

Boron/Calcium ratios in *Globigerinoides ruber* from the Arabian Sea: Implications for controls on Boron incorporation

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Abstract

Culture and downcore studies have been used to argue that B/Ca ratios in planktic foraminifera are correlated with seawater pH and may record seawater borate/bicarbonate ratios, although other factors may also control B/Ca. Specimens of *Globigerinoides ruber* from the Ocean Drilling Program (ODP) Site 723A (western Arabian Sea) and Core AAS9/21 (eastern Arabian Sea) from the last 22 kyr were analysed for B/Ca, $\delta^{18}\text{O}$ and Mg/Ca. B/Ca was compared to reconstructed salinity and sea surface temperature (SST) records, to gain insight into the processes controlling the incorporation of boron. In both cores, B/Ca and Mg/Ca is positively correlated which suggests that temperature governs the incorporation of boron in *G. ruber* to some extent. Higher B/Ca ratios at the site affected by upwelling (ODP 723A) than in the non-upwelling region (Core AAS9/21), and a positive correlation between B/Ca and shell size in *G. ruber* are observed. We observe no significant correlation between B/Ca in *G. ruber* and salinity, pH or dissolved inorganic carbon (DIC) in either the western or eastern Arabian Sea which throws considerable doubt on the utility of B/Ca ratios as a pH or pCO₂ proxy.

Keywords: B/Ca, *G. ruber*, Arabian Sea, shell size, SST, DIC.

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1. Introduction

Oceans may be a source or sink of CO₂ depending on the relative partial pressure of this gas in the atmosphere and seawater. An increase of CO₂ in seawater decreases its pH and leads to a decrease in carbonate ion concentration ([CO₃²⁻]) (Zeebe and Wolf-Gladrow, 2001) which in turn may inhibit the shell growth of calcareous organisms or even dissolve their shells (Broecker and Clark, 2001). In order to measure past variations in pH and [CO₃²⁻], empirically-validated and robust carbonate system proxies are required. Boron isotope ($\delta^{11}\text{B}$) values of planktic foraminifera (Sanyal et al., 1996) and a few others like B/Ca, U/Ca and Zn/Ca in planktic foraminiferal tests have been used or suggested as potential proxies to understand the pH variability of past oceans (see Katz et al., 2010 for a review). Out of these the B/Ca proxy shows great promise as a pH proxy (Yu et al., 2007). Boron exists in seawater as borate (B(OH)₄⁻) or boric acid (B(OH)₃), with the proportions of each varying with seawater pH. B(OH)₃ is more abundant at lower pH and B(OH)₄⁻ is abundant at higher pH. Dissolved B(OH)₄⁻ is considered to be the species incorporated into foraminiferal calcite and hence B/Ca should increase with greater abundance of borate. Boron incorporation in foraminifera shells will thus be greater if the seawater is more alkaline (see Hemming and Hanson, 1992).

Using B/Ca ratios in *G. bulloides* and *G. inflata* and the empirical boron partition coefficient, K_D ($= [\text{B}/\text{Ca}_{\text{CaCO}_3}] / [\text{B}(\text{OH})_4^-]/\text{HCO}_3^-]_{\text{seawater}}$), Yu et al. (2007) reconstructed pH and pCO₂ of seawater and showed that during the Last Glacial Maximum (LGM), pH was 0.15 units higher and aqueous pCO₂ was 95 μatm lower in the southern Pacific Ocean. They attributed core-top K_D variability to the influence of temperature on boron partitioning. Further, Tripathi et al. (2009) have used B/Ca ratios in *G. ruber* and *G. sacculifer* from the western tropical Pacific and revealed that during the Middle Miocene, atmospheric pCO₂ may have been similar to modern levels. However, recent studies have demonstrated that B/Ca in planktic foraminifera may be affected by factors such as carbonate ion, dissolved inorganic carbon (DIC; in seawater DIC = [CO₃²⁻] + [HCO₃⁻]), temperature, salinity and growth rate, complicating the interpretation of this proxy (Ni et al., 2007; Foster 2008; Tripathi et al., 2011; Allen and Hönisch, 2012). Allen and Hönisch, (2012) suggest that B/Ca could potentially be applied to upwelling regions where carbonate system shifts can be several times larger than those driven by atmospheric CO₂; for e.g. the northern Arabian Sea where only one study (Palmer et al., 2010) exists to date.

The aim of the present communication is to understand whether B/Ca ratios in *G. ruber* respond to the pH changes between the Holocene and LGM or whether the incorporation of boron is controlled by processes other than pH. Two high-resolution sediment cores, one from the western Arabian Sea (WAS) and the other from the eastern Arabian Sea (EAS), were used in this study. The planktic foraminifera species *Globigerinoides ruber* (white) was selected as it dwells in the surface seawater and is present all year round in the Arabian Sea (Curry et al., 1992).

2. Regional settings:

The Arabian Sea is influenced by the south-west (SW) monsoon winds during the northern hemisphere summer and north-east (NE) monsoon winds during winter and the associated water circulation patterns (Wyrтки, 1973). The strong southwesterly monsoon winds blow across the Arabian Sea, causing offshore Ekman transport and intense seasonal upwelling along the Oman and Somalia margins and weak upwelling along some parts of the east coast of India (Wyrтки, 1973). The upwelled waters are cold and nutrient-rich and also laden with higher CO₂ (Peeters et al., 2002). The WAS is an intense CO₂ source to the atmosphere with pCO₂ values reaching ~600 µatm during the SW monsoon (Sarma, 2003). During the NE monsoon the upwelling in the WAS is suppressed and there is a convective mixing due to surface cooling in the EAS (Madhupratap et al. 1996). The EAS, unlike the WAS, is influenced by heavy precipitation during the SW monsoon and is also fed by numerous rivers from the Indian subcontinent. Upwelling of cooler subsurface waters in the western Arabian Sea creates an east-west temperature gradient in the region (Cullen and Prell, 1984). Associated with SW monsoon upwelling conditions in the WAS, is an increase in *G. bulloides* abundance (Curry et al., 1992). Since *G. bulloides* is a reliable upwelling tracer and the SW monsoon is coupled to upwelling, the relative abundance of *G. bulloides* was used to reconstruct upwelling intensity and hence palaeomonsoon (Prell, 1984; Anderson and Prell, 1993). In the WAS, an increase in *G. bulloides* abundance/flux was observed during ~12 to 5 kyr and is associated with an increase in intensity of upwelling (Naidu and Malmgren, 1996, Gupta et al., 2003).

3. Materials and Methods

The WAS core (Ocean Drilling Program (ODP) Site 723A; 18°03'N and 57°37'E; wd = 808 m) and the EAS core (AAS9/21; 14°30'N and 72°39'E; wd = 1807 m) are from above lysocline depths (Fig. 1). The age model of ODP Core 723A was taken from Naidu and Malmgren (2005) and *G. bulloides*

flux and *G. ruber* shell size data was taken from Naidu and Malmgren (1995). The age model, Mg/Ca SSTs and reconstructed salinity from AAS9/21 were taken from Govil and Naidu (2010). Sediment trap samples were obtained from a Western Arabian Sea Trap (WAST) (location: 16°20'N and 60°20'E) placed at 4020 m below the sea surface.

The sediment sample was wet sieved (150 µm sieve), dried and again sieved in a narrow size range of 300-355 µm. This fraction was sonicated in methanol for ~8 s at 40 Hz to clean the shells. The cleaned shells were oven dried at 50°C. Whole *G. ruber* (white) shells were picked (n = 60) and weighed on a microbalance (1σ precision = ± 2 µg, n = 10) and the individual shell weight was averaged out. Foraminiferal element/Ca ratios were measured using a Varian 820MS quadrupole Inductively Coupled Plasma -Mass Spectrometer (ICP) at the State University of New York, Oswego using intensity ratio calibration. Introduction system was a Quartz spray chamber/torch, and PFA 50 µl/min nebulizer with self aspiration. *Globigerinoides ruber* shells (n = 60) were crushed using pre-cleaned glass plates. Successive deionized water and methanol washes were carried out to remove clays followed by coarse grained silicate removal under a binocular microscope (Barker et al., 2003). Rigorous oxidative steps were carried out using alkali buffered 1% H₂O₂ in the clean laboratory to remove organic matter (Barker et al., 2003). The reductive cleaning step was not carried out (see Yu et al., 2007). Before dissolution, samples were rinsed twice with acid (0.001M HNO₃) to remove any adsorbed contaminants. Finally, cleaned samples were dissolved in 200 ml 0.075M HNO₃ for measurements in the ICP-MS (Yu et al., 2005). Precision for B/Ca is <2%, based on replicate measurements (n=16) of a standard with B/Ca =150 µmol/mol. Background of B is <2% of consistency standard (B/Ca = 150 µmol/mol). Precision for Mg/Ca is <1% (n=16), of a standard with Mg/Ca = 1.89 mmol/mol. The calibration standards are identical to those used in Cambridge (Yu et al., 2005), thus no inter-lab offset. B/Ca or Mg/Ca do not covary with Al/Ca or Mn/Ca indicating there is no contamination from diagenetic coatings or silicates.

Oxygen and carbon isotopes were analysed on an 'Isoprime' mass spectrometer at the LDEO. Reproducibility (1σ; n = 9) of carbonate standard was ±0.05‰ and ±0.03‰ for δ¹⁸O and δ¹³C, respectively. The Mg/Ca ratios from ODP 723A were converted to sea surface temperature (SST) values using the equation, $T = (1/0.09) * \text{LN}(\text{Mg/Ca}/0.449)$ (Anand et al., 2003 for *G. ruber*) and for AAS9/21 the temperature equation used was; $T = (1/0.09) * \text{LN}(\text{Mg/Ca}/0.38)$ (Dekens et al., 2002). These calibration equations provided temperature estimates of core tops close to the modern values at

respective core locations. Measured foraminiferal oxygen isotope values ($\delta^{18}\text{Oc}$) were corrected for continental ice volume using the dataset of Waelbroeck et al. (2002). The residual $\delta^{18}\text{O}$ values thus obtained were then used to compute a local $\delta^{18}\text{Ow}$ using the Mg/Ca-derived SST by applying the equation, $\delta^{18}\text{Ow} = 0.27 + ((T - 16.5 + 4.8 \cdot \delta^{18}\text{Oc})/4.8)$ (Bemis et al., 1998). Based on the error estimates of Mg/Ca analyses and $\delta^{18}\text{Oc}$, an overall error estimate (1σ) for reconstructed $\delta^{18}\text{Ow}$ is $\pm 0.1\%$. The $\delta^{18}\text{Ow}$ values were then converted into salinity using the equation, $S = (\delta^{18}\text{Osw} + 15.2)/0.45$ (Rostek et al., 1993). The salinity analysed from core-tops using these calibrations give the closest modern values.

In order to calculate borate concentrations, data from Rixen et al., (2006) along the Western Arabian Sea transect were used. CO_2 system calculations were performed using a Microsoft Excel-based programme (CO₂sys_v2.1; Lewis and Wallace, 1998). Input parameters were salinity, temperature, alkalinity, TCO₂ and nutrients, and the constants used were as follows : pK^*B and KHSO_4 are from Dickson (1990), the relationship between total B in seawater and chlorinity from Lee et al. (2010) and K1 & K2 carbonate disassociation constants from Leuker et al. (2000). pH calculations were done on the 'total scale'.

4. Results

B/Ca ratios in ODP Core 723A ranged from 124 to 179 $\mu\text{mol/mol}$ (Fig. 3a). A clear increase in B/Ca is seen during the period from 5 to 12 kyr. This period coincides with an increase in the intensity of upwelling (see Fig. 3b), as indicated by an increase in *G. bulloides* flux (Naidu and Malmgren, 1996). We have compared B/Ca_{G. ruber} ratios from the present study to earlier published records for the same time interval. As seen from Table 1, highest B/Ca ratios from ODP 723A are followed by AAS9/21 for the Late Holocene as well as LGM. Temperature, salinity and pH difference between these sites is $\sim 2.5^\circ\text{C}$, 1 psu and 0.3 units respectively whereas the B/Ca difference is $\sim 40 \mu\text{mol/mol}$. Furthermore, the B/Ca difference in Late Holocene and LGM ranges between 1 and 10 $\mu\text{mol/mol}$.

Mg/Ca ratios from ODP Core 723A ranged from 4 to 5.5 mmol/mol and the reconstructed SSTs varied from 24 to 28°C for the last 22 kyr (Fig. 3c). Reconstructed salinity values varied from 34.4 to 37.5 psu (Fig. 3d). B/Ca is weakly correlated to Mg/Ca (SSTs) ($R^2 = 0.24$; $n = 39$; P-value = 0.007) (Fig. 5a) whereas there is no relationship with reconstructed salinity ($R^2 = 0.03$; $n = 16$). In Core AAS9/21, B/Ca ranged from 117 to 132 $\mu\text{mol/mol}$ (Fig. 4a) and SST varied from 25°C to 29°C (Fig.

4b). In this core B/Ca and Mg/Ca show significant correlation ($R^2 = 0.4$; $n = 23$; P-value = 0.005) (Fig. 5b). However, B/Ca and salinity (Fig. 4c) did not show any correlation ($R^2 = 0.07$; $n = 18$). In ODP Core 723A, shell weights of *G. ruber* varied from 12 to 19 μg (Fig. 3e). In Core AAS9/21 shell weights varied from 13 to 16 μg (Fig. 4d). Shell weights do not show any correlation to B/Ca at both the sites (ODP 723A; $R^2 = 0.04$; $n = 39$) (AAS9/21; $R^2 = -0.1$; $n = 21$). B/Ca ratios measured from the WAST were higher during the SW monsoon and lower during the inter monsoon period (Table 2).

5. Discussion

A major influence on boron incorporation could be calcification temperature (Wara et al., 2003). Existence of significant correlation between the B/Ca and SST derived from Mg/Ca at ODP Site 723A and Core AAS9/21 is consistent with a possible influence of SSTs on boron incorporation in *G. ruber* shells. Our data shows that SSTs at WAS were lower than that at EAS. Therefore, we would expect as per the study of Wara et al. (2003), that the B/Ca concentrations at WAS should be lesser in comparison to those at EAS. But, on the contrary, the B/Ca values at WAS are much higher which suggests that temperature is not the only factor controlling boron incorporation (Foster, 2008; Tripathi et al., 2009; Allen et al., 2012).

ODP Site 723A has been subjected to a number of important studies, aimed at reconstruction of the Indian monsoon based on upwelling records from LGM to present (Naidu and Malmgren, 1996; Gupta et al., 2003). These studies have used the *G. bulloides* flux in marine sediment as an indicator of upwelling and hence a proxy for monsoon strength. Their results show that upwelling intensity was weak during the last glacial period and it strengthened from 12 to 5 kyr and then eventually weakened after 5 kyr (Fig. 3b). We examined the down core B/Ca ratios from ODP Core 723A where substantial information on upwelling strength variability is available. Strikingly high B/Ca values were noticed during an intense upwelling period from 12 to 5 kyr (Fig. 3a). One would expect lower pH values of seawater due to increased CO_2 concentrations in surface waters as a result of upwelling. We have calculated carbonate ion $[\text{CO}_3^{2-}]$ and borate concentrations $[\text{B}(\text{OH})_4^-]$ of the surface water along a transect perpendicular to the coast of Oman to 1200 km offshore (Rixen et al., 2006). The $[\text{CO}_3^{2-}]$ ranges from 140 to 257 $\mu\text{mol/kg}$ and $[\text{B}(\text{OH})_4^-]$ from 64 to 112 $\mu\text{mol/kg}$ (Fig. 2). The $[\text{CO}_3^{2-}]$ and $[\text{B}(\text{OH})_4^-]$ show similar behavior with lower concentrations in the upwelling region near the Oman coast and increasing concentrations further offshore where upwelling ceases. It is known that as pH increases, the

proportion of boron in the form of borate increases, while boric acid decreases (Dickson, 1990). So in the past as upwelling became more intense, the concentration of $[B(OH)_4^-]$ as well as $[CO_3^{2-}]$ must have decreased due to a decrease in pH and therefore the incorporation of boron in foraminifera shells must have also decreased. Contrary to this, upwelling periods at ODP 723A display higher B/Ca. Furthermore, in both cores, B/Ca and reconstructed salinity do not show any relationship. Comparison of B/Ca_{G. ruber} ratios from the present study to earlier published records shows a large difference in B/Ca between sites for the Late Holocene as well as LGM which cannot be explained by a temperature/ salinity/ pH effect (Table 1).

Culture experiments of *G. ruber* and *G. sacculifer* show that B/Ca in shells increases with increasing pH but decreases with increasing DIC (Allen et al., 2012). They find an interplay between borate and carbonate species for inclusion into the crystal lattice and hence they conclude that B/Ca of calcite depends on the relative abundance of $B(OH)_4^-$ and DIC. In our study region we expect DIC to be high during upwelling times and hence if there is a DIC control in *G. ruber*, B/Ca ratios are expected to be lower during upwelling periods. We plotted B/Ca data from the ODP 723A core-top and from the WAST sediment traps against pH and $[B(OH)_4^-]/DIC$ (calculated using data from Takahashi et al., 2009 and Rixen et al., 2006) to test the reproducibility of the relationships by Allen et al., (2012) outside of culture studies. Interestingly, results are contrary to their findings (Fig. 6). We observe negative relationships between B/Ca:pH and B/Ca: $[B(OH)_4^-]/DIC$.

Another factor which could be important in this regard is foraminiferal growth rate or size-related changes in B/Ca. It is known from ODP Core 723A that foraminifera grew larger in size during upwelling (Naidu and Malmgren, 1995). The correlation between B/Ca and shell sizes (shell area) of *G. ruber* exhibit significant correlation ($R^2 = 0.40$; $n = 33$; P-value = 0.0005) (see Fig. 3f) suggesting that the B/Ca ratio increases when foraminifera grow a larger test. B/Ca ratios are shown to increase with increasing shell size in *G. ruber* possibly due to higher overall growth rate in larger individuals than in small ones, resulting in less efficient discrimination of the trace elements during their incorporation into the calcite lattice in overall faster growing organisms (Ni et al., 2007). This size-fraction related bias could be associated with enhanced symbiont photosynthetic activity in large specimens which raises the pH of the foraminiferal microenvironment and elevates B/Ca in its shell (Hönisch and Hemming, 2004; Henehan et al., 2013). Our study suggests that though temperature seems to have a control on boron incorporation in *G. ruber* in the Arabian Sea, growth rate may play a role in upwelling regions with

higher boron in shells during intense upwelling periods. This inference is also supported by the seasonal sampling by sediment traps from the western Arabian Sea wherein higher B/Ca ratios are noted in shells during the upwelling periods (Table 2).

6. Conclusions

B/Ca from two sediment cores from the Arabian Sea is positively correlated to Mg/Ca derived SSTs. There also seems to be a lack of a significant correlation between B/Ca and salinity, pH or DIC. Significant positive correlation between B/Ca ratios and shell sizes of *G. ruber* in the upwelling region suggests that boron incorporation in planktic foraminifera maybe size-related and could arise from an effect of growth rate on B/Ca in *G. ruber*. In summary, then, our data do not appear to support the use of B/Ca ratios in foraminifera to estimate ocean carbonate system changes.

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Table 1: Range of B/Ca ($\mu\text{mol/mol}$) concentrations in *G. ruber* at different core sites for the Late Holocene and the LGM. Numbers in closed brackets denote average concentrations. Also provided are the modern day seawater temperature, salinity and pH whereas for ODP668B and Site 806 are reconstructed values*.

Study	Core	Late Holocene B/Ca ($\mu\text{mol/mol}$)	n	Temp ($^{\circ}\text{C}$)	S (psu)	pH (total scale)	LGM B/Ca ($\mu\text{mol/mol}$)	n
Yu et al., 2007	ODP668B (Eastern Equatorial Atlantic)	104	1	26.5*	35.7*	8.15*	103	1
Foster, 2008	ODP999A (Caribbean Sea)	120-123 (121)	2	28.63	35.4	8.16	111-111 (111)	2
Tripati et al., 2009	Site 806 (Western Tropical Pacific)	119	1	29*	34.5*	8.21*	~114	1
Present	ODP 723A (WAS)	143-152 (147)	7	26.63	35.8	7.87	124-148 (137)	4
Present	AAS9/21 (EAS)	117-132 (125)	6	28.50	35.3	8.06	117-121 (119)	4

Table 2: B/Ca concentrations from planktic foraminifera *G. ruber* shells collected from the WAST during SW monsoon and post-monsoon seasons. Also shown are approximated pH, DIC, TA, Borate/DIC and Salinity (data from Takahashi et al., 2009). * marks upwelling periods.

Trap sample collection date (dd/mm/yy) –period	B/Ca ($\mu\text{mol/mol}$)	Temp ($^{\circ}\text{C}$)	pH (total scale)	DIC ($\mu\text{mol/kg}$)	Total Alkalinity ($\mu\text{mol/kg}$)	Borate/DIC	Salinity (psu)
31/07/97 to 12/08/97 - 13 days	*125	25.8	8.02	2066	2377	0.0468	36.28
17/09/97 to 29/09/97 - 13 days	*138	26.5	8.04	2038	2363	0.0491	36.07
16/11/97 to 28/11/97 - 13 days	122	27.7	8.07	2009	2372	0.0547	36.22

Figure Captions

Fig. 1. Core sites and sediment trap location used in the present study indicated by black filled circles. U.S. JGOFS sampling stations are shown as grey stars.

Fig. 2. Carbonate and borate ion concentrations calculated for stations along the U.S. JGOFS transect.

Fig. 3. a) B/Ca b) *G. bulloides* flux c) Mg/Ca and reconstructed SSTs d) reconstructed salinity e) *G. ruber* shell weights and f) *G. ruber* shell size from ODP Core 723A.

Fig. 4. a) B/Ca b) reconstructed SSTs c) reconstructed salinity and d) *G. ruber* shell weights from Core AAS9/21.

Fig. 5. Correlations between B/Ca and Mg/Ca in a) ODP 723A and b) AAS9/21

Fig. 6. B/Ca plotted against pH and $[\text{B}(\text{OH})_4^-]/\text{DIC}$ shows negative relationships contradictory to culture studies.

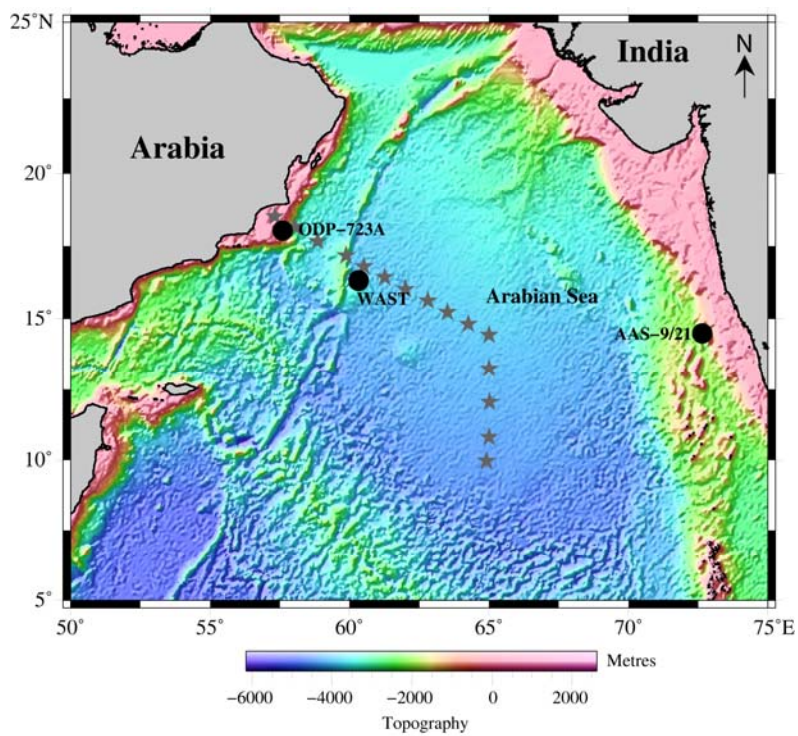


Fig. 1

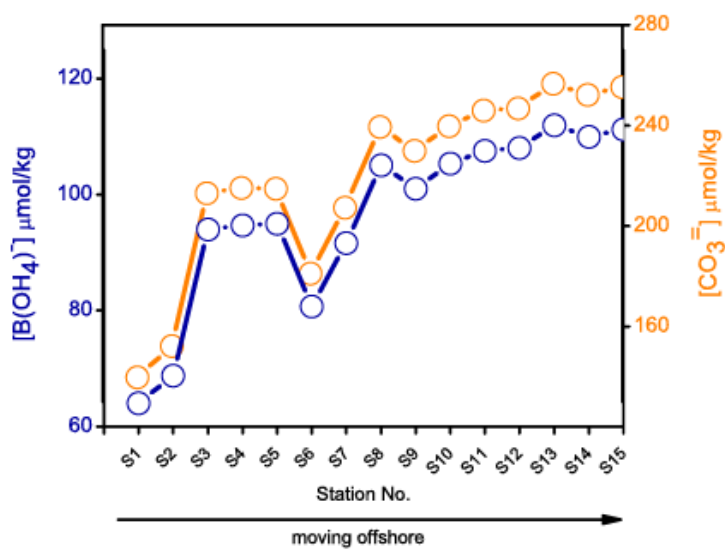


Fig. 2

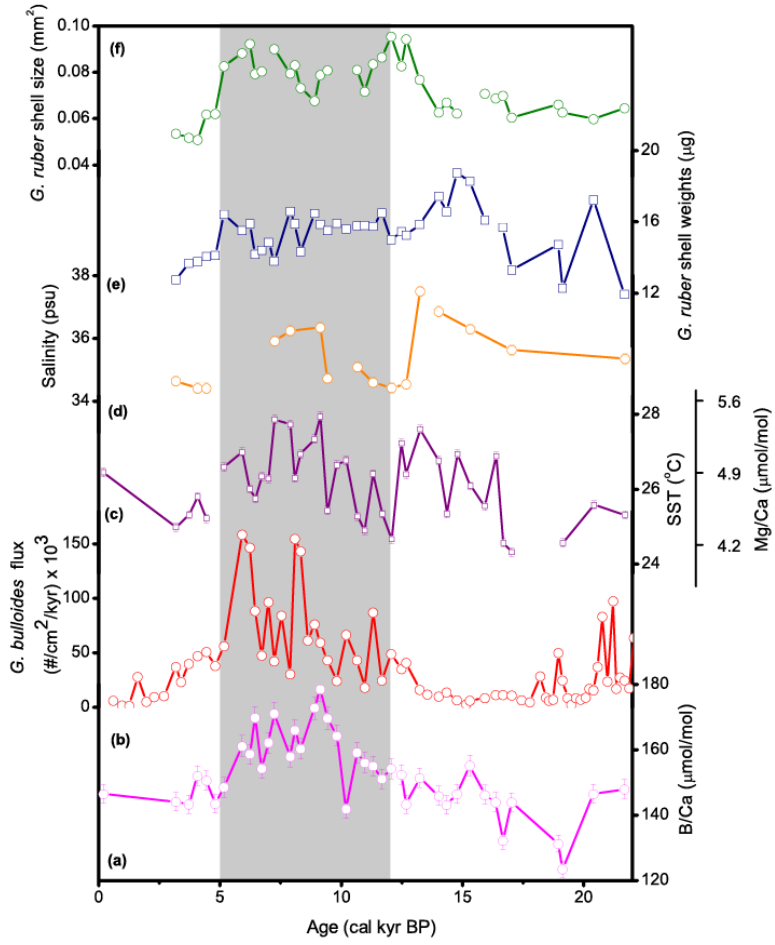


Fig. 3

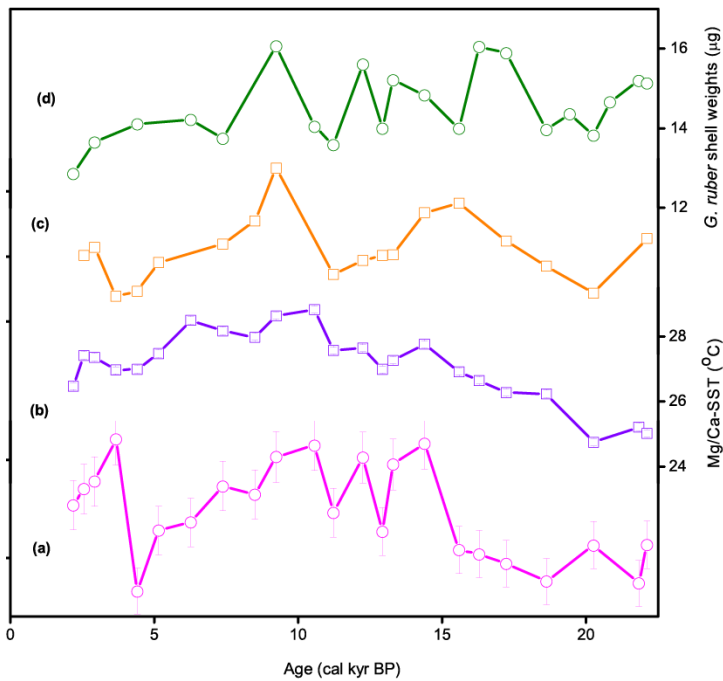


Fig. 4

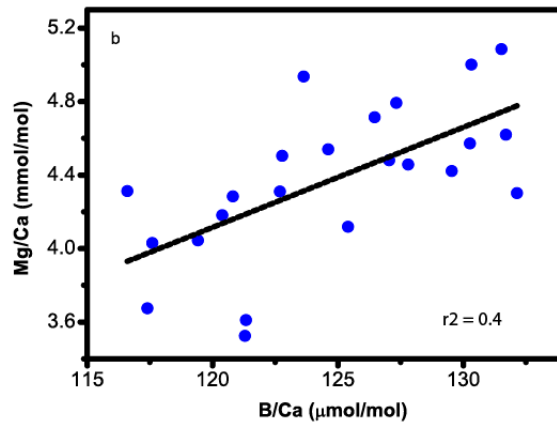
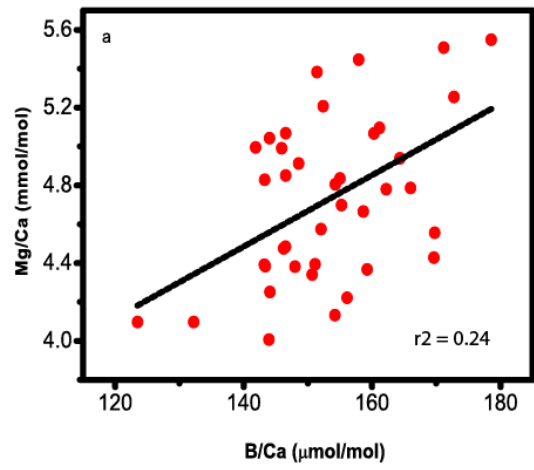


Fig. 5 a and b

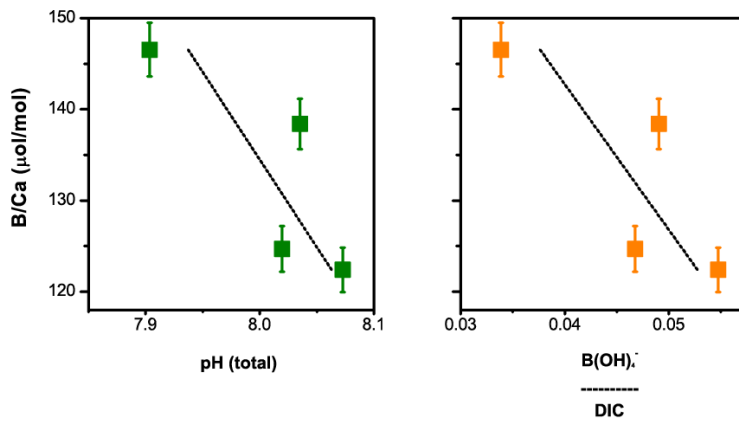


Fig. 6