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Letter

Relationship between weights of planktonic foraminifer shell and surface water $CO_3^{=}$ concentration during the Holocene and Last Glacial Period

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ABSTRACT

Shell weights of *Globigerinoides sacculifer* and the elemental concentration of magnesium and calcium (Mg/Ca) from *Globigerinoides ruber* measured from an Arabian Sea sediment core, AAS9/21, exhibit an inverse relationship with each other, which reveals that shell weights are mainly controlled by surface water $[CO_3^{=}]$ rather than calcification temperature. Down core shell weight variations of Core AAS9/21 show an excellent correspondence with CO_2 concentrations in an Antarctic Ice Core, which reveals that planktic forminifera shells can trace atmospheric CO_2 due to the resultant change in surface water $[CO_3^{=}]$. Hence, shell weights of *G. sacculifer* can be used as a proxy to reconstruct atmospheric CO_2 concentrations in the past. Here, based on the shell weights, surface water $[CO_3^{=}]$ change in the Arabian Sea is quantified and found that a $[CO_3^{=}]$ variation of ~8 µmol/kg occurred during the Holocene and a ~36 µmol/kg variation occurred during the last glacial period.

1. Introduction

CO_2 dissolved in the surface ocean waters is known to be in equilibrium with the atmospheric CO_2 content. As atmospheric CO_2 dissolves in seawater, it influences the dissolved inorganic carbon (DIC) species; CO_2 (aq), H_2CO_3, HCO_3^- and $CO_3^{=}$ (Broecker and Peng, 1982). The increased dissolution of CO_2 consequently decreases the pH and carbonate ion concentration $[CO_3^{=}]$ of surface and deep waters. Records from Antarctic ice cores indicate that the concentration of CO_2 in the atmosphere has varied in step with the waxing and waning of ice ages, fluctuating between 180 ppmv to 280 ppmv during glacial and interglacial time periods respectively (Barnola et al., 1987; Petit et al., 1999).

It was first shown by using the planktic foraminifer *Orbulina universa* in culture experiments that increase in shell weights can be due to increase in shell thickness as a result of increase in $[CO_3^{=}]$ (Spero et al., 1997). Later it was demonstrated that shell weights of several planktic foraminifera species from narrow size fractions from the North Atlantic varied systematically as a function of latitude (Barker and Elderfield, 2002). These findings were combined with a record of shell weight across glacial–interglacial Termination-I to demonstrate that the changes are a result of ambient $[CO_3^{=}]$ changes rather than calcification temperature and are consistent with known changes in atmospheric pCO_2.

Subsequent studies have shown that factors which control shell weights are more complex than previously thought (de Villiers, 2003). It was also suggested that shell calcification is apparently a function of complex interplay of environmental parameters (de Villiers, 2004). This study was followed by a study from the tropical Indian Ocean, which demonstrated that *Globigerinoides sacculifer* shell weights were indeed controlled by $[CO_3^{=}]$ of surface waters (Naik and Naidu, 2007). These conflicting results led to another study which employed different foraminifer species, viz, *Globigerina bulloides*, *Globigerinoides ruber* and *Neogloboquadrina pachyderma* to gain a better understanding of the control of calcification rate (Gonzalez-Mora et al., 2008). It was shown that in general, $[CO_3^{=}]$ of surface waters controls shell weights in *G. bulloides* and *G. ruber*, but *N. pachyderma* thrives on optimum growth conditions. All these studies basically point out that factors controlling shell calcification may vary from species to species. In the present study we make use of the planktic foraminifer *G. sacculifer* and provide evidence for the dependency of shell weights on surface water $[CO_3^{=}]$ over calcification temperature, on a glacial/interglacial timescale and further use it as proxy to quantify the $[CO_3^{=}]$ change during Holocene and last glacial period in the Arabian Sea.

2. Methods

The sediment core AAS9/21 was recovered from the Arabian Sea in the northern Indian Ocean (14.51°N and 72.65°E) from a water depth of 1807 m (Fig. 1). This core, of 2.16 m length was sub-sampled at every 10 cm interval. All the samples were disaggregated by soaking

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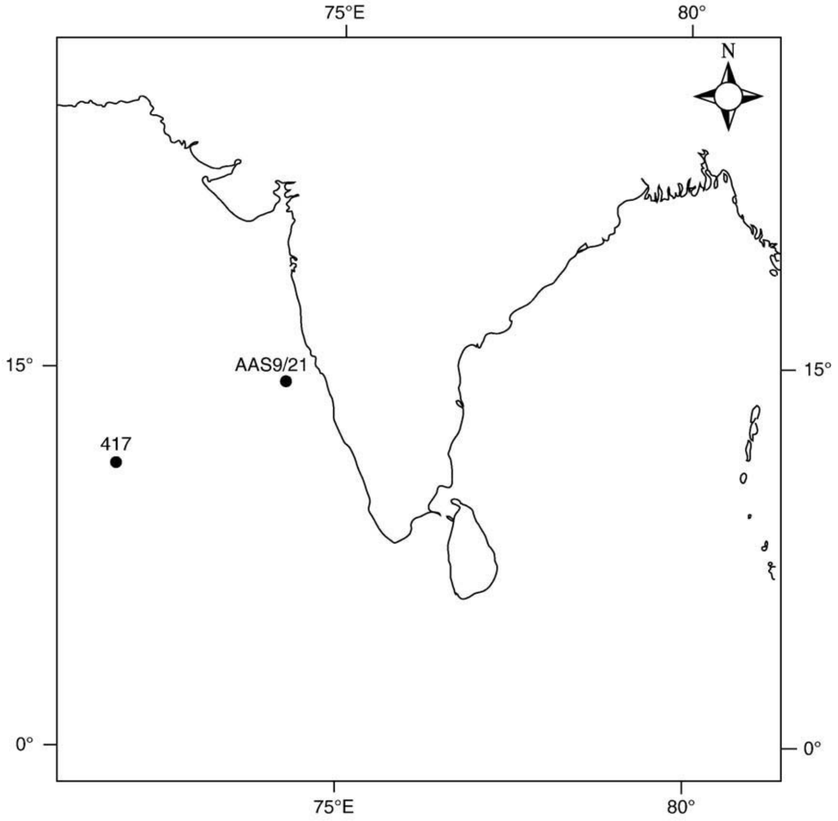

Fig. 1. Map showing location of Core AAS9/21 and GEOSECS station 417.

in distilled water and then wet sieved through a >63 µm sieve. Shell weight measurements were made following the procedure of Lohmann (1995). A portion of the coarse fraction (>63 µm) was cleaned and sonicated in methanol at 40 hz for 8 s in order to remove fines that could fill the last chambers. The material was then oven dried at 50 °C and passed through sieves in order to isolate 350–420 µm size fractions. Fifty shells of *G. sacculifer* were picked under a Stereo Binocular Microscope and weighed on a microbalance (1σ precision: ±2 µg, n = 10).

Chronology was established using Carbon-14 dates obtained by Accelerator Mass Spectrometry (AMS) at Kiel University. Monospecific samples of the planktic foraminifera *G. ruber* in the size range of 250–350 µm, was used for AMS carbon dates. These ^{14}C dates were converted to calendar years by using the calibration program; CalPal, quickcal 2005 ver 1.4 (Weninger et al., 2006).

Mg/Ca ratios of foraminifera are a rather well established proxy for Sea Surface Temperature (SST) (Nürnberg et al., 1996). We have used Mg/Ca ratios data published from AAS9/21 by Govil and Naidu (2010) for comparing with shell weights of *G. sacculifer*. For determination of the Mg/Ca ratios, 30 to 40 individuals of planktic foraminiferal species; *G. ruber* (white variety) within a size range of 250 to 350 µm were picked and gently crushed while viewing through a binocular microscope. Clay lumps and shell fragments containing clays were removed manually. Crushed samples were cleaned following the protocol described by Barker et al. (2003). 0.2 N HNO_3 was added to the cleaned samples and left overnight, allowing foraminiferal shell fragments to dissolve completely. The solutions were later transferred into clean vials and diluted with HNO_3. 'Mg' and 'Ca' analyses were carried out on a Thermo Finnigan Element 2, sector field, Inductively Coupled Plasma-Mass Spectrometer. Elemental concentrations were derived from the isotopes, ^{25}Mg and ^{43}Ca; ^{89}Y served as internal standard in order to correct for instrument drift. ^{27}Al and ^{55}Mn were also measured simultaneously, to monitor the effectiveness of the cleaning protocol. Long-term repeatability of sample solutions yielded a 1σ precision of ±0.1 mmol/mol Mg/Ca (n = 40).

To convert shell weights into surface water $[\mathrm{CO_3^{=}}]$ this study has adopted the slope derived from the relationship between pressure-normalized $[\mathrm{CO_3^{=}}]^*$ and *G. sacculifer* shell weights, from the East Tropical Indian Ocean by Broecker and Clark (2001):

$$G.\ sacculifer\ \text{shell weight} = 0.223 \times [\mathrm{CO_3^{=}}]^* + 7.464$$

The pressure-normalized $[\mathrm{CO_3^{=}}]^*$ obtained from the above equation is then converted to in situ $[\mathrm{CO_3^{=}}]$ from the equation given by Broecker and Clark, (1999): $[\mathrm{CO_3^{=}}]^* = [\mathrm{CO_3^{=}}] + 20\ (4\text{-}h)$; where h is the water depth in km and 20 µmol/kg/km is the increase with water depth of the solubility of calcite. We obtain a $[\mathrm{CO_3^{=}}]$ value of 61 µmol/kg for the core top sample of AAS9/21. The in situ carbonate ion concentration was calculated from the nearest GEOSECS station (No.417) using a programme designed by Taro Takahashi of Lamont Doherty Earth Observatory. The following parameters were the inputs for the programme: Depth (dB), Temperature (°C), Salinity (‰), Alkalinity (µEq/kg), Total CO_2 (µmol/kg), Silicate (µmol/kg) and Phosphate (µmol/kg). It was found that in situ $[\mathrm{CO_3^{=}}]$ at a depth of 1.8 km was 65 µmol/kg, which is near to the value of 61 µmol/kg obtained using shell weight data, which proves that our measurements are reliable.

3. Results

G. sacculifer shell weights from the Core AAS9/21 show an increase downcore with a weight range from 31 to 41 µg, which corresponds to lower values during Holocene and higher values during last glacial period (Fig. 2a; Table 1). The *G. ruber* Mg/Ca values range from 3.4 to 5.2 mmol/mol, with minimum values during last glacial period and maximum values during Holocene. From 15 kyr onwards, Mg/Ca values have increased towards the core top (Fig. 2b; Table 2). The Mg/Ca ratio in foraminifera is controlled by water temperature during