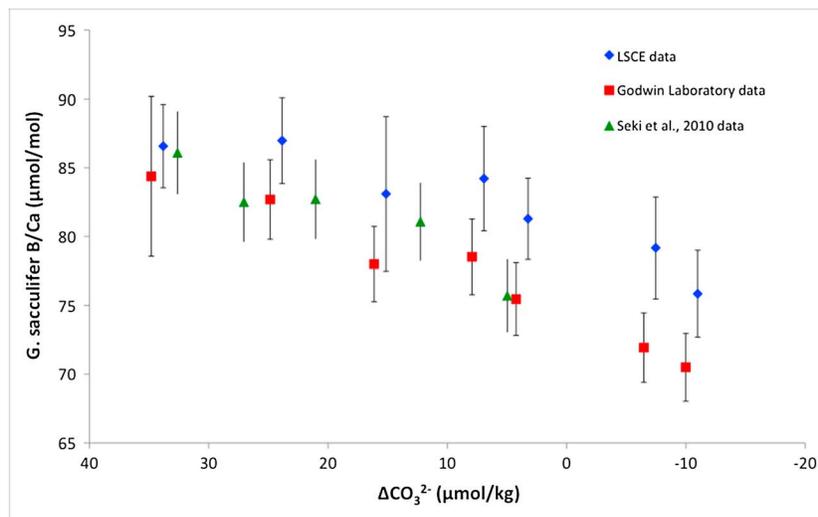
Figure 8. Comparison of *G. sacculifer* B/Ca profiles obtained on two different depth transects: (i) Sierra Leone Rise (blue diamonds for LSCE data and red squares for Godwin Laboratory data, this work) and (ii) Ceara Rise (green triangle) [*Seki et al.*, 2010]. In order to compare the B/Ca evolutions, B/Ca values are plotted versus bottom water ΔCO_3^{2-} estimated with CO_2calc software using GLODAP nearby sites. For more readability, ΔCO_3^{2-} values for Godwin laboratory data were increased by 1 μmol/kg.

a reference (non-dissolved) end-member for B/Ca and Mg/Ca. This assumption is based on the high level of ΔCO_3^{2-}, 35 μmol/kg, at this water depth (Figure 3), well above the average ΔCO_3^{2-} critical value of 15–20 μmol/kg below which dissolution severely increases in modern pelagic deposits [*Regenberg et al.*, 2006].

[38] We used the calibration of *Anand et al.* [2003] to calculate the sea-surface temperature (*T*, in °C) for *G. sacculifer* without sac-like chamber:

$$T = \ln(\text{Mg/Ca}/0.347)/0.09 \qquad (4)$$

[39] The reconstructed temperature of 25.5 °C for station A agrees within 3% with the annual mean temperature of the upper layer of the ocean upon the Sierra Leone Rise [World Ocean Atlas; *Boyer et al.*, 2009]. Due to the dissolution effect on Mg/Ca, station G shows a lower reconstructed temperature of 22.9 °C. This 2.6 °C difference with Mg/Ca-T for station A is much higher than the Atlas-derived temperature difference between the two sites (0.7 °C).

[40] The exact temperature effect on the K_D for *G. sacculifer* is still under debate [*Yu et al.*, 2007; *Foster*, 2008; *Tripati et al.*,]. Among the available K_D calibrations, that of *Foster* [2008], used with our B/Ca data, provided us with reconstructed surface water $[B(OH)_4^-/HCO_3^-]$, and subsequent pH

estimates, that were the closest to modern pH values obtained from the GLODAP database. The potential temperature dependence (*T*) of the K_D is expressed as [*Foster*, 2008]

$$K_D = -0.0654T + 3.0661 \qquad (5)$$

[41] We used *G. sacculifer* B/Ca to reconstruct the pH at stations A and G based on the specific, temperature-dependent relationship between pH and the $[B(OH)_4^-/HCO_3^-]$ of seawater (Figure 9) and the K_D coefficients estimated for stations A and G based on Mg/Ca-reconstructed temperatures. Using this method, the drop of *G. sacculifer* B/Ca and Mg/Ca values between station A and station G translates into an estimated pH drop of about 0.11 units (8.13 to 8.02) when using B/Ca data obtained at the LSCE and a pH drop of about 0.11 units also (8.09 to 7.98) when considering the B/Ca data from the Godwin Laboratory. The Mg/Ca decrease due to dissolution contributes for ~25% of this reconstructed pH difference, whereas the B/Ca decrease contributes for ~75%.

[42] As can be readily seen, the dissolution-induced change in B/Ca results in a pH difference between the upper part and the lower part of the transect (~0.11 pH unit) with a similar order of magnitude as the expected glacial/interglacial surface water pH changes [*Sanyal et al.*, 1997; *Hönisch and Hemming*, 2005]. Because glacial-interglacial changes in oceanic
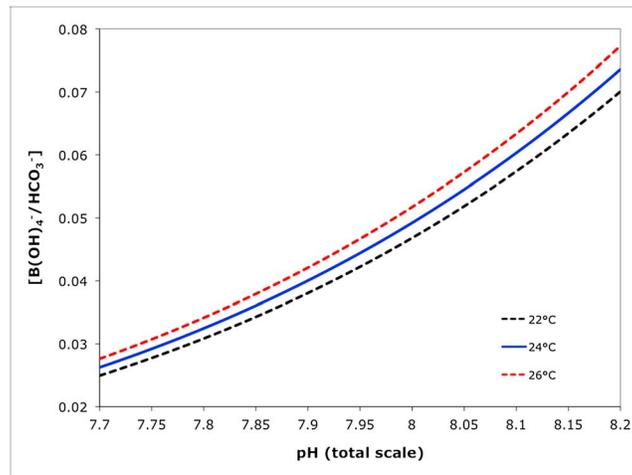
Figure 9. Variations of $[B(OH)_4^-/HCO_3^-]$ with seawater pH assuming constant DIC ($2000\,\mu mol\cdot kg^{-1}$), salinity (35.9 psu) and $[B]_{tot}$ ($434\,\mu mol\cdot kg^{-1}$), but with differing temperature (°C).

circulation and carbon reservoirs have induced changes in carbonate saturation and lysocline depth [e.g., *Farrell and Prell*, 1989; *Bassinot et al.*, 1994; *Hodell et al.*, 2001], one can expect that if not corrected for dissolution, the paleo-pH reconstructions of surface water using *G. sacculifer* B/Ca ratios can be substantially biased.

4.4. A Potential Dissolution Correction Approach for Planktonic Foraminifer B/Ca?

[43] Several authors have used the size-normalized weight of planktonic foraminifers as a proxy for quantifying past dissolution intensity [e.g., *Lohmann*, 1995; *Broecker and Clark*, 2001]. *Rosenthal and Lohmann* [2002] used this proxy to develop a correction approach for dissolution effects on the Mg/Ca thermometer, allowing for more accurate paleo-temperature reconstructions of the surface ocean. In a similar way, one could envision development of a procedure to correct B/Ca for dissolution effects on *G. sacculifer* using its size-normalized shell weight as a dissolution proxy. However, recent studies have suggested that the initial shell weight of several planktonic foraminifer species may co-vary with surface water $[CO_3^=]$ and, therefore, pH [e.g., *Lohmann*, 1995; *Barker* and *Elderfield*, 2002; *Bijma et al.*, 2002]. In other words, such a proxy used to correct B/Ca for dissolution bias would not be independent from past variations of surface water pH that one wants to reconstruct.

[44] Another way to correct for dissolution effects on the planktonic foraminifer Mg/Ca and B/Ca data could be the use of benthic foraminiferal B/Ca obtained on the same samples. *Yu and Elderfield*

[2007] showed that the B/Ca of benthic foraminifers is linearly linked to the carbonate ion saturation of bottom waters and is not affected by dissolution. Since the post-depositional dissolution of planktonic foraminifers is related to bottom water ΔCO_3^{2-}, it should be possible to use B/Ca measured from benthic foraminifer to estimate ΔCO_3^{2-} and correct for the dissolution effect on *G. sacculifer* foraminifer B/Ca. The principal difficulty of this correction approach is the lower abundances of benthic compared to planktonic foraminifers. However, it has the advantages that it is quantitative and independent of sea surface conditions. This approach will be tested in a future research project.

5. Conclusion

[45] Mg/Ca and B/Ca of *G. sacculifer* retrieved from multi-core tops along the Sierra Leone Rise (i) confirm the well-known influence of dissolution on Mg/Ca ratio of planktonic foraminifera and (ii) unambiguously show that B/Ca of *G. sacculifer* is also sensitive to post-depositional dissolution. The reconstruction of surface seawater pH from our B/Ca and Mg/Ca data reveals a difference of roughly 0.11 pH units between the shallowest and the most dissolved core top samples along the Sierra Leone Rise, which is the order of magnitude expected for glacial-interglacial pH changes. For paleo-pH reconstruction, a correction procedure is therefore mandatory if one wants to quantify the surface water pH changes over different timescales using this planktonic species.

Acknowledgments

References

Allen, K.A., B. Hönisch, S.M. Eggins, and Y. Rosenthal (2011), Environmental controls on B/Ca in calcite tests of the tropical planktic foraminifer species *Globigerinoides ruber* and *Globigerinoides sacculifer*, *Earth Planet. Sci. Lett.*, *351–352*, 270–280.

Allen, K.A., B. Hönisch, S. Eggins, and Y. Rosenthal (2012a), The planktic foraminiferal B/Ca proxy for seawater carbonate chemistry: A critical evaluation, *Earth Planet. Sci. Lett.*, *345–348*, 203–211.

Allen, K.A., B. Hönisch, S. Eggins, and Y. Rosenthal (2012b), Environmental controls on B/Ca in calcite tests of the tropicaal planktic foraminifer species *Globigerioides ruber* and *Globigerioides sacculifer*, *Earth Planet. Sci. Lett.*, *351–352*, 270–280.

Anand, P., H. Elderfield, and M. Conte (2003), Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series, *Paleoceanography*, *18*, 1050, doi:10.1029/2002PA000846.

Barker, S., and H. Elderfield (2002), Foraminiferal calcification response to glacial-interglacial changes in atmospheric CO₂, *Science*, *297*(5582), 833–836.

Barker, S., M. Greaves, and H. Elderfield (2003), A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry, *Geochem. Geophys. Geosyst. 4*, doi:10.1029/2003GC000559.

Bassinot, F. C., L. D. Labeyrie, E. Vincent, X. Quidelleur, N. J. Shackleton, and Y. Lancelot (1994), The astronomical theory of climate and the age of the Brunhes-Matuyama magnetic reversal, *Earth Planet. Sci. Lett.*, *126*, 91–108.

Bassinot F. C., F. Mélières, M. Gehlen, C. Levi, L. Labeyrie (2004), Crystallinity of foraminifera shells: A proxy to reconstruct past bottom water CO₃⁼ changes?, *Geochem. Geophys. Geosyst.*, *5*, Q08D10, doi:10.1029/2003GC000668.

Berger, W. H. (1968), Planktonic foraminifera—Selective solution and paleoclimatic interpretation, *Deep-Sea Res.*, *15*(1), 31–43.

Bijma, J., B. Hönisch, and R. Zeebe (2002), Impact of the ocean carbonate chemistry on living foraminiferal shell weight: Comment on "Carbonate ion concentration in glacial-age deep waters of the Caribbean Sea" by W.S. Broecker and E. Clark, *Geochem. Geophys. Geosyst.*, *3*(11), 1064, doi:10.1029/2002GC000388.

Bourdin C., E. Douville, and D. Genty (2011), Alkaline-earth metaland rare-earth element incorporation control by ionic radius and growth rate on a stalagmite from the Chauvet Cave, Southeastern France, *Chem. Geol.*, *290*(1–2) 1–11.

Boussetta, S., F. Bassinot, A. Sabbatini, N. Caillon, J. Nouet, N. Kallel, H. Rebaubier, G. Klinkhammer, and L. Labeyrie (2011), Diagenetic Mg-rich calcite in Mediterranean sediments: Quantification and impact on foraminiferal Mg/Ca thermometry, *Mar. Geol.*, *280* (1–4), 195–204, doi:10.1016/j.margeo.2010.12.011.

Boyer, T. P., et al. (2009), World Ocean Database 2009, *NOAA Atlas NESDIS*, 66. U.S. Department of Commerce. NOAA. National Environmental Satellite, Data, and Information Service: Silver Spring. 219 pp (+2 CD).

Boyle, E. A. (1983), Manganese carbonate overgrowths on foraminifera tests, *Geochim. Cosmochim. Acta*, *47*(10), 1815–1819.

Broecker, W. S., and E. Clark (2001), An evaluation of Lohmann's foraminifera weight dissolution index, *Paleoceanography*, *16*(5), doi:10.1029/2000PA000600.

Broecker, W. S., R. Anderson, E. Clark, and M. Fleisher (2001), Record of seafloor CaCO₃ dissolution in the equatorial Pacific, *Geochem. Geophys. Geosyst.*, *2*(6), doi:10.1029/2000GC000151.

Brown, S. J., and H. Elderfield (1996), Variations in Mg/Ca and Sr/Ca ratios of planktonic foraminifera caused by postdepositional dissolution: Evidence of shallow Mg-dependent dissolution, *Paleoceanography*, *11*(5), 543–551.

Cléroux, C., E. Cortijo, P. Anand, L. Labeyrie, F. Bassinot, N. Caillon, and J.-C. Duplessy (2008), Mg/Ca and Sr/Ca ratios in planktonic foraminifera: Proxies for upper water column temperature reconstruction, *Paleoceanography*, *23*, PA3214, doi:10.1029/2007PA001505.

Curry, W. B., and G. P. Lohmann (1986), Late Quaternary carbonate sedimentation at Sierra Leone Rise (eastern equatorial Atlantic Ocean), *Mar. Geol.*, *70*, 223–250.

Curry, W. B., and G. P. Lohmann (1990), Reconstructing past particles fluxes in the tropical Atlantic Ocean, *Paleoceanography*, *5*, 487–505.

Dekens, P. S., D. W. Lea, D. K. Pak, H. J. Spero (2002), Core top calibration of Mg/Ca in tropical foraminifera: Refining paleotemperature estimation, *Geochem. Geophys. Geosyst.*, *3*(4), doi:10.1029/2001GC000200.

De Villiers, S., M. Greaves, and H. Elderfield (2002), An intensity ratio calibration method for the accurate determination of Mg/Ca and Sr/Ca of marine carbonates by ICP-AES, *Geochem. Geophys. Geosyst.*, *3*(8), doi:10.1029/2001GC000169.

Dickson, A. G. (1990), Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K, *Deep-Sea Res. 37*, 755–766.

Dickson, A. G., and F. J. Millero (1987), A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, *Deep-Sea Res. 34*, 1733–1743. (Corrigenda. *Deep-Sea Res*. 36, 983, 1989).

Dickson, A. G., C. L. Sabine, and J. R. Christian (2007), *Guide to best practice for CO2 measurements*, PICES Special Publication, *3*, 191 pp.

Elderfield, H., and G. Ganssen (2000), Past temperature and δ¹⁸O of surface ocean waters inferred from foraminiferal Mg/Ca ratios, *Nature*, *405*, 441–445.

Emerson, S., and M. Bender (1981), Carbon fluxes at the sediment-water interface of the deep-sea—Calcium carbonate preservation, *J. Mar. Res.*, *39*(1), 139–162.

Farrell, J. W. and W. L. Prell (1989), Pacific CaCO₃ preservation and δ¹⁸O since 4 Ma: Paleoceanic and paleoclimatic implications, *Paleoceanography*, *6*(4), 485–498.

Foster, G. (2008), Seawater pH, pCO₂ and [CO₃²⁻] variations in the Caribbean Sea over the last 130 kyr: A boron isotope and

B/Ca study of planktic foraminifera, *Earth Planet. Sci. Lett.*, *271*(1–4), 254–266.

Gehlen, M., F. Bassinot, L. Beck, and H. Khodja (2004), Trace element cartography of *Globigerinoides ruber* shells using particle-induced X-ray emission, *Geochem. Geophys. Geosyst.*, *5*, Q12D12, doi:10.1029/2004GC000822.

Gehlen, M., F. Bassinot, L. Chou, and D. McCorkle (2005), Reassessing the dissolution of marine carbonates: I. Solubility, *Deep-Sea Res. I*, *52*(8), 1445–1460, doi:10.1016/j.dsr.2005.03.010.

Greaves, M., et al. (2008), Interlaboratory comparison study of calibration standards for foraminiferal Mg/Ca thermometry, *Geochem. Geophys. Geosyst.*, *9*(8), Q08010, doi:10.1029/2008GC001974.

Harding, D. J., J. W. Arden, and R. E. M. Rickaby (2006), A method for precise analysis of trace element/calcium ratios in carbonate samples using quadrupole inductively coupled plasma mass spectrometry. *Geochem. Geophys. Geosyst.*, *7*, Q06003, doi:10.1029/2005GC001093.

Hemming, N. G., and G. N. Hanson (1992), Boron isotopic composition and concentration in modern marine carbonates, *Geochim. Cosmochim. Acta*, *56*(1), 537–543.

Hodell, D. A., C. D. Charles, and F. J. Sierro (2001), Late Pleistocene evolution of the ocean's carbonate system, *Earth Planet. Sci. Lett.*, *192*(2), 109–124.

Hönisch, B., and N. G. Hemming (2004), Ground-truthing the boron isotope-paleo-pH proxy in planktonic foraminifera shells: Partial dissolution and shell size effects, *Paleoceanography*, *19*(4), PA4010, doi:10.1029/2004PA001026.

Hönisch, B., and N. Hemming (2005), Surface ocean pH response to variations in pCO₂ through two full glacial cycles, *Earth Planet. Sci. Lett.*, *236*(1–2), 305–314.

Key, R. M., A. Kozyr, C. L. Sabine, K. Lee, R. Wanninkhof, J. Bullister, R. A. Feely, F. Millero, C. Mordy, T.-H. Peng (2004), A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), *Global Biogeochem. Cycl.*, *18*(4), 1–23.

Klochko, K., G. D. Cody, J. A. Tossell, P. Dera, and A. J. Kaufman (2009), Re-evaluating boron speciation in biogenic calcite and aragonite using ^{11}B MAS NMR, *Geochim. Cosmochim. Acta*, *73*(7), 1890–1900.

Le, J., and N. Shackleton (1992), Carbonate dissolution fluctuations in the western equatorial Pacific during the Late Quaternary, *Paleoceanography*, *7*(1), 21–42.

Levi, C. (2003), Etude des variations climatiques de la zone Indo-Pacifique: role des basses latitudes dans la variabilité millénaire du climat, PhD thesis, Université Paris XI, Orsay, France, 181 pp.

Lohmann, G. P. (1995), A model for variation in the chemistry of planktonic foraminifera due to secondary calcification and selective dissolution, *Paleoceanography*, *10*(3), 445–457.

Marchitto, T., J. Lynchstieglitz, and S. Hemming (2005), Deep Pacific CaCO₃ compensation and glacial-interglacial atmospheric CO₂, *Earth Planet. Sci. Lett.*, *231*(3–4), 317–336.

Mathien-Blard, E., and F. Bassinot (2009), Salinity bias on the foraminifera Mg/Ca thermometry: Correction procedure and implications for past ocean hydrographic reconstructions, *Geochem. Geophys. Geosyst.*, *10*, Q12011, doi:10.1029/2008GC002353.

Mehrbach, C., C. H. Culberson, J. E. Hawley, and R. M. Pytkowicz (1973), Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol. Oceanogr.*, *18*, 897–907.

Ni, Y., G. L. Foster, T. Bailey, T. Elliott, D. N. Schmidt, P. Pearson, B. Haley, and C. Coath (2007), A core top

assessment of proxies for the ocean carbonate system in surface-dwelling foraminifers, *Paleoceanography*, *22*(3), PA3212, doi:10.1029/2006PA001337.

Nouet, J., and F. Bassinot (2007), Dissolution effects on the crystallography and Mg/Ca content of planktonic foraminifera *Globorotalia tumida* (Rotaliina) revealed by X-ray diffractometry, *Geochem. Geophys. Geosyst.*, *8*, Q10007, doi:10.1029/2007GC001647.

Okai, T., A. Suzuki, M. Inoue, H. Kawahata, and N. Imai (2004), Collaborative analysis of GSJ/AIST geochemical reference materials JCp-1 (Coral) and JCt-1 (Giant Clam), *Chikyu Kagaku (Geochemistry)*, *38*(4), 281–286.

Östlund H. G., C. Craig, W. S. Broecker, and D. Spencer (Eds) (1987), *GEOSECS Atlantic, Pacific and Indian Ocean Expeditions. Shorebased Data and Graphics*, GEOSECS Atlas Series, vol. *7*, 200p, U.S. Government Printing Office, Washington D.C.

Palmer, M. R., and P. N. Pearson (2003), A 23,000-year record of surface water pH and pCO₂ in the western equatorial Pacific Ocean, *Science*, *300*(5618), 480–482.

Palmer, M. R., G. J. Brummer, M. J. Cooper, H. Elderfield, M. J. Greaves, G. J. Reichart, S. Schouten, and J. M. Yu (2010), Multi-proxy reconstruction of surface water pCO₂ in the northern Arabian Sea since 29 ka, *Earth Planet. Sci. Lett.*, *295*(1–2), 49–57.

Pearson, P. N., and M. R. Palmer (1999), Middle Eocene seawater pH and atmospheric carbon dioxide concentrations, *Science*, *284*(5421), 1824–1826.

Pearson, P. N., and M. R. Palmer (2000), Atmospheric carbon dioxide concentrations over the past 60 million years, *Nature*, *406*(6797), 695–699.

Regenberg, M., D. Nürnberg, S. Steph, J. Groeneveld, D. Garbe-Schönberg, R. Tiedemann, and W.-C. Dullo (2006), Assessing the effect of dissolution on planktonic foraminiferal Mg/Ca ratios: Evidence from Caribbean core tops, *Geochem. Geophys. Geosyst.*, *7*, Q07P15, doi:10.1029/2005GC001019.

Robbins, L. L., M. E. Hansen, J. A. Kleypas, and S. C. Meylan (2010), CO2calc—A user-friendly seawater carbon calculator for Windows, Max OS X, and iOS (iPhone), *U.S. Geological Survey Open-File Report* 2010–1280, 17 p.

Rollion-bard, C., D. Blamart, J. Trebosc, G. Tricot, A. Mussi, and J.-P. Cuif (2011), Boron isotopes as pH proxy: A new look at boron speciation in deep-sea corals using 11B MAS NMR and EELS, *Geochim. Cosmochim. Acta*, *75*(4), 1003–1012.

Rosenthal, Y., and G. P. Lohmann (2002), Accurate estimation of sea surface temperatures using dissolution-corrected calibrations for Mg/Ca paleothermometry, *Paleoceanography*, *17*, 1044, doi:10.1029/2001PA000749.

Rosenthal, Y., M. P. Field, and R. M. Sherrell (1999), Precise determination of element/calcium ratios in calcareous samples using sector field inductively coupled plasma mass spectrometry, *Anal. Chem.*, *71*, 3248–3253.

Rosenthal, Y., G. P. Lohmann, K. C. Lohmann, and R. M. Sherrell (2000), Incorporation and preservation of Mg in *Globigerinoides sacculifer*: Implications for reconstructing the temperature and ^{18}O/^{16}O of seawater, *Paleoceanography*, *15*(1), 135–145.

Rosenthal, Y., et al. (2004), Interlaboratory comparison study of Mg/Ca and Sr/Ca measurements in planktonic foraminifera for paleoceanographic research, *Geochem. Geophys. Geosyst.*, *5*, Q04D09, doi:10.1029/2003GC000650.

Russell, A. D., S. Emerson, B. K. Nelson, J. Erez, D. W. Lea (1994), Uranium in foraminiferal calcite as recorder of seawater uranium concentrations, *Geochim. Cosmochim. Acta*, *58*(2), 671–681.

Sabbatini, A., F. Bassinot, S. Boussetta, A. Negri, H. Rebaubier, F. Dewilde, J. Nouet, N. Caillon, and C. Morigi (2011), Further constraints on the diagenetic influences and salinity effect on *Globigerinoides ruber* (white) Mg/Ca thermometry: Implications in the Mediterranean Sea, *Geochem. Geophys. Geosyst.*, *12*, Q10005, doi:10.1029/2011GC003675.

Sabine, C. L., R. M. Key, A. Kozyr, R. A. Feely, R. Wanninkhof, F. J. Millero, T.-H. Peng, J. L. Bullister, and K. Lee (2005), Global Ocean Data Analysis Project: Results and Data, ORNL/CDIAC-145, NDP-083, *Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee*, 110 pp.

Sadekov, A., Eggins, S. M., de Deckker, P., Ninnemann, U., Kuhnt, W., and F. Bassinot (2009), Surface and subsurface seawater temperature reconstruction using Mg/Ca microanalysis of planktonic foraminifera *Globigerinoides ruber*, *Globigerinoides sacculifer*, and *Pulleniatina obliquiloculata*, *Paleoceanography*, *24*, PA3201, doi:10.1029/2008PA001664.

Sanyal, A., N. G. Hemming, W. S. Broecker, and G. N. Hanson (1997), Changes in pH in the eastern equatorial Pacific across stage 5–6 boundary based on boron isotopes in foraminifera, *Global Biogeochem. Cycl.*, *11*(1), 125–133.

Seki, O., G. L. Foster, D. N. Schmidt, A. Mackensen, K. Kawamura, and R. D. Pancost (2010), Alkenone and boron-based Pliocene pCO₂ records, *Earth Planet. Sci. Lett.*, *292*(1–2), 201–211.

Shackleton, N. J. (1974), Attainment of isotopic equilibrium between ocean water and benthonic foraminifera genus Uvigerina: Isotopic changes in the ocean during the last glacial, in: *Les méthodes quantitatives d'étude des variations du climat au cours du Pleistocène*, edited by L. Labeyrie, CNRS-Paris, pp. 203–209.

Spivack, A. J., and C.-F. You (1997), Boron isotopic geochemistry of carbonates and pore waters, Ocean Drilling Program Site 851, *Earth Planet. Sci. Lett.*, *152*(1–4), 113–122.

Spivack, A. J., C.-F. You, and H. J. Smith (1993), Foraminiferal boron isotope ratios as a proxy for surface ocean pH over the past 21 Myr, *Nature*, *363*(6425), 149–151.

Tripati, A. K., C. D. Roberts, and R. A. Eagle (2009), Coupling of CO₂ and ice sheet stability over major climate transitions of the last 20 million years, *Science*, *326* (5958), 1394–1397.

Wara, M. W., M. L. Delaney, T. D. Bullen, and A. C. Ravelo (2003), Possible roles of pH, temperature, and partial dissolution in determining boron concentration and isotopic composition in planktonic foraminifera, *Paleoceanography*, *18*(4), 1100, doi:10.1029/2002PA000797.

Yu, J., and H. Elderfield (2007), Benthic foraminiferal B/Ca ratios reflect deep-water carbonate saturation state, *Earth Planet. Sci. Lett.*, *258*(1–2), 73–86.

Yu, J., J. Day, M. Greaves, and H. Elderfield (2005), Determination of multiple element/calcium ratios in foraminiferal calcite by quadrupole ICP-MS, *Geochem. Geophys. Geosyst.*, *6*, Q08P01, doi:10.1029/2005GC000964.

Yu, J., H. Elderfield, and B. Hönisch (2007), B/Ca in planktonic foraminifera as a proxy for surface seawater pH, *Paleoceanography*, *22*, PA2202, doi:10.1029/2006PA001347.

Yu, J., H. Elderfield, Z. D. Jin, and L. Booth (2008), A strong temperature effect on U/Ca in planktonic foraminifer carbonates, *Geochim. Cosmochim. Acta*, doi:10.1016/j.gca.2008.4907.4011.