

## **Relationship between Weights of Planktonic Foraminifer Shell and Surface Water $\text{CO}_3^{=}$ 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 [ $\text{CO}_3^{=}$ ] rather than calcification temperature. Down core shell weight variations of Core AAS9/21 shows an excellent correspondence with  $\text{CO}_2$  concentrations in an Antarctic Ice Core, which reveals that planktic foraminifera shells can trace atmospheric  $\text{CO}_2$  due to the resultant change in surface water [ $\text{CO}_3^{=}$ ]. Hence, shell weights of *G. sacculifer* can be used as a proxy to reconstruct atmospheric  $\text{CO}_2$  concentrations in the past. Here, based on the shell weights, surface water  $\text{CO}_3^{=}$  change in the Arabian Sea is quantified and found that a [ $\text{CO}_3^{=}$ ] variation of  $\sim 8 \mu\text{mol/kg}$  occurred during the Holocene and a  $\sim 36 \mu\text{mol/kg}$  variation occurred during the last glacial period.

**Keywords:** *Atmospheric  $\text{CO}_2$  proxy, carbonate ion concentration, Indian Ocean, *Globigerinoides sacculifer* shell weights.*

## 1. Introduction:

CO<sub>2</sub> dissolved in the surface ocean waters is known to be in equilibrium with the atmospheric CO<sub>2</sub> content. As atmospheric CO<sub>2</sub> dissolves in seawater it influences the dissolved inorganic carbon (DIC) species; CO<sub>2</sub> (aq), H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>=</sup> (Broecker and Peng, 1982). The increased dissolution of CO<sub>2</sub> consequently decreases the pH and carbonate ion concentration [CO<sub>3</sub><sup>=</sup>] of surface and deep waters. Records from Antarctic ice cores indicate that the concentration of CO<sub>2</sub> in the atmosphere has varied in step with the waxing and waning of ice ages, fluctuating between 180ppmv to 280ppmv 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<sub>3</sub><sup>=</sup>] (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<sub>3</sub><sup>=</sup>] changes rather than calcification temperature and are consistent with known changes in atmospheric pCO<sub>2</sub>.

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<sub>3</sub><sup>=</sup>] of surface waters (Naik and Naidu, 2007). These conflicting results led to another study which employed different foraminifer species, viz, *Globigerina bulloides*, *Globigerina 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<sub>3</sub><sup>=</sup>] 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<sub>3</sub><sup>=</sup>] over calcification temperature, on a glacial/interglacial timescale and further use it as proxy to quantify the [CO<sub>3</sub><sup>=</sup>] 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 1807m (Fig.1). This core, of 2.16m length was sub-sampled at every 10cm interval. All the samples were disaggregated by soaking in distilled water and then wet sieved through a >63µm sieve. Shell weight measurements were made following the procedure of Lohmann (1995). A portion of the coarse fraction (>63µm) was cleaned and sonicated in methanol at 40hz for 8secs 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 *Globigerinoides sacculifer* were picked under a Stereo Binocular Microscope and weighed on a microbalance (1σ precision: ±2µg, n=10).

Chronology was established using Carbon-14 dates, obtained by Accelerator Mass Spectrometry (AMS) at Kiel University. About 10 mg of planktic foraminifera, consisting of diverse species in the size range of 250-350µm, were used for AMS carbon dates. These <sup>14</sup>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; *Globigerinoides ruber* (white variety) within a size range of 250 to 350µm 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<sub>3</sub> 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<sub>3</sub>. '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 <sup>25</sup>Mg and <sup>43</sup>Ca; <sup>89</sup>Y served as internal standard in order to correct for instrument drift. <sup>27</sup>Al and <sup>55</sup>Mn were also measured simultaneously, to monitor the effectiveness of the cleaning protocol. Long-term repeatability of sample solutions yielded a 1σ precision of ±0.1mmol/mol Mg/Ca (n=40).

To convert shell weights into surface water  $[\text{CO}_3^{2-}]$  this study has adopted the slope derived from the relationship between pressure-normalized  $[\text{CO}_3^{2-}]^*$  and *G. sacculifer* shell weights, from the East Tropical Indian Ocean by Broecker and Clark (2001):

$$G. \text{ sacculifer shell weight} = 0.223 * [\text{CO}_3^{2-}]^* + 7.464$$

The pressure-normalized  $[\text{CO}_3^{2-}]^*$  obtained from the above equation is then converted to in situ  $[\text{CO}_3^{2-}]$  from the equation given by Broecker et al. (1999):  $[\text{CO}_3^{2-}]^* = [\text{CO}_3^{2-}] + 20 (4-h)$ ; where  $h$  is the water depth in  $km$  and  $20 \mu\text{mol/kg/km}$  is the increase with water depth of the solubility of calcite. We obtain a  $[\text{CO}_3^{2-}]$  value of  $61 \mu\text{mol/kg}$  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 ( $^{\circ}\text{C}$ ), Salinity ( $\text{‰}$ ), Alkalinity ( $\mu\text{Eq/kg}$ ), Total  $\text{CO}_2$  ( $\mu\text{mol/kg}$ ), Silicate ( $\mu\text{mol/kg}$ ) and Phosphate ( $\mu\text{mol/kg}$ ). It was found that in situ  $[\text{CO}_3^{2-}]$  at a depth of  $1.8 \text{ km}$  was  $65 \mu\text{mol/kg}$ , which is near to the value of  $61 \mu\text{mol/kg}$  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  $41 \mu\text{g}$ , 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  $5.2 \text{ mmol/mol}$ , with minimum values during last glacial period and maximum values during Holocene. From  $15 \text{ kyr}$  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 shell formation and the lower and higher Mg/Ca values represent lower and higher temperatures respectively. Therefore Mg/Ca values from Core AAS9/21 denote an obvious SST increase from the last glacial period to the Holocene.

### 4. Discussion:

In an attempt to understand the effect of calcification temperature on planktic foraminifera shell weights, we compared the *G. sacculifer* shell weight and *G. ruber* Mg/Ca values obtained from the Core AAS9/21. The shell weight values and the Mg/Ca ratios show a significant negative correlation ( $r^2 = -$

0.6; Fig. 2c), which indicates that higher shell weights are associated with colder temperatures and vice versa. The regional foraminiferal lysocline depth lies around 3300m in the Arabian Sea (Cullen and Prell, 1984) and the present core was raised from 1807m depth, hence one can rule out the effect of dissolution on foraminifer shell weights. In addition, significant negative relationship between *G. sacculifer* shell weights and Mg/Ca of *G. ruber* also provides an evidence for the absence of dissolution, since Mg-rich calcite is more prone to dissolution (Brown and Elderfield, 1996) and hence samples affected by dissolution present lower Mg/Ca ratios.

Due to strong temperature dependence of CO<sub>2</sub> solubility in seawater and the subsequent dissolution of CO<sub>2</sub> (aq) into HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>=</sup>, modern open ocean surface water [CO<sub>3</sub><sup>=</sup>] varies as a function of temperature (Broecker and Peng, 1982). In the present study shell weights were reported to be highest during the last glacial period and show a large decrease in the early Holocene. During the last glacial period, temperatures were colder and surface water [CO<sub>3</sub><sup>=</sup>] was higher as compared to the Holocene (Broecker and Peng, 1982). Also due to a temperature control more CO<sub>2</sub> readily dissolved during glacials thus decreasing the [CO<sub>3</sub><sup>=</sup>]. Therefore a temperature control on shell weights would show lower shell weights during glacial and a carbonate ion control would show higher shell weights during glacial (Barker and Elderfield, 2002). In the present study we have noticed heavier shell weights during the last glacial period and lower during the Holocene. Therefore, we argue that surface water carbonate ion concentration play an important role in controlling the shell weights of planktonic foraminifer species *G. sacculifer*, rather than calcification temperature in the Arabian Sea, in response to changing atmospheric CO<sub>2</sub> during glacials and interglacials.

As discussed above in the present study, since dissolution does not affect shell weights, this core was expected to provide manifestation of CO<sub>2</sub> dissolution in the surface seawaters and should give a CO<sub>3</sub><sup>=</sup> variation in surface waters during the Holocene and the last glacial period. Therefore, we use planktonic foraminifera shell weights as a proxy of pCO<sub>2</sub> variations during the Holocene and the last glacial period. Using the *G. sacculifer* shell weight data from the present study, for a shell weight variation of 10 ± 0.2 µg, the CO<sub>3</sub><sup>=</sup> variation from the last glacial period to the Holocene is calculated to be ~36 µmol/kg. This means that during the glacial, the surface water [CO<sub>3</sub><sup>=</sup>] was ~36 µmol/kg higher than during the Holocene (Table 1). The large difference in shell weight of ~10 µg from the last glacial period to Holocene signifies that the opposite or dampening effect from water temperature, as seen in species like *G. bulloides* and *G. ruber* reported by Gonzalez-Mora et al. (2008), is at minimum.

During the Holocene the atmospheric  $p\text{CO}_2$  was typically close to 280 ppmv, whereas during the last glacial period atmospheric  $p\text{CO}_2$  was 180 to 200 ppmv (Petit et al., 1999). Glacial to Holocene surface water carbonate ion concentration calculated from AAS9/21 was compared to the  $\text{CO}_2$  record from Taylor Dome Ice Core from Antarctica (Smith et al., 1999) and the results show a good match between the two (Fig.3). It is seen that, corresponding to an 80 to 100 ppmv change from the glacial to Holocene in atmospheric  $\text{CO}_2$ , a change of  $\sim 36 \mu\text{mol/kg}$  in  $\text{CO}_3^{=}$  occurred. This is consistent with Spero et al. (1997) estimates based on culture experiments of planktonic foraminifera *Orbulina universa* and *Globigerina bulloides*, wherein it is shown that glacial to interglacial change in  $[\text{CO}_3^{=}]$  was around  $40 \mu\text{mol/kg}$ . In addition, during the course of Holocene a shell weights change of  $\sim 2 \mu\text{g}$  is noticed. This  $2 \mu\text{g}$  change in shell weights during the course of the Holocene calculates to a  $\text{CO}_3^{=}$  concentration of  $\sim 8 \mu\text{mol/kg}$ . In terms of atmospheric  $\text{CO}_2$  change, this difference between Holocene to present corresponds to 20 ppmv (Smith et al., 1999). The results from the Core AAS9/21 are in agreement with the changes discussed from ice cores as well as the results from Broecker and Clark (2007), which suggest that this  $\text{CO}_3^{=}$  change during the course of the Holocene is from 6 to  $13 \mu\text{mol/kg}$ .

## 5. Conclusions:

The present study suggests that the *G. sacculifer* shell weights variations during Holocene – last glacial period- are mainly related to the variations in surface water  $[\text{CO}_3^{=}]$  through time, in response to the changing atmospheric  $\text{CO}_2$ . Accordingly, we estimated the variations of  $[\text{CO}_3^{=}]$  during Holocene and last glacial period in the Arabian Sea. Our estimates show that a variation of  $\sim 8 \mu\text{mol/kg}$  of  $[\text{CO}_3^{=}]$  and  $\sim 36 \mu\text{mol/kg}$  of  $[\text{CO}_3^{=}]$  occurred during Holocene and last glacial period respectively, in the Arabian Sea.

## 5. Acknowledgements:

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**Table captions:**

Table 1. *G. sacculifer* shell weights from the Core AAS9/21 and estimated water [ $\text{CO}_3^{=}$ ] with relation to age.

Table 2. *G. ruber* Mg/Ca data for the Core AAS9/21 with relation to age.

**Figure captions:**

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

Fig. 2. Fluctuations in a) *G. sacculifer* shell weights, b) *G. ruber* Mg/Ca with relation to age and, c) *G. sacculifer* shell weights at selective sections showing a linear relation to *G. ruber* Mg/Ca ratio at corresponding depths ( $r^2 = -0.6$ ).

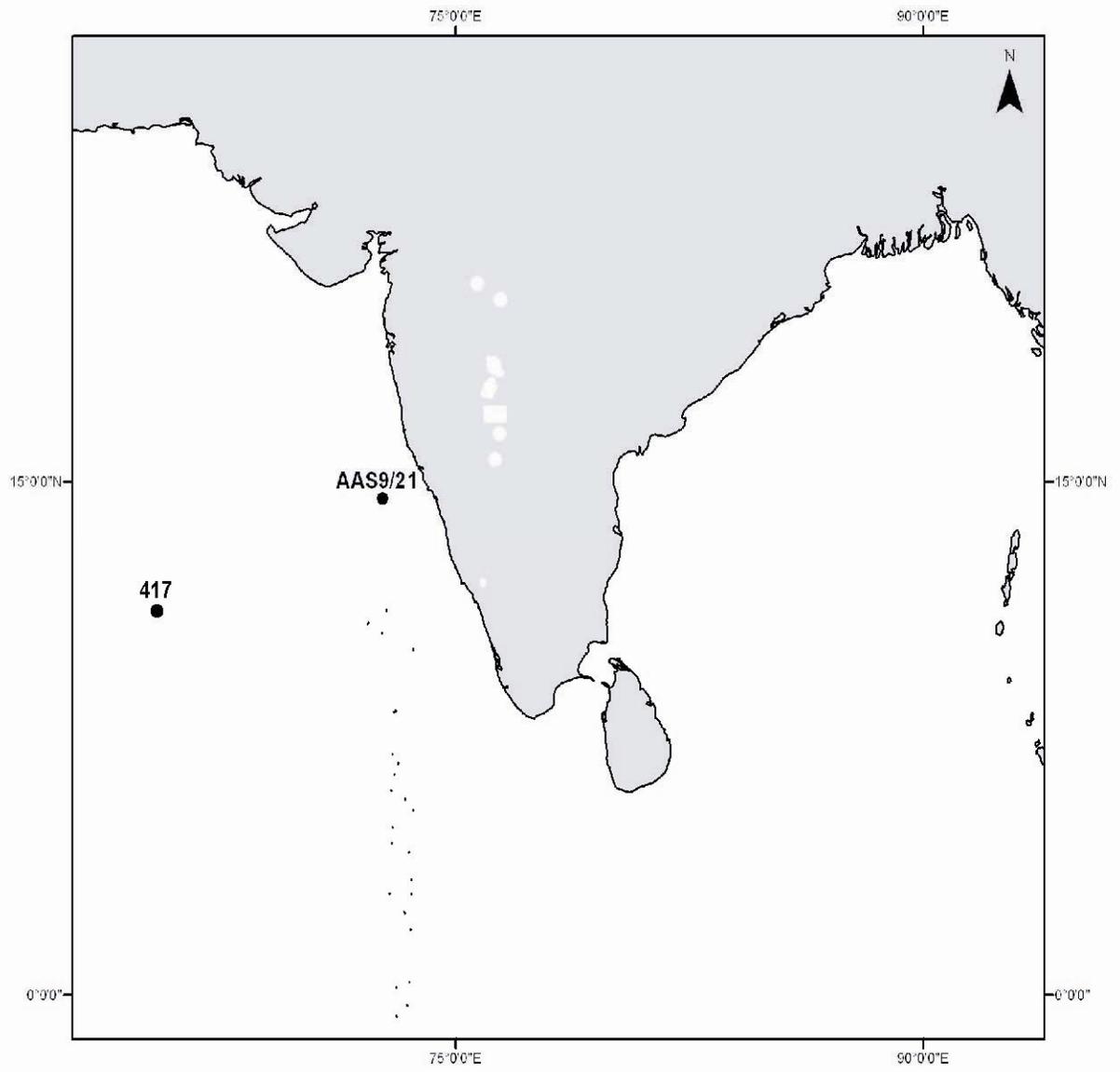
Fig. 3. Estimated water [ $\text{CO}_3^{=}$ ] showing a close relation to  $\text{CO}_2$  measurements from an ice core (Taylor Dome, Antarctica. \* see text)

Table 1. *G. sacculifer* shell weights from the Core AAS9/21 and estimated water [CO<sub>3</sub><sup>2-</sup>] with relation to age.

AAS9/21		
Age (kyr)	<i>G. sacculifer</i> Shell weights (μg)	[CO <sub>3</sub> <sup>2-</sup> ] (μmol/kg) calculated from shell weights
1.068	31	61
2.181	31	61
2.923	32	66
4.407	31	61
6.262	33	70
8.117	33	70
10.343	34	75
11.224	32	66
11.812	35	79
12.839	33	70
13.06	34	75
13.941	36	84
14.879	35	79
15.9298	35	79
17.214	37	88
18.265	40	102
19.15	41	106
20.261	40	102
21.278	41	106
22.111	40	102
23.129	38	93
23.962	39	97
25.639	37	88

Table 2. *G. ruber* Mg/Ca data for the Core AAS9/21 with relation to age.

AAS9/21	
Age (kyr)	<i>G. ruber</i> Mg/Ca (mmol/mol)
0.512	5.18
1.068	5.16
1.81	4.91
2.552	5.04
2.923	4.95
3.665	4.41
4.407	4.34
5.149	4.74
5.891	4.55
7.375	4.75
7.746	4.75
8.488	4.80
9.23	4.99
11.224	4.43
12.252	4.59
12.693	4.41
12.913	4.43
13.281	4.00
13.721	4.88
14.382	4.58
15.58	4.23
17.214	3.74
18.615	3.57
18.965	3.99
19.428	3.80
20.261	3.67
20.816	3.80
22.111	3.39
23.129	3.90
23.407	3.58
23.962	3.72
24.517	3.73
24.98	3.85
25.639	4.84



**Fig. 1**

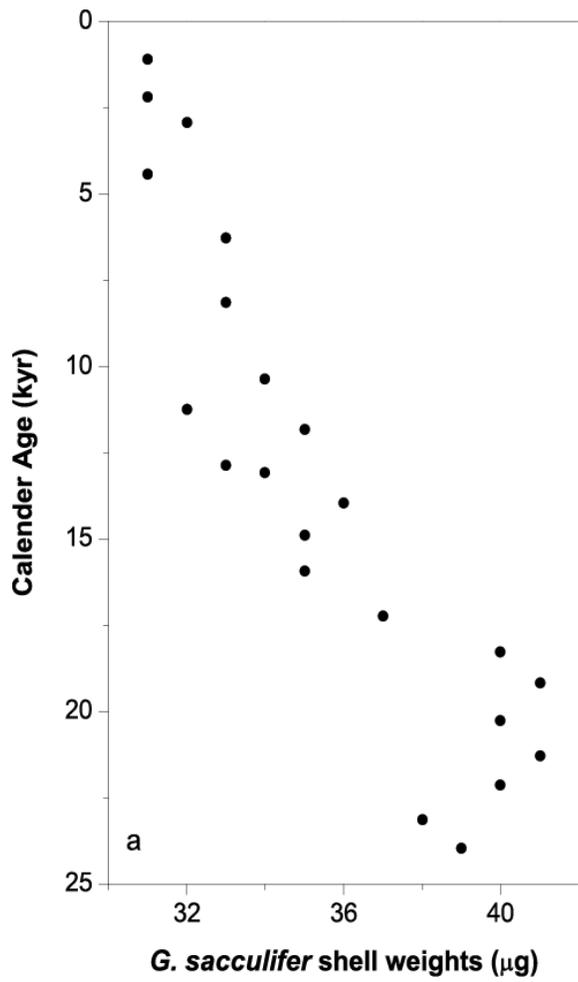
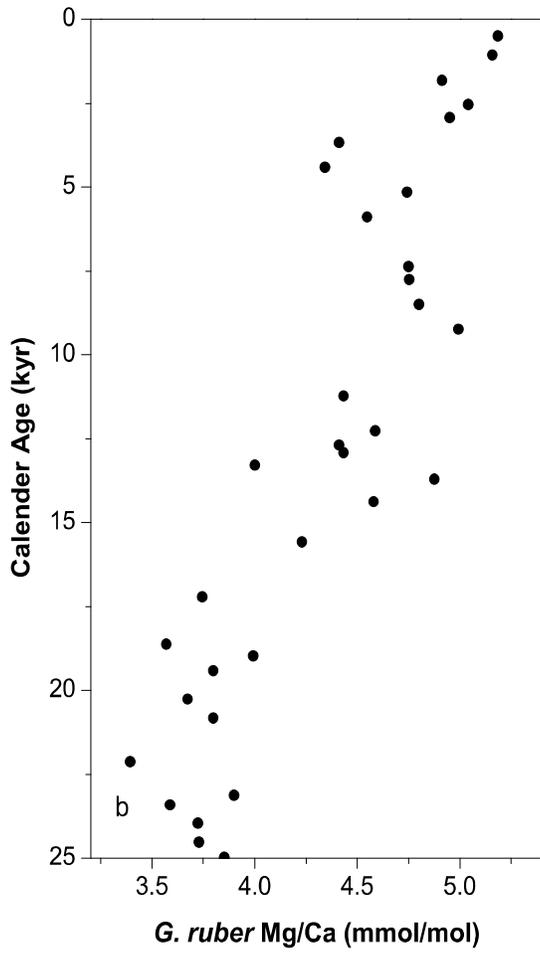
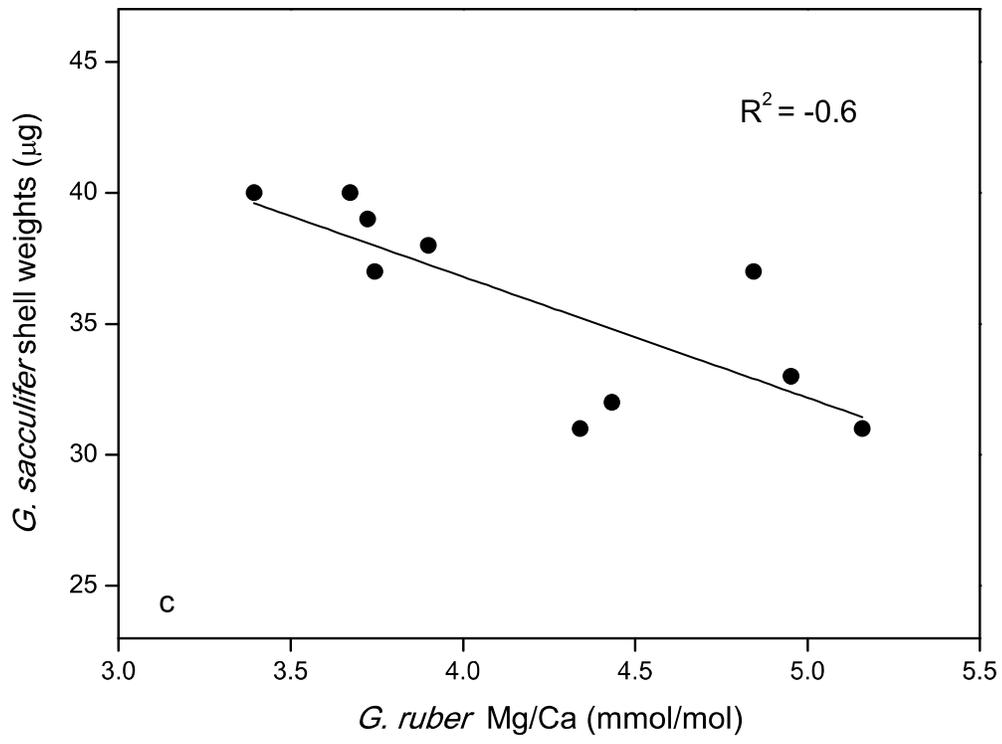


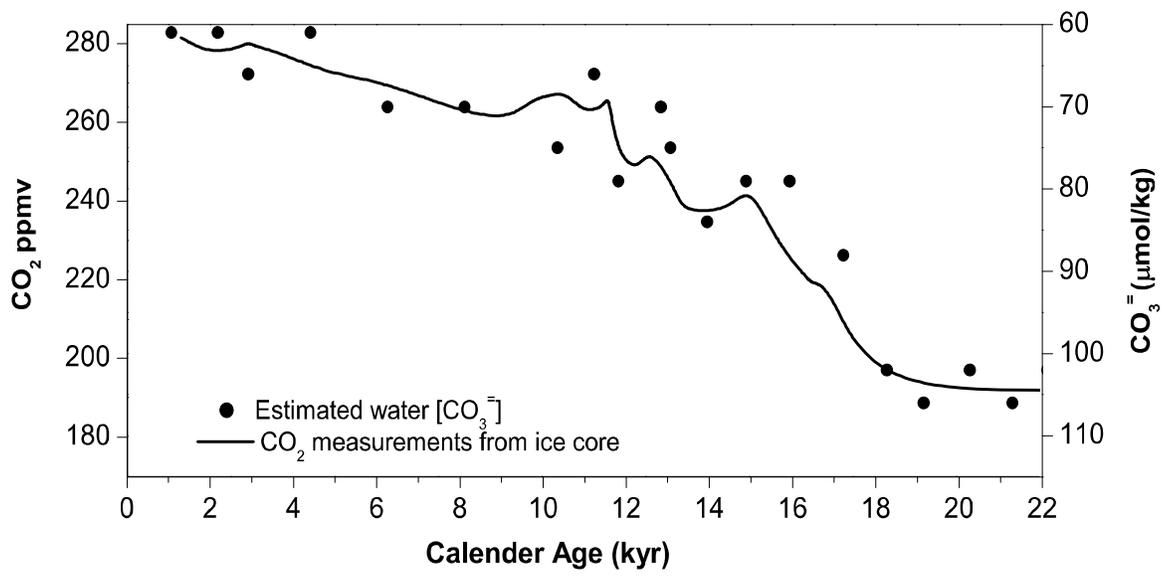
Fig. 2a



**Fig. 2b**



**Fig. 2c**



**Fig. 3**