Effet de la dissolution sur le B sur Ca des foraminifères planctoniques

Introduction

Le rapport B/Ca des foraminifères planctoniques est étroitement lié au pH des eaux de surface, et représente donc un proxy prometteur pour la reconstruction des variations du cycle du carbone. Néanmoins, la qualité de ce proxy ne dépend pas que des conditions initiales, c'est à dire l'incorporation du bore dans les foraminifères vivants, mais dépend également du processus de sédimentation des tests de foraminifère et de leur préservation dans le sédiment. En effet, de nombreuses études ont montré l'influence de la dissolution des carbonates sur les proxies géochimiques, tant en matière d'isotopie que d'analyse élémentaire. Ainsi, l'effet de la dissolution tend à diminuer la composition isotopique du bore dans les carbonates (e.g. Spivack and You, 1997 ; Wara et al., 2003 ; Hönisch et al., 2004), mais diminue également les valeurs d'autres traceurs comme le rapport Sr/Ca (E.G. Lohmann 1995 ; Brown and Elderfield, 1996 ; Rosenthal et al., 2000), le rapport U/Ca (Russell et al., 1994) ou encore le proxy de température Mg/Ca (Brown and Elderfield, 1996 ; Dekens et al., 2002 ; Gehlen et al., 2005a ; Regenberg et al., 2006 ; Nouet and Bassinot, 2007).

Nous avons souhaité savoir si ce biais potentiel possédait ou non une influence sur le rapport B/Ca des foraminifères planctoniques. Nous avons utilisé des sommets de carottes issues d'un transect de profondeur sur la Sierra Leone Rise (SLR), dans l'Atlantique Est équatorial. Ces carottes ont été prélevées par le R/V *Knorr* à l'aide d'un préleveur à multitubes (Figure 30), qui présente l'avantage de pénétrer le sédiment sur quelques centimètres sans en perturber la surface. Une fois que l'on a vérifié que ce sédiment est en place (pas de turbidites, nodules sédimentaires ou autres) on a donc l'assurance que ce sédiment est récent. Des études antérieures basées sur des carottes sédimentaires datées au ^{14}C ou calées stratigraphiquement grâce au $\delta^{18}O$ montrent que les taux de sédimentation oscillent entre 2 et 5 cm par mille ans sur SLR, le premier ½ cm peut donc contenir des foraminifères ayant vécu au cours des deux cents dernières années.
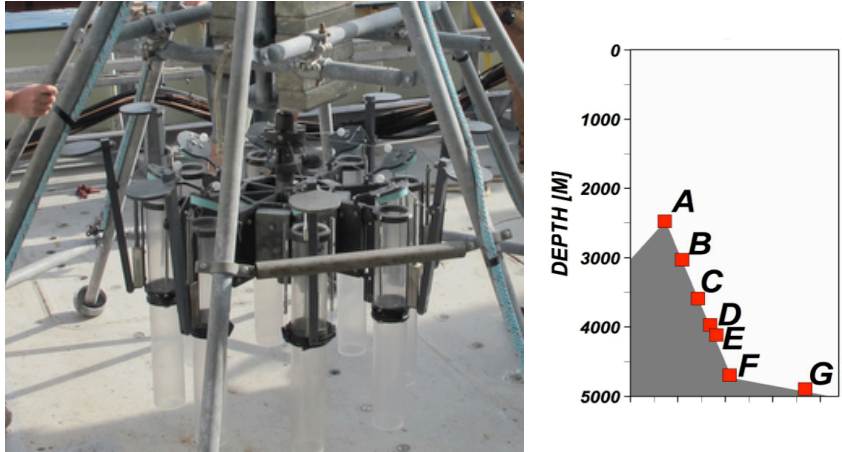
Figure 30 : A gauche : Multicorer présent sur le R/V *Knorr* : les tubes s'enfoncent lentement dans le sédiment une fois le carottier posé au fond. A droite : profondeurs des sept stations de prélèvement sur le transect de profondeur de la Sierra Leone Rise

Sur ce transect en zone oligotrophe, les foraminifères ont connu les mêmes conditions de vie en surface, en termes de température (0.5°C d'amplitude maximale), de salinité (0.4 d'amplitude maximale)(voir Figure 2, section 2.1 de la section suivante) et de pH. Ainsi, ces foraminifères doivent posséder un rapport B/Ca initial sensiblement équivalent, et les seuls procédés pouvant influencer ce paramètre sont donc ceux ayant lieu au cours du processus de sédimentation ou après déposition sur le sédiment. Or, la dissolution des carbonates augmente lorsque la saturation diminue, c'est à dire lorsque la solubilité du $CaCO_3$ augmente lorsque la profondeur augmente (cf chapitre 1).

Le profil bathymétrique le long de la Sierra Leone Rise a permis de recueillir des échantillons à des profondeurs comprises entre 2500 et 5000m et représente donc un site d'étude idéal pour l'impact de la dissolution. Cette hypothèse a pu être vérifiée par la quasi absence de l'espèce *Globigerinoides ruber* à sur les échantillons les plus profonds, cette espèce étant particulièrement sensible à la dissolution (Berger, 1968, 1970). De plus, de précédentes études sur ce transect avaient déjà mis en évidence l'influence de la dissolution sur la cristallographie et le Mg/Ca des foraminifères (Nouet and Bassinot, 2007). Pour connaître l'état de saturation en carbonates des eaux baignant les sites de carottages, nous avons recherché l'ensemble des stations voisines ou les mesures de deux paramètres du système des carbonates ont été réalisées afin de pouvoir tracer le profil en profondeur des concentrations en ion carbonate. Sur la figure 31 sont représentées l'ensemble des mesures de la base GLODAP pour la zone ainsi que la courbe de l'horizon de saturation (cf chapitre 1).
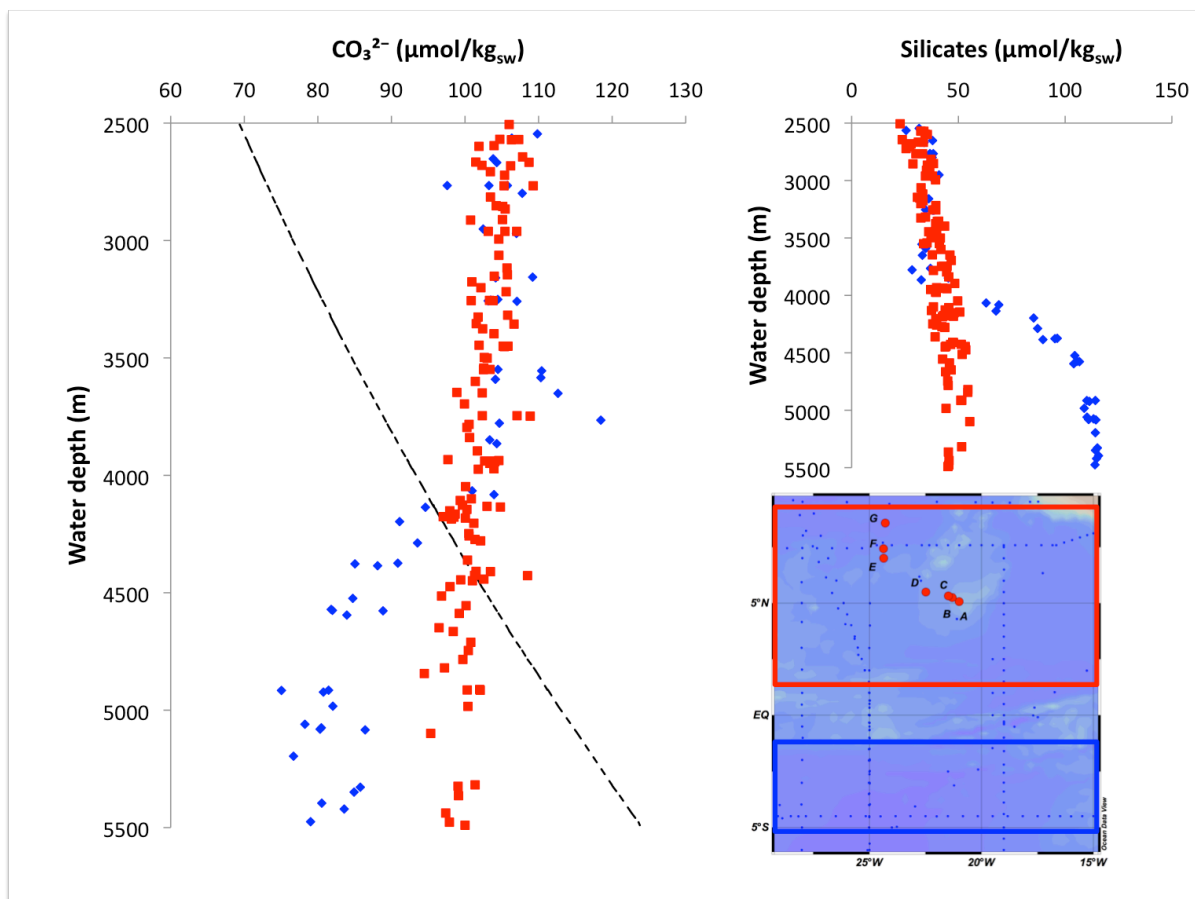
Figure 31 : Profil de $[CO_3^{2-}]$ et silicates dans la région de la Sierra Leone Rise. La ligne pointillée représente la concentration en ions carbonates à saturation pour la calcite ($[CO_3^{2-}]_{sat}$), le croisement avec la série de données rouges à ~4500m correspond au passage de l'horizon de saturation.

Les deux couleurs de points montrent les mesures des stations de la base de données GLODAP situées dans les deux cadres géographiques. Les stations au sud de la dorsale (située sur l'Equateur) montrent un changement de masse d'eau à ~4000m, avec le passage de la North Atlantic Deep Water à l'Antarctic Bottom Water (cf chapitre I), avec les eaux originaires de l'océan austral riches en silicates et pauvres en carbonates (losanges bleus). La zone contenant nos stations montre des concentrations homogènes (carrés rouges), toutes nos stations sont donc baignées par l'eau profonde Nord Atlantique.

Dans ce chapitre, nous présentons tout d'abord les mesures de B/Ca de l'espèce G. sacculifer effectuées sur ce transect de profondeur. Nous verrons dans quelle mesure le B/Ca est affecté par le phénomène de dissolution, et les implications de cet effet en terme de paléocéanographie. Nous proposons ensuite une procédure basée sur la mesure du B/Ca des foraminifères benthiques, qui permettrait potentiellement de corriger les mesures de B/Ca des foraminifères planctoniques de l'effet de la dissolution.

A. Publication: "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."

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Abstract

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

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., 2009; Palmer et al., 2010*).

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):

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

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.

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

$$K_D = [B/Ca]_{CaCO3} / [B(OH)_4^-/HCO_3^-]_{seawater} \qquad (2)$$

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 $(B(OH)_4^-/HCO_3^-)$:

$$[B(OH)_4^-/HCO_3^-]_{seawater} = [B/Ca]_{CaCO3} / K_D \qquad (3)$$

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.* (2009) 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.

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 δ^{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*, 2000; *Dekens et al.*, 2002; *Gehlen et al.*, 2005a; *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.

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

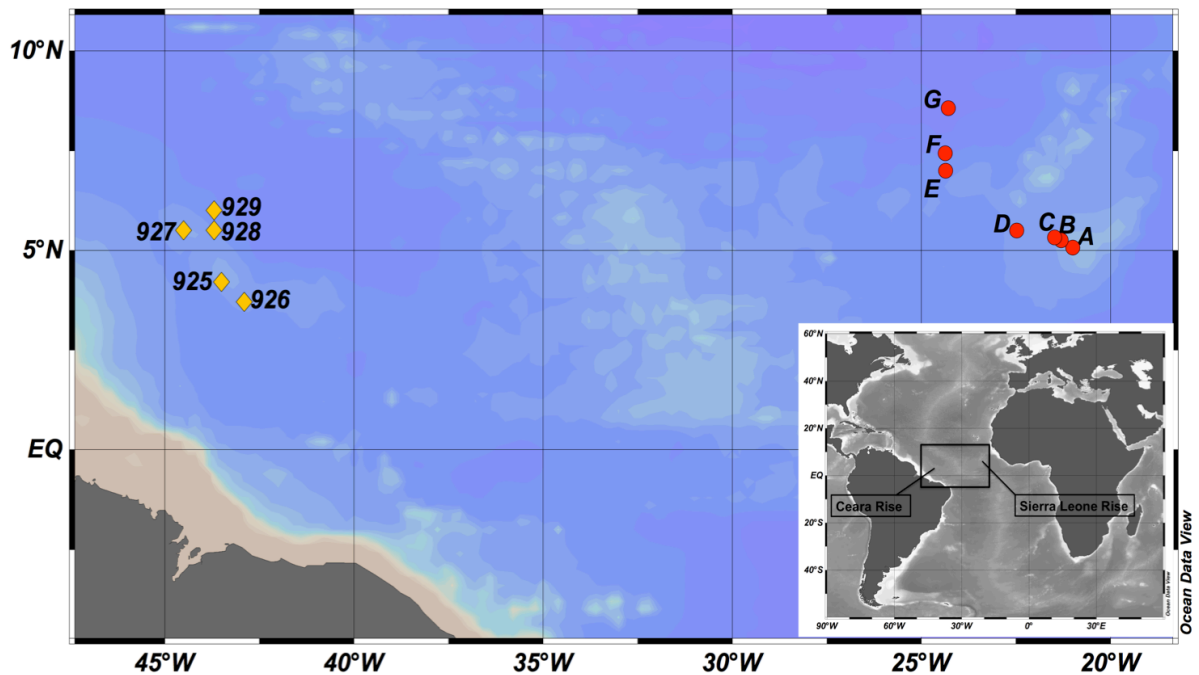### 2.1. Site locations and hydrographic settings

Figure 32 : Location of sites on the Sierra Leone Rise (this study) and ODP Sites from the Ceara Rise (Seki et al., 2010).

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 on Figure 32 and listed in Table 7.

Station	Latitude	Longitude	Water depth (m)	Deep water ΔCO_3^{2-} ($\mu mol.kg_{sw}^{-1}$)	Cibicidoides oxygen isotopic composition (‰ versus 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

Table 7 : Location and depth (m) of sampling sites. The carbonate ion composition of bottom waters ($\mu mol.kg_{sw}^{-1}$) is estimated using the GLODAP data base (see section 2.4 : Hydrographic data). *C. wullerstörfi* and *C. kullenbergi* oxygen isotopic analysis, expressed in ‰ versus VPDB. The reproducibility is given from 2 to 5 replicates.

Because of the close vicinity of the seven sites, there are no significant differences in sea surface temperature (SST, ≤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 µmol/k) obtained from the Global Ocean Data Analysis Project database (GLODAP; *Key et al.,* 2004; *Sabine et al.,* 2005) (Figure 33).
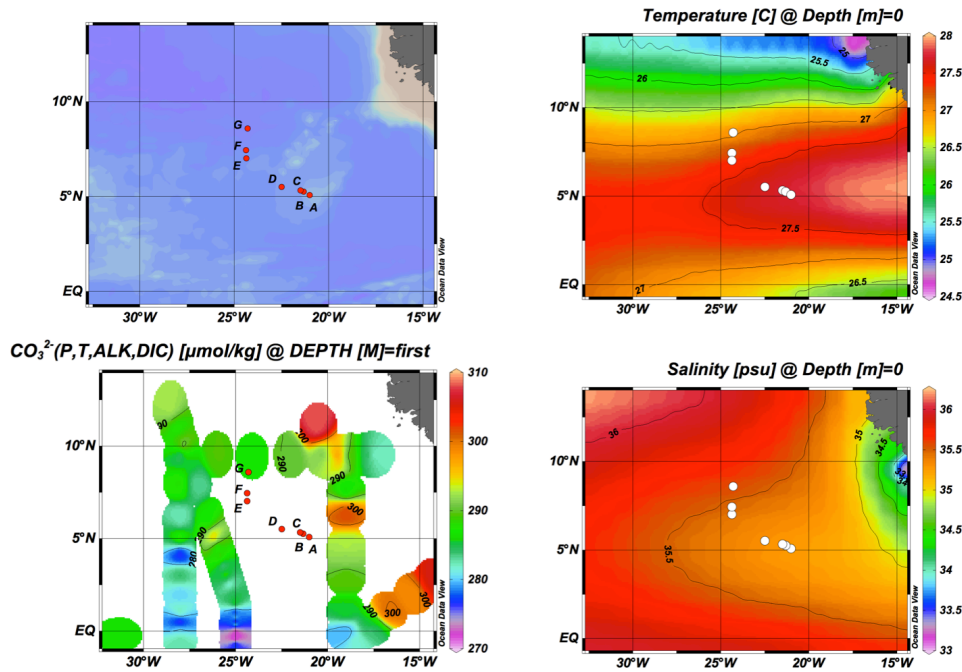

Figure 33 : Surface water mean annual temperature and salinity over the Sierra Leone Rise obtained with the World Ocean Atlas 2009 (*Boyer et al.*, 2009), and surface water carbonate ion concentration calculated from the GLODAP data set (Key et al., 2004). Temperatures and salinities are from the World Ocean Atlas and represent a climatic average over past decades. Carbonate ion concentrations are calcultated from the GLODAP data set following equilibrium constants recommended by Dickson et al., 2007. As shown in the figure, only few, ponctual 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 mean $[CO_3^{2-}]$ of 289±4 µmol/kg (1σ)

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 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).
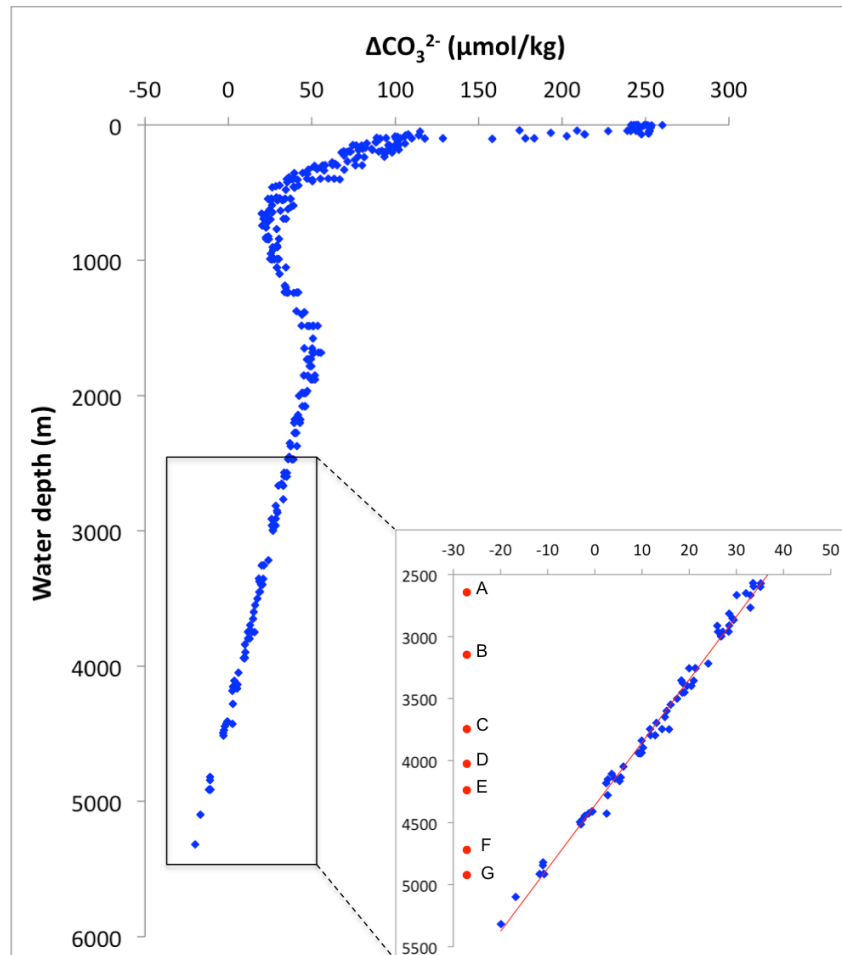
Figure 34 : Water depth (m) versus ΔCO_3^{2-} ($\mu mol.kg_{sw}^{-1}$) in the vicinity of the Sierra Leone Rise estimated from the GLODAP data set (*Sabine et al.*, 2005). Figure inset represents the ΔCO_3^{2-} trend change between 2500 and 5000 m of water depth, red circles represent the station depths.

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 $\mu mol.kg^{-1}$ at the shallowest site (A) to -11 $\mu mol.kg^{-1}$ at the deepest one (G; Figure 34). 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

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 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 hours at 50°C and stored for analysis. C. *wuellerstorfi* 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, 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 7) 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.

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.

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 eight 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 (*Ghelen et al.,* 2004), nor through X-Ray

Diffractometry analyses (*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. *Gehlen et al.*, 2005; *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

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.

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

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.

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 10000 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.

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 a Xseries II from Thermo-Scientific, and at the Godwin Laboratory it is an Elan DRC II from Perkin Elmer.

Because boron is leached from glassware under acidic conditions, a mini cyclonic quartz spraychamber 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 $\sim 5\%$, compared with $\sim 30\%$ when using a glass spray chamber. In order to minimize the memory effect, acid (0.1M HNO_3) washout time between samples was set to at least 60 seconds. 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 ~50µl/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 hours (Yu *et al*., 2005).

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 5 samples. Drift along a typical analytical session (~6 hours) is less than 5% for boron and 1% for magnesium. In the LSCE analytical protocol we also measured, every ten 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., *in prep*.) and LSCE mean value for standard JCt-1 was 189 µmol/mol, close to the resulting average value of 191 µmol/mol (from only 3 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-1 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 five 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

G. sacculifer Mg/Ca and B/Ca data obtained on the Sierra Leone Rise core tops are presented in Table 8, and plotted versus water depth in Figures 35 and 36, respectively. Values in this 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.

Station	Water depth (m)	Deep water ΔCO_3^{2-} ($\mu mol/kg_{sw}^{-1}$)	LSCE, Gif-sur-Yvette			Godwin Lab., Cambridge		
			B/Ca ($\mu mol/mol$)	Mg/Ca (mmol/mol)		B/Ca ($\mu mol/mol$)	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

Table 8 : B/Ca ($\mu mol.mol^{-1}$) and Mg/Ca ($mmol.mol^{-1}$) data, measured per station at both LSCE and the Godwin laboratory. Errors are the maximum between standard reproducibility (±3.5% at 2σ) and replicates standard deviation (2 S.D.)

3.1. Profile of Mg/Ca versus water depth

Mg/Ca data obtained at LSCE and at the Godwin Laboratory are plotted on Figure 35. 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 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).
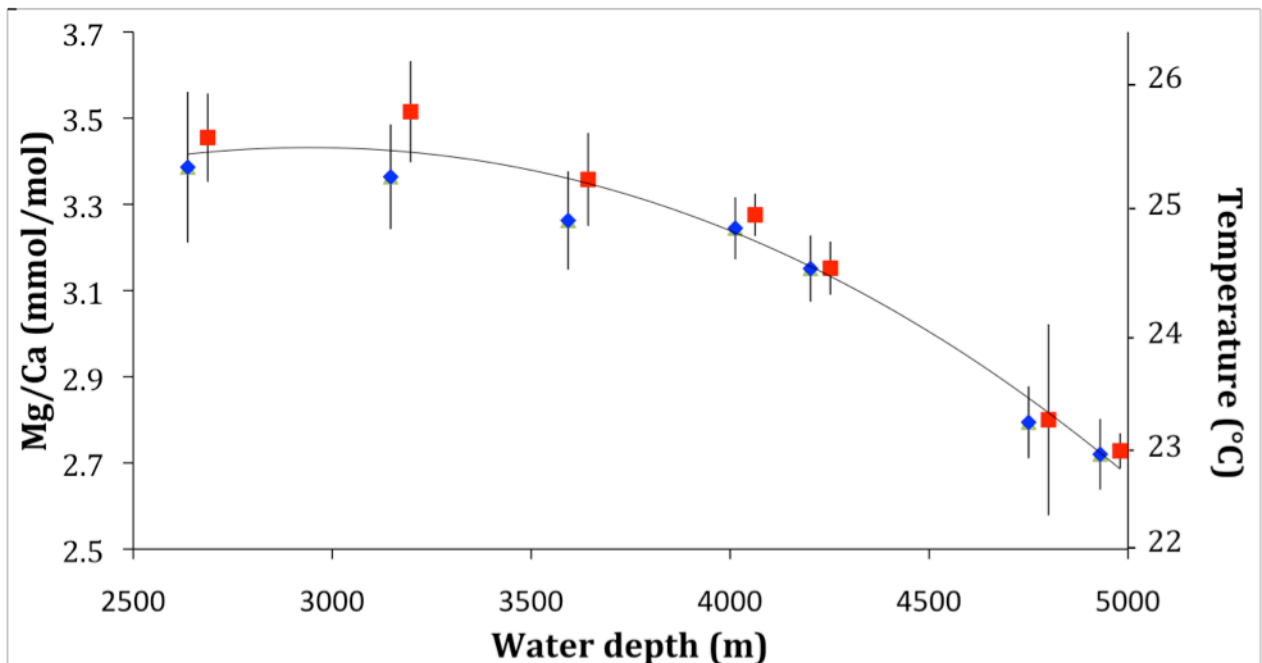

Figure 35 :   Mg/Ca ratio (mmol.mol^{-1}) profiles of *G. sacculifer* versus water depth (m). Mg/Ca values obtained at the Godwin laboratory (Red squares) and at LSCE (Blue diamonds). Error bars represent the larger of the standard deviation of the replicates and standard reproducibility (1.5%). For more readability, Godwin's stations have been deepened by 50 m. Lines represent two possible trends for the data sets. On the right axis temperature calculated from Mg/Ca *G. sacculifer* values.

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 4.1).

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 ~ -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

The trend of B/Ca data with water depth observed in the LSCE and the Godwin Laboratory data are comparable although the values show an offset; the Godwin Laboratory B/Ca being ~ 6 μmol/mol lower in average than the LSCE values (Figure 36). 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 36 (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 prep) 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)).
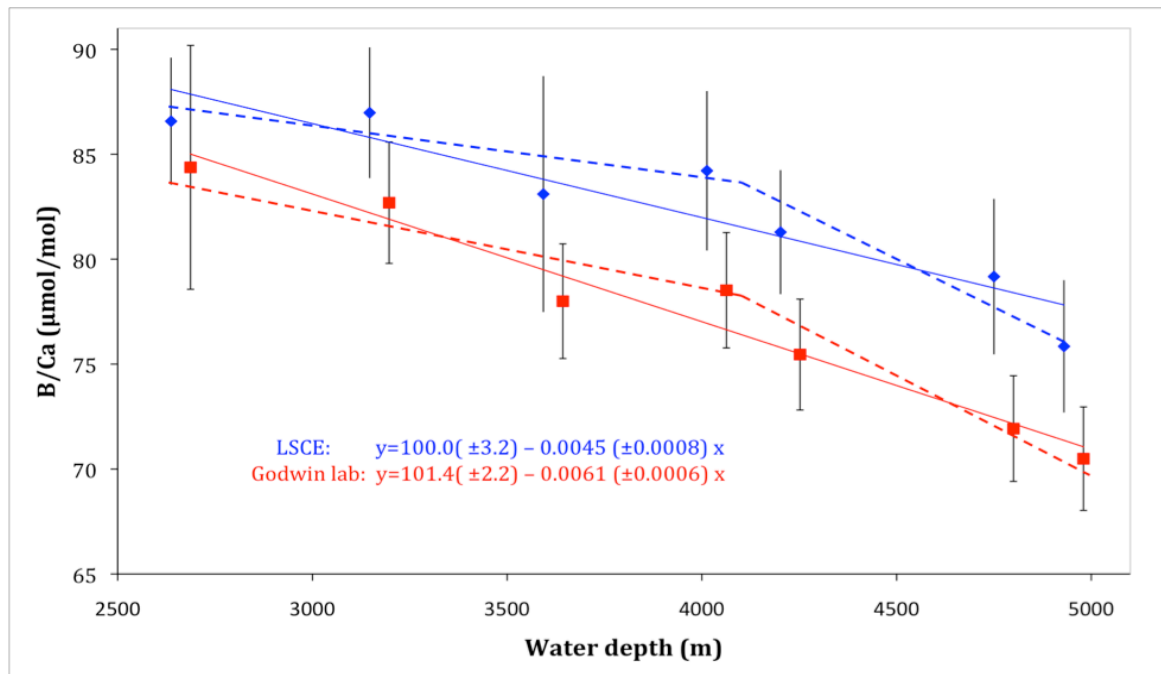
Figure 36 : B/Ca (μmol.mol^{-1}) profiles of *G. sacculifer* versus water depth (m): B/Ca values obtained at the Godwin laboratory (Red squares), and at LSCE (Blue diamonds). Error bars represent the maximum between the standard deviation of the replicates and the standard reproducibility (3.5%). For more readability, Godwin's stations have been deepened by 50 m. Blue and red lines represent the possible trends for different sets of results.

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 μmol/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 μmol/mol (from 84.4 to 70.5 μmol/mol and 87 to 75.8 μmol/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.

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 36). 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 4000m (Figure 36). Such a two-step evolution is similar to that shown by the *G. sacculifer* Mg/Ca profile along the Sierra Leone Rise (Figure 35). 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

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 et al.*, 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 37; data from this study and from *Gehlen, et al., 2005a*). (i) The first proxy is the relative amount (weight percentage) of the coarse, > 150 μm size fraction (*Gehlen et al.,* 2005a). This coarse fraction is chiefly foraminifer-dominated. The decreasing coarse fraction % 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.*, 2005a). (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.,* 2005a). 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.

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 37). There are, however, differences between the profiles which may reflect either the various proxy responses, or sediment heterogeneity. Such a 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 (cristallinity and shell weight) show a more constant evolution with increasing water depth (Figure 37).
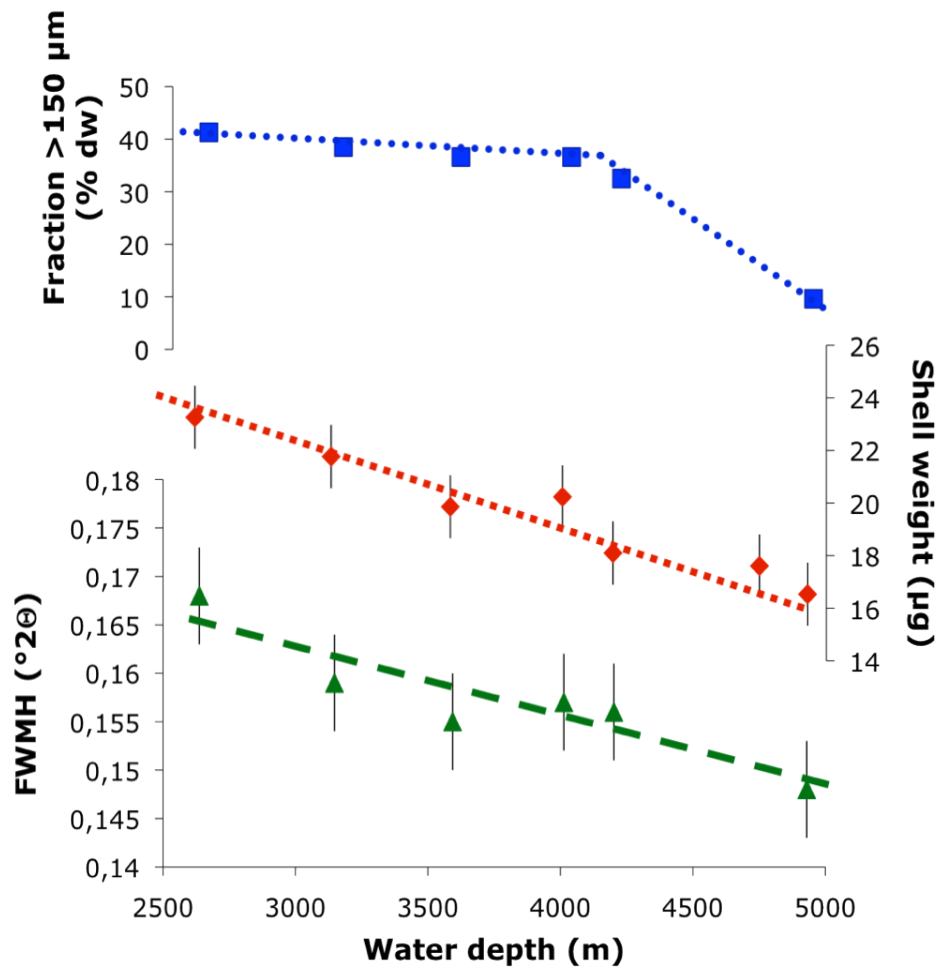
Figure 37 : Dissolution proxies versus water depth (m): Relative amount of fraction >150 μm (% dry weight) (Top, blue squares), shell weight (μg) of *G. sacculifer* from our samples (middle, red diamonds) and full width at half maximum (FWMH, °2θ) of the calcite peak (bottom, green triangle).

These three proxies (cristallinity, >150μm 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^{2-}), 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 % coarse fraction (>150μm) showing the lowest (R^2=0.88).

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

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 ±2.6s 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.

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 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 34). This seems to be in good agreement, therefore, with previous studies which have shown that there exists a threshold for supra-lysoclinal dissolution of pelagic carbonates at around ~ 15-20 µmol/kg (*Regenberg et al.,* 2006).
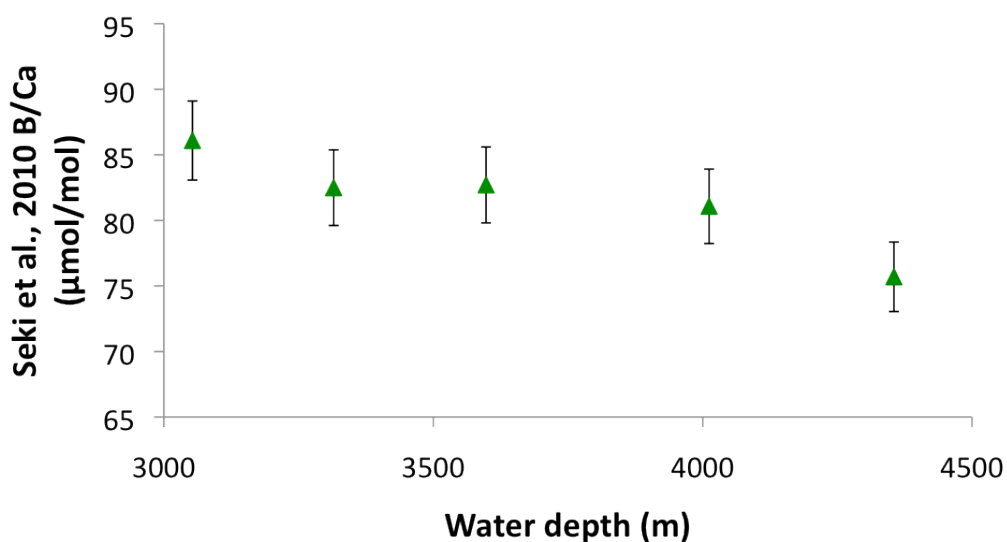

Figure 38 : *G. sacculifer* B/Ca versus water depth measured by *Seki et al.* (2010), on a depth transect of five ODP sites of the Ceara Rise (west equatorial Atlantic ocean). Errors bars are ± 4 µmol/mol.

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 38). 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 39). 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).
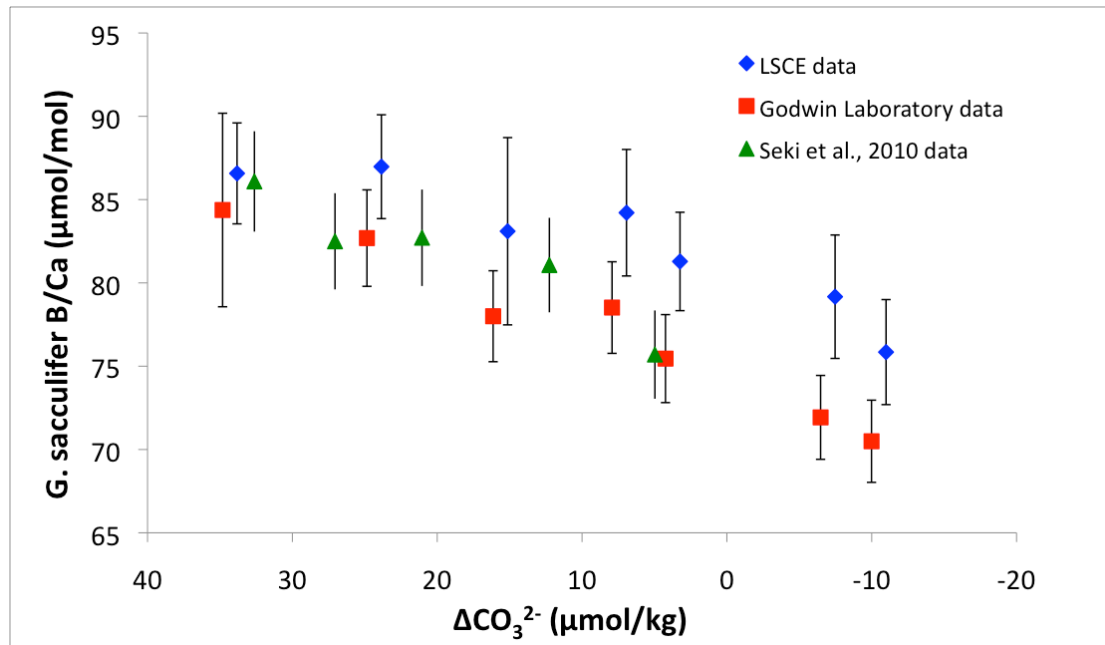

Figure 39 : Comparison of the B/Ca profiles obtained on the two different depth transects ((i) Sierra Leone Rise: blue diamonds for LSCE's data and red squares for Godwin Laboratory's data; and (ii) Ceara Rise: green triangle). In order to compare the B/Ca evolutions, B/Ca values are plotted versus ΔCO_3^{2-} 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.

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; *Gehlen et al.*, 2005a; *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*

We have shown that both the B/Ca and the Mg/Ca composition 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.*, 2009; *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. 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 reconstruction of K_D and (ii) to the B/ Ca ratio.

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 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 34), well above the average ΔCO_3^{2-} critical value of 15-20 µmol/kg below which dissolution severely increases in modern pelagic deposits (*Regenberg*, 2006).

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:

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

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).

The exact temperature effect on the K_D for *G. sacculifer* is still under debate (*Yu et al.*, 2007; *Foster*, 2008; *Tripati et al.*, 2009). 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):

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

We used *G. sacculifer* B/Ca to reconstruct the pH at station A and G based on the two relationships between pH and the $[B(OH)_4^-/HCO_3^-]$ of seawater (Figure 40) and the two partition coefficients derived from stations A and G, with 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 (8.11 to 8.00) 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% .
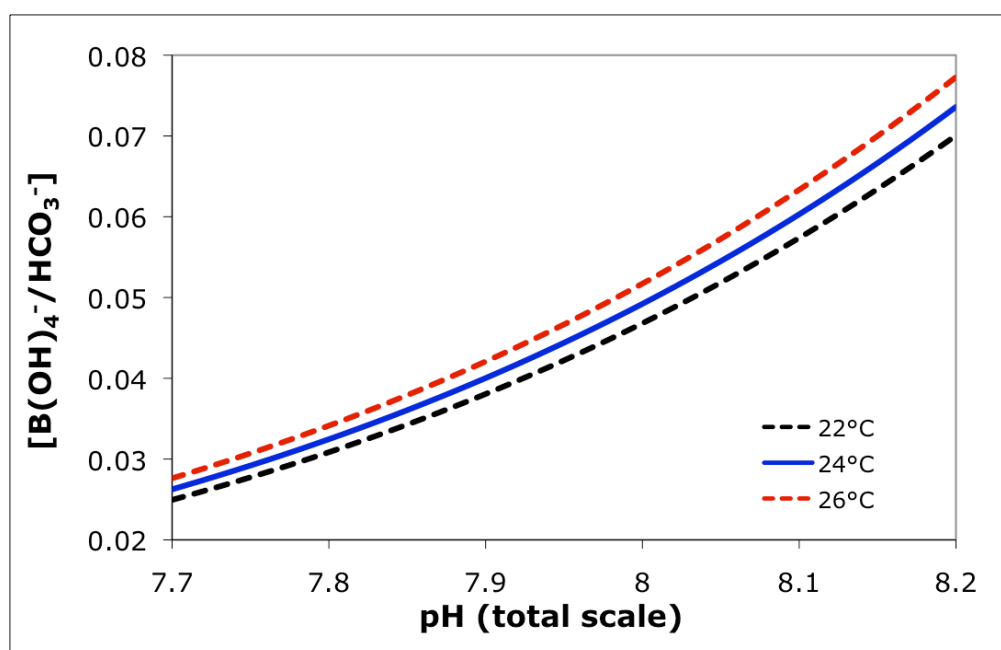

Figure 40 : Variations of $[B(OH)_4^-/HCO_3^-]$ with seawater pH assuming constant DIC (2000 μmol.kg^{-1}), salinity (35.9 psu) and $[B]_{tot}$ (434 μmol.kg^{-1}), but with differing temperature (°C).

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; *Hönish and Hemming*, 2005). Because glacial-interglacial changes in oceanic circulation and carbon reservoirs have induced changes in carbonate saturation and lysocline depth (e.g. *Farrell and Prell*, 1991; *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?

Several authors have used the size-normalized weight of planktonic foraminifers as a proxy for quantifying past dissolution intensity (e.g. *Lohman*, 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 & 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.

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

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.

B. Etablissement d'une procédure potentielle de correction du B/Ca

Les résultats précédents ont mis en évidence l'influence de la dissolution sur le B/Ca des foraminifères planctoniques, avec une perte de B/Ca de l'ordre de 10 µmol/mol entre les stations les moins profondes et les plus profondes. Cet écart génère une erreur sur les reconstructions de pH de ~0.11 unités pH, ce qui correspond à l'ordre de grandeur des variations de pH attendues sur des échelles glaciaires-interglaciaires (Sanyal et al., 1995 ; Hönisch and Hemming, 2005), et limite donc les reconstructions de paleo-pH aux sites non affectés par la dissolution si l'on ne tient pas compte de son effet.

Rosenthal et al., 1997 ont proposé d'utiliser le poids des tests de foraminifères planctoniques pour corriger les valeurs de Mg / Ca de la dissolution, afin d'obtenir plus de précision lors de la reconstruction des paléo-températures de la surface de l'océan. Le poids des foraminifères a été utilisé avec succès par plusieurs auteurs pour quantifier l'intensité de la dissolution (e.g. Lohman et al, 1995 ; Broecker and Clark, 2002). De la même manière, il est possible d'envisager d'élaborer une procédure de correction pour corriger le B/Ca des effets de la dissolution. L'utilisation du poids normalisé du test comme un proxy de dissolution présente plusieurs avantages: elle est non destructrice, quantitative, indépendante de l'opérateur et peut être dérivée de la même espèce que celles sur laquelle les analyses de B/Ca sont effectuées. Elle a, cependant, un potentiel inconvénient pour des paléo-reconstructions, d'autres études ayant suggéré que le poids initial du test de foraminifère planctonique peut co-varier avec la concentration en ion carbonate des eaux de surface et, par conséquent, le pH (Bijma et al, 1999;. Barker and Elderfield, 2002; Dissard et al, 2010). En d'autres termes, le proxy permettant de corriger B/Ca du biais de dissolution ne serait pas indépendant des variations passées du pH des eaux de surface que l'on souhaite reconstruire.

Une autre façon de corriger l'effet de la dissolution sur les rapports Mg/Ca et B/Ca des foraminifères planctoniques peut être l'utilisation du B/Ca des foraminifères benthiques des échantillons issus des mêmes sites. Le processus de dissolution intervenant après déposition est fortement lié à la saturation en ion carbonate des eaux de fond (ΔCO_3^{2-}) (Regenberg et al., 2006). Yu and Elderfield (2007) ont montré que le B/Ca des foraminifères benthiques est proportionnel à la saturation en ions carbonates, et que le B/Ca des foraminifères benthiques n'était pas influencé par la dissolution. Le principal inconvénient de cette procédure de correction est la relative faible abondance des foraminifères benthiques par rapport

aux foraminifères planctoniques. Toutefois, elle a les avantages d'être quantitative et indépendante des conditions de surface de l'océan.

Site	Water depth (m)	GLODAP ΔCO_3^{2-} ($\mu mol/kg_{sw}^{-1}$)	C. wuellerstorfi B/Ca ($\mu mol/mol$)	Reconstructed ΔCO_3^{2-} ($\mu mol/kg_{sw}^{-1}$)	Calculated Ω
Station A	2637	34	233	49.4	1.48
Station B	3147	24	223	40.1	1.31
Station C	3593	15	218	36.3	1.18
Station D	4013	7	207	26.1	1.07
Station E	4202	3	198	18.5	1.03
Station F	4750	-7	187	8.4	0.93
Station G	4930	-11	185	6.8	0.90

Table 9 : ΔCO_3^{2-} calculé à partir des données de la base GLODAP ; rapport B/Ca mesuré sur l'espèce C. wuellerstorfi ; ΔCO_3^{2-} calculée à l'aide de la calibration établie par Yu et Elderfield, 2007 ; et Ω calculé à l'aide de la calibration entre les données GLODAP et le B/Ca de C. *wuellerstorfi*.

Nous avons mesuré le rapport B/Ca sur l'espèce de foraminifère benthique *Cibicidoides wuellerstorfi*. Les ratios B/Ca obtenus varient entre 223 et 180 µmol/mol, et diminuent lorsque la profondeur augmente (table 9). Ces mesures de B/Ca montrent une très forte relation avec le ΔCO_3^{2-} (Figure 41), évalué à partir de la base de données GLODAP (Key et al., 2004). Cette calibration donne une pente semblable mais une droite de calibration différente de celle établie par Yu et Elderfield (2007) (table 9, figure 41). L'offset obtenu récemment entre le Godwin Laboratory et le LSCE n'explique pas moins du tiers de cette différence. Soit l'écart entre les mesures B/Ca de Yu et Elderfield (2007) et du LSCE est plus important que l'écart actuel entre les laboratoires, soit une partie de la différence est due au fait que la calibration établie par Yu et Elderfield (2007) comprend des mesures pour des carottes prélevées dans les différents bassins océaniques tandis que nos mesures sont restreintes à l'Atlantique tropical. Cependant, conserver uniquement les points Atlantiques de la calibration de Yu et Elderfield (2007) (voir chapitre V de cette thèse, partie 4.4) ne permet pas de gommer la différence avec la courbe de calibration pour les points de la Sierra Leone Rise. Ces écarts devront être de nouveau analysés lorsqu'une calibration internationale aura été effectuée entre les différents laboratoires pour la mesure du B/Ca des foraminifères.

Pour l'instant, pour calculer une correction de l'effet de la dissolution sur les rapports B/Ca et le Mg/Ca des foraminifères planctoniques, nous allons nous focaliser sur les mesures obtenues ici sur la SLR.
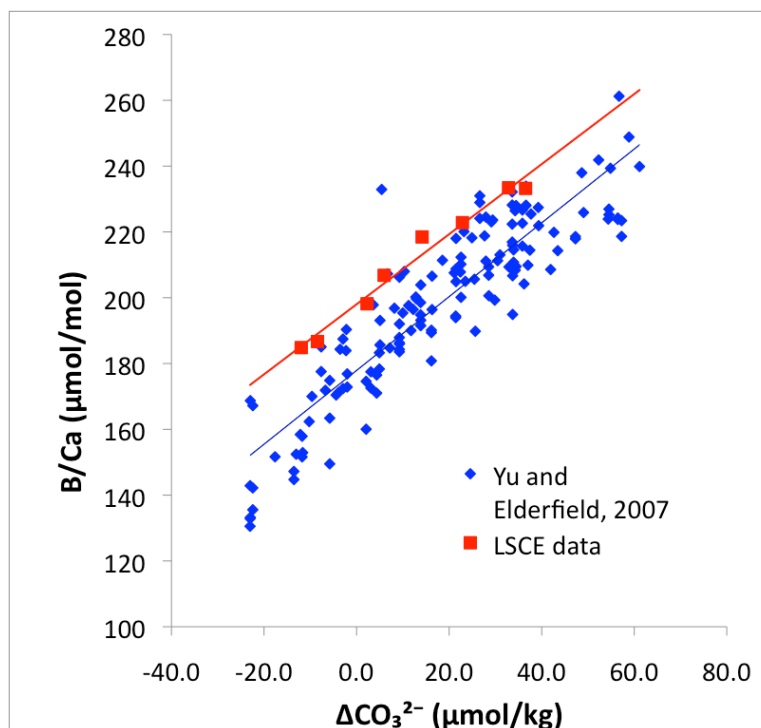
Figure 41 : Rapport B/Ca en fonction de la saturation en ion carbonate. Les carrés rouges représentent les données issues de la Sierra Leone Rise, les losanges bleus proviennent de la calibration de Yu et Elderfield, 2007. Les droites représentent les régressions linéaires de ces deux séries de données.

Nous avons calculé les pertes relatives en B/Ca et en Mg/Ca des foraminifères planctoniques par rapport à la station A, la moins profonde du transect (~2640 m), considérée comme référence non dissoute. Nous pensons que cette hypothèse est justifiée, compte tenu de la saturation relativement élevée de l'eau par rapport à la calcite à la station A, ainsi que les faibles variations des différents proxies de dissolution dans la partie supérieure du transect de profondeur (figure 37 de la partie 1). La perte d'un élément X par rapport au calcium est donc exprimée comme :

$$\Delta X/Ca = \frac{\left(\left[X/Ca\right]_{station} - \left[X/Ca\right]_{station\,A}\right)}{\left[X/Ca\right]_{station\,A}} \times 100 \qquad (6)$$

Pour faciliter l'obtention des relations liant saturation en ion carbonates des eaux profondes et perte relative en X/Ca, nous avons choisi d'utiliser la saturation en ion carbonate sous sa forme Ω. En effet, les variations de ΔCO_3^{2-} montrent une large gamme de variations (~40 μmol/kg$_{sw}$), et qui plus est des valeurs négatives qui interdisent l'utilisation de certains types de régression. Dans l'océan, le degré de saturation en ion carbonate Ω ne varie elle qu'entre 0 et 7, et peut être obtenue par la mesure du B/Ca, qui permet l'obtention du ΔCO_3^{2-}, et par le calcul du $[CO_3^{2-}]_{sat}$, fonction de la profondeur. L'effet de la dissolution avec la profondeur le long du transect a comme conséquence une forte relation entre la saturation Ω en ion carbonate et la perte relative de B/Ca de l'espèce (Figure 42). Le rapport B/Ca des

échantillons peut alors être corrigé de la perte relative de B/Ca due à la dissolution et, de la même manière, les valeurs de Mg/Ca peuvent également être corrigées.
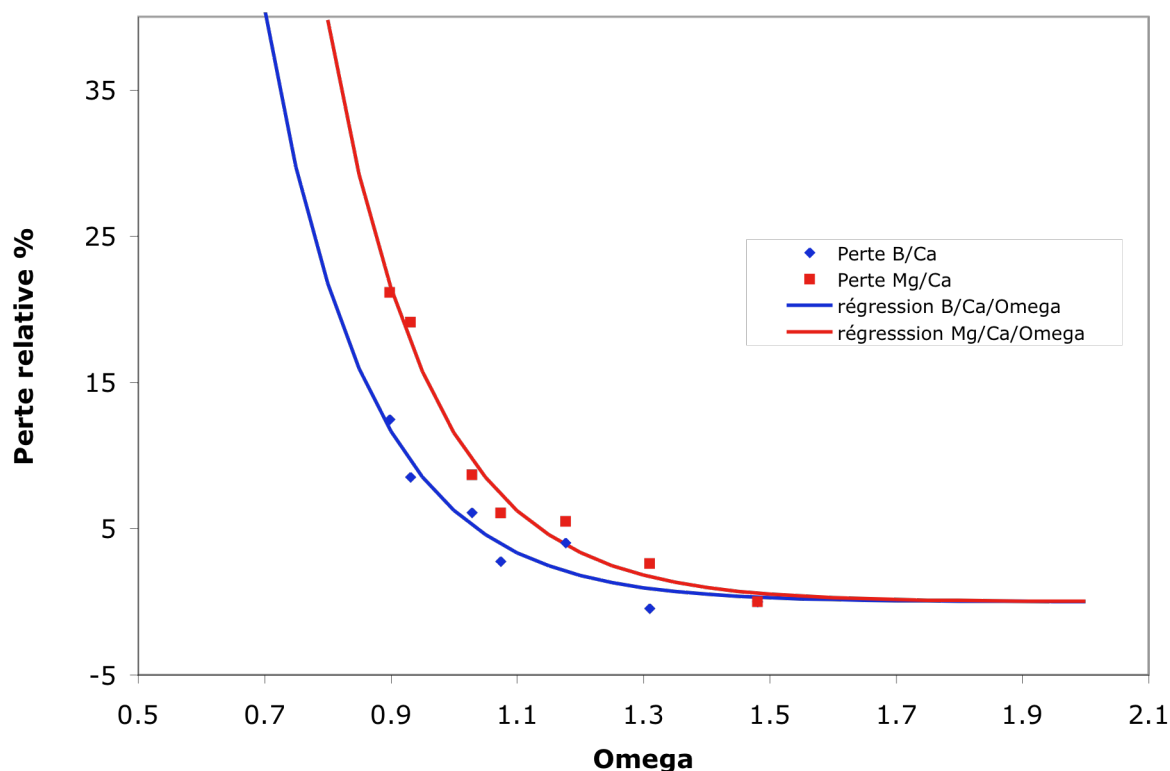

Figure 42 : Perte relative de B/Ca par rapport à la station A en fonction de la saturation Ω pour les stations de SLR et régression de type exponentielle.

Les valeurs corrigées des rapports B/Ca et Mg/Ca sont présentées sur la figure 43. La procédure de correction permet de ramener l'ensemble des mesures de B/Ca à un niveau similaire à celui de la station A, avec une moyenne de 86.6 µmol/mol et un écart type sur les stations de 2.2 µmol/mol (2σ). De même, les mesures de Mg/Ca sont ramenées à des niveaux similaires à la station A, avec une moyenne de 3 .45 ±0.09 µmol/mol (2σ). Seuls les résultats de la station C semblent avoir une plus grande dispersion au regard des autres points, mais les résultats sont indiscernables du fait des barres d'erreurs.
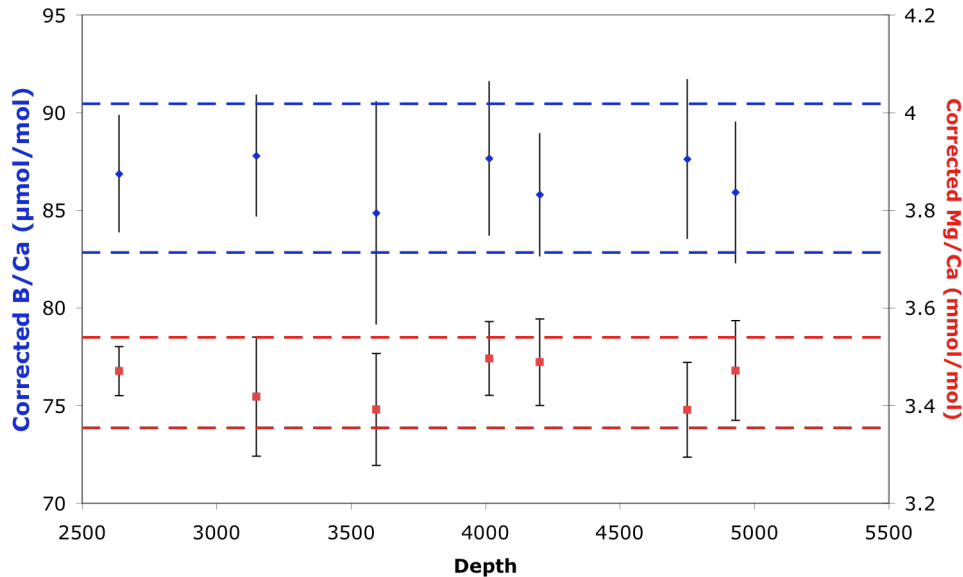
Figure 43 : Mesures de B/Ca et de Mg/Ca corrigée de l'effet de la dissolution en fonction de la profondeur. Les barres d'erreurs représentent l'écart type entre les différentes répliques de chaque station. Les lignes pointillés montrent l'écart type obtenu pour les valeurs corrigées.

Afin de valider notre approche de correction, nous avons calculé le pH en utilisant les valeurs corrigées de B/Ca et Mg/Ca puis nous les avons comparé avec le pH calculé en utilisant les données GLODAP. La valeur moyenne des Mg/Ca corrigés conduit à une température de 25.5 °C, ce qui correspond à la température moyenne des 60 premiers mètres de la colonne d'eau. La valeur moyenne de B/Ca corrigée conduit elle à un pH de 8.10 ± 0,02 (échelle totale), très proche du pH de 8.11 des eaux de surface obtenu à partir des données GLODAP de sites proche de la Sierra Leone Rise.

L'approche de correction de l'effet de dissolution par l'usage du B/Ca des foraminifères benthiques s'est donc montré concluante et permet de pleinement contrer le biais généré par la dissolution, en reconstruisant parfaitement le pH des eaux de surface à partir de sommets de carotte. Néanmoins, les équations décrites ici pour la procédure de correction sont spécifiques à la Sierra Leone Rise, et d'autres études sur d'autres transects de profondeur provenant de différents bassins océaniques, notamment pacifique dont les eaux profondes sont davantage sous saturées vis-à-vis des carbonates, sont nécessaires pour vérifier la compatibilité, le potentiel ainsi que les limites de cette approche, notamment dans le cas de reconstruction de paléo-pH.