

**Temperature and stable isotope variations in different water masses from the  
Alboran Sea (Western Mediterranean) between 250 and 150 ka**

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## **Abstract**

Mg/Ca, Sr/Ca and stable isotope measurements have been performed on tests from the planktonic foraminifers *Globigerinoides ruber* (white), *Globigerina bulloides*, and *Neogloboquadrina pachyderma* (right coiling) in samples from ODP site 977A in the Alboran Sea (Western Mediterranean). The evolution of different water masses between 250 and 150 ka is described. Warm substages were characterized by strong seasonality and thermal stratification of the water column. By contrast, less pronounced seasonality and basin stratification seem to prevail during cold substages. Several periods of stratification due to the low salinity of the upper water mass occurred during the formation of organic-rich layers and also during a possible Heinrich-like event at 220 ka. The three foraminifer species studied show a common and large shell Sr/Ca variability in short timescales, suggesting changes in the global ocean Sr/Ca ratio as one of the main causes of variations in shell composition.

**Keywords:** Mg/Ca paleothermometry, stable isotopes, Sr/Ca, marine isotope stage 7, Alboran Sea.

## **1. Introduction**

Mg/Ca paleothermometry on planktonic foraminifer shells is a relatively recent proxy for reconstructing past sea surface temperatures (SST). The uptake of  $Mg^{2+}$  into the foraminifer shell is influenced by the temperature of the seawater in which the foraminifer lives. The Mg/Ca ratio increases with temperature. The temperature sensitivity of the foraminifer Mg/Ca ratio was first reported by Chave [1954] after X-ray diffraction studies. In the past decade, Mg/Ca paleothermometry has been developed and used in many paleoceanographic studies [e.g. Nürnberg et al., 1996; Lea et al., 1999; Elderfield and Ganssen, 2000]. This method has an important advantage in that if the Mg/Ca ratio and stable isotopes are measured in the same calcite test, then the seawater  $\delta^{18}O$  can be reconstructed over time, guaranteeing a common source of the signal [e. g. Mashiotta et al., 1999; Elderfield and Ganssen, 2000]. Thus, the errors for seawater  $\delta^{18}O$  reconstructions can be minimized [Barker et al., 2005]. Moreover, this proxy permits study of the evolution of different water masses on the basis of the species analysed [e. g., Elderfield and Ganssen, 2000; Martin et al., 2002]. One of the aims of the present work is to analyse the evolution of different water masses in the Alboran Sea between 250 and 160 ka, based on the Mg/Ca ratio and stable isotope records, especially at times of striking events such as the formation of organic-rich layers (ORL) or possible Heinrich-like Events (HE). This study also pretends to obtain some conclusions about Sr/Ca controls on foraminifer shells.

Several studies based on alkenone and pollen records have been published about paleotemperature estimates during marine isotopic stages 6 and 7 in the Iberian Margin [Martrat et al., 2004; Martrat et al., 2007; Roucoux et al., 2006; Desprat et al., 2006].

Here we reconstruct sea surface temperatures in the Alboran Sea between 250 and 160 ka based on Mg/Ca paleothermometry.

## **2. Regional setting**

The Mediterranean Sea is a semi-enclosed evaporative basin governed by its connection with the Atlantic Ocean through the Strait of Gibraltar. The Alboran Sea is the westernmost sub-basin of the Western Mediterranean and its surface circulation shows two anticyclonic gyres that remain stable over time [Heburn and La Violette, 1990] (figure 1). A two-layered flow develops at the Strait of Gibraltar: less saline surface waters enter the Alboran Sea from the Atlantic and more saline and cooler Mediterranean waters flow out [Wüst, 1961; Béthoux, 1979]. The Atlantic waters, which occupy the uppermost 200 m, are gradually modified along their flow eastwards due to vertical water mixing and heat interchange with the atmosphere [Pierre, 1999]. The Mediterranean outflow is mainly formed by the Levantine Intermediate Water and the Tyrrhenian Dense Water [Millot, 1999], which flows westwards in the Alboran basin at depths between 200 and 1000 m. Below these water masses, the Western Mediterranean Deep Water also proceeds to the Strait of Gibraltar. This water mass is formed in the Gulf of Lions and constitutes 10 % of the Mediterranean Outflow [Millot, 1999].

In the past, the climate in the Mediterranean Sea has been strongly controlled by the atmospheric circulation at higher latitudes [e.g., Rohling et al., 1998; Sierro et al., 2005; Frigola et al., 2007], demonstrating the rapid teleconnection between high- and mid-latitudes. In particular, the migration of pressure systems in the Northern Hemisphere

over time has also conditioned warming and cooling periods in the Alboran basin, both at millennial and astronomical time scales [Cacho et al., 1999; Moreno et al., 2005]

### **3. Material and Methods**

Around 40 individuals of the planktonic foraminifer species *Neogloboquadrina pachyderma* (right coiling) and *Globigerinoides ruber* (white) were picked from the 250-300  $\mu\text{m}$  fraction of sediment samples in order to perform paired Mg/Ca and stable isotope analyses. By this method, we cannot avoid picking different genotypes of the same species but this is an inevitable error (less than 2%) in this kind of studies [Darling et al., 2003]. Twenty individuals of *Globigerina bulloides* were picked for Mg/Ca analyses, since the stable isotope analyses were already available [Martrat et al., 2004]. The *Globigerinoides ruber* record is discontinuous because in many samples this species was very scarce and hence, there were insufficient individuals to perform the analyses. All samples were ultrasonically cleaned with hydrogen peroxide and methanol. Specimens of *Globigerina bulloides*, *Globigerinoides ruber* and *Neogloboquadrina pachyderma* were crushed between clean glass plates and homogenized, and then split into two aliquots, one for Mg/Ca and the other for stable isotope measurements. This ensured that both analyses would be carried out on the same samples and eliminated possible discrepancies due to the measurement of different individuals in each analysis. When the samples were too small to be split they were used for either Mg/Ca or  $\delta^{18}\text{O}$  measurements only. We applied the Mg/Ca cleaning protocol after Barker et al. [2003], which consisted of: 1) repeated clay removal with ultra-pure de-ionised water; 2) removal of organic matter with 250 ml of alkali-buffered 1%  $\text{H}_2\text{O}_2$  solution (kept in water at 90°C for 10 minutes and then rinsed); 3) weak acid leaching using 250 ml of 0.001M  $\text{HNO}_3$  followed by a rinse; 4) immediately prior to the

analysis, dissolution in 0.075M HNO<sub>3</sub>, centrifugation, and transfer to a clean vial. The sample solutions were conditioned to a [Ca<sup>2+</sup>] concentration of ca. 60 ppm, and intensity calibrations were carried out following de Villiers et al. [2002] in order to limit the “matrix effect”. Minor elements analyses were carried out on an ICP-AES device (Varian Vista AX CCD simultaneous) at the University of Cambridge, as described by de Villiers et al. [2002]. The standards of Mg/Ca ratio=5.130 mmol/mol and Sr/Ca ratio=2,088 mmol/mol analysed in parallel with the samples were reproducible in the long-term, with a relative standard deviation (RSD) better than 0.23% ( $\pm 0.012$  mmol/mol) and 0.19% ( $\pm 0.004$  mmol/mol), respectively. The blank contamination effect was very small (less than 1.0 ppb Mg) despite this it was removed from the temperature estimates.

Stable isotope analyses in *Globigerinoides ruber* and *Neogloboquadrina pachyderma* were carried out at the isotope laboratory at IFM-GEOMAR with a CARBO KIEL automated carbonate preparation device linked on-line to a FINNIGAN MAT 252 mass spectrometer. External reproducibility was 0.06 ‰ for  $\delta^{18}\text{O}$  (1-sigma values), as calculated from replicate analyses of the internal carbonate standard (Solnhofen Limestone). The isotope data are referred to the Vienna PeeDee Belemnite (VPDB) scale [Coplen, 1996]. Most foraminifer species secrete their calcite test out of isotopic equilibrium for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ; nonetheless, the  $\delta^{18}\text{O}$  disequilibrium offset can be considered to remain constant over time for each species. Therefore, the relative trends in isotopic records are independent of such systematic disequilibria, which only affect the absolute values. No correction was made for disequilibrium effects in this study since no values based on Mediterranean specimens are available and it is likely that certain endemic genotypes with different disequilibrium effects would have developed

in the Mediterranean Sea due to the quasi-isolation over 5 million years [Rohling et al., 2004]. Considering this uncertainty, we considered it more appropriate to work with the measured values.

The water  $\delta^{18}\text{O}$  was obtained from the equation of Shackleton [1974], subtracting the ice-volume [Siddall et al., 2003] and temperature effect from the  $\delta^{18}\text{O}$  composition, where SST estimates were based on the Mg/Ca ratios measured in each species. Sea surface salinity estimates were calculated using the empiric water  $\delta^{18}\text{O}$ -salinity relationship for the Mediterranean Sea given by Pierre [1999].

We used the age model established by Martrat et al. [2004], based on the correlation between the SPECMAP stacked curve [Martinson et al., 1987] and the *Globigerina bulloides*  $\delta^{18}\text{O}$  curve from this core (ODP site 977A). According to this age model, the interval studied here spans between 245 and 160 ka, and the averaged sample resolution is 720 years.

The fragmentation index was calculated as the “number of foraminifer shell fragments/number of foraminifer shell fragments + number of complete foraminifer shells”, considering the  $>150\mu\text{m}$  size-fraction.

#### **4. Species ecology**

*Globigerinoides ruber* (white) is a spinous symbiont-bearing species that proliferates in warm, usually stratified, oligotrophic waters [Bé, 1977]. This species inhabits shallow waters (first 50 m of water depth). In the Alboran Sea, it is more abundant at the end of

the summer [Barcena et al., 2004] at around 23 °C [García-Gorriz and Carr, 2001], although its abundance is always low [Pujol and Vergnaud-Grazzini, 1995].

*Globigerina bulloides* is a spinous species that lacks symbionts. This species is characteristic of upwelling situations, responding to high fertility periods. It is more abundant within the first 50-100 m, although it can occupy lower levels since it is not restricted to the photic zone [Hemleben et al., 1989]. In the Alboran Sea, *Globigerina bulloides* proliferates below the thermocline in spring, when it starts to form, or in summer, when a strong pycnocline is established [Pujol and Vergnaud-Grazzini, 1995]. This species may also show a strong unique bloom in May however [Hernández-Almeida et al., 2005].

*Neogloboquadrina pachyderma* (right coiling) is a non-spinose planktonic foraminifer that usually lives in subpolar-tropical regions [Bé, 1977]. It proliferates when the water temperature below the thermocline is lower than 12 °C. It is considered a deep-water species (below 100 m), although during its reproduction and the juvenile stadials it lives in the first 100 m [Pujol and Vergnaud-Grazzini, 1995]. It develops especially within the Deep Chlorophyll Maximum (DCM), which appears at the base of the euphotic zone when the upper part of the water column is well stratified. In the modern Alboran Sea, this species does not exist, but in the Gulf of Lions it is quite abundant in winter due to the very low water temperature in that area; in summer it only develops at great depth. In the rest of the Mediterranean Sea, *Neogloboquadrina pachyderma* only appears during winter, and at great depths. This kind of behavior suggests that water temperature is a limiting factor to this species, at least in the Mediterranean Sea [Pujol and Vergnaud-Grazzini, 1995].



## **5. Results**

### **5.1 Shell dissolution and contamination**

Mg-rich calcite is more prone to dissolution [Brown and Elderfield, 1996] and hence samples affected by dissolution present lower Mg/Ca ratios. In this case, a negative correlation between the Mg/Ca ratio and fragmentation index is expected, and when this occurs, paleotemperature calculations based on this ratio are underestimated. In core ODP site 977A, the samples are not subjected to significant dissolution since no correlation was observed between the Mg/Ca ratio and the fragmentation index in the three species selected (figure 2).

To evaluate possible persistent contamination in the samples after the cleaning procedure, we compared the Mg/Ca ratios with the Al/Ca, Fe/Ca and Mn/Ca values. Al, Fe and Mn indicate the presence of clays and/or autigenic minerals, which usually include Mg in their composition. This contribution would increase the calcite Mg/Ca ratio of the samples, introducing an error in the final paleotemperature estimates. In our measurements, no correlation was seen between the Mg/Ca and the Al/Ca, Fe/Ca and Mn/Ca ratios (figure 3), meaning that contamination did not control the variations in the Mg/Ca ratio in this core.

### **5.2 Calibration equations**

For the Alboran Sea, there are very few core tops available for obtaining a good regional Mg/Ca-temperature calibration for the three species selected here. Accordingly, we had to use previous equations developed in other parts of the world. We decided to use the equation of von Langen et al. [2005] for *Neogloboquadrina pachyderma* (r.c.),

since this expression was obtained from living cultures of this species between 9 and 19 °C, comparing the results with those of sediment traps from the Santa Barbara Strait; this temperature range is fairly similar to that of intermediate waters in the Alboran Sea. For *Globigerina bulloides* we used the Elderfield and Ganssen [2000] specific equation, which is based on measurements in a set of core tops from the Atlantic Ocean between 32 and 62°N. We consider this equation appropriate for the Alboran Sea since this basin has been strongly affected by North Atlantic waters throughout the late Pleistocene [Cacho et al., 1999; Martrat et al., 2004]. The equation of Anand et al. [2003] (constant A assumed, 250-350 µm) was used for *Globigerinoides ruber* (white). This calibration was performed on six-year sediment traps from the Sargasso Sea, and the temperature range in that area (18 to 26 °C) is not very different from that of summer surface waters in the Alboran Sea.

The error associated with temperatures obtained by these calibration equations is driven by uncertainties on the Mg/Ca measurements and the calibration equations, which causes an error of ±0.2-0.7 °C (Elderfield and Ganssen, 2000; Anand et al., 2003; von Langen et al., 2005] exceeding the analytical measurement precision. But in this study we have to consider another uncertainty derived from the utilization of an equation developed in another geographical area where the species considered might have a different geochemical response to temperature than the Alboran Sea species. Unfortunately this error cannot be calculated and therefore, we assume that the error of the final temperature estimates is ±1.5 °C (twice the calibration equation maximal error).

### **5.3 Mg/Ca ratios and paleotemperature estimates**

The results on Mg/Ca ratios differ considerably, depending on the species analysed (figure 4). In *Globigerinoides ruber*, the most superficial species, this ratio ranges between 2 and 4.5 mmol/mol during warm substages, which is the widest range of the three species studied. The Mg/Ca ratio measured in *Globigerina bulloides* ranges between 1.8 and 4 mmol/mol. By contrast, the Mg/Ca ratio in *Neogloboquadrina pachyderma* (r.c.) is lower, and ranges between 1.3 and 2.4 mmol/mol. Therefore, the Mg/Ca ratios range apparently became narrower the deeper the species lived. Moreover the Mg/Ca ratio patterns are different from one species to the other.

The *Globigerinoides ruber* calcification temperature ranges between 25.3 °C at the beginning of warm substage 7.3, and 17.4 °C at the end of 7.4 (figure 5a). Although this curve is very discontinuous, profound variability is observed between substages. The temperature amplitude recorded by this species is large, even though its record is reduced to warm interglacial periods. In substages 7.5 and 7.3, the warmest period is observed at the beginning, and throughout the substages a gradual cooling took place. In substage 7.1, the warmest values are recorded in the middle and at the very end of the substage.

The *Globigerina bulloides* record shows very subtle variations in the period studied (figure 5a); although stage 6, as well as substage 7.4, is clearly identified. However, the cold substage 7.2 cannot be identified in this record since the averaged calcification temperature during this period was 17 °C, very similar to the mean values observed for substages 7.1 and 7.3. During warm substages the temperature record seems to have been very stable. The highest value reaches 20.2 °C, coinciding with the highest temperature recorded for *Globigerinoides ruber* at the beginning of substage 7.3, and

the lowest temperature is 12 °C, recorded at around 172 ka (stage 6); however, the lowest temperature reached during stage 7 is 13.3 °C, at 221 ka (second half of substage 7.4). During warm substages 7.5 and 7.3, the calcification temperature of both species (*Globigerina bulloides* and *Globigerinoides ruber*) was slightly higher at the beginning of the intervals. The paleotemperature estimates for the three warm substages (7.5, 7.3 and 7.1) based on these two species follows the same pattern as the alkenone-derived sea surface temperatures for the same core [Martrat et al., 2004].

The *Neogloboquadrina pachyderma* calcification temperature follows a different trend, since no clear variability between substages is observed (figure 5a). However, millennial changes are quite frequent. The highest value is 15.34 °C, recorded at the middle of substage 7.3, whereas the lowest one is 9.31 °C at 223 ka. Compared with the other species studied, *Neogloboquadrina pachyderma* shows great variability within the warm substages.

#### **5.4 Stable isotopes and salinity**

The lightest oxygen isotope values are recorded by the surface species *Globigerinoides ruber* (figure 5b), whereas the other two species show very similar values. The heaviest values are observed close to the cold substages, whereas the lightest appear at the beginning of substages 7.5 and 7.3, in the middle of 7.1, and also in substage 7.4. The isotopic pattern shown by the three species is asymmetric between substages 7.5 and 7.2, since the transitions from light to heavy values are more gradual than the transitions from heavy to light values. However within substage 7.1 the isotopic record is symmetric. The lightest oxygen isotope values from the period studied are recorded at 220 ka (-0.82 ‰), during the cold substage 7.4. Between 190 and 160 ka, the

*Globigerina bulloides*  $\delta^{18}\text{O}$  is the only record available, and it reveals millennial changes between 2.73 and 0.67 ‰. A special period with very light oxygen isotope values is observed between 165 and 175 ka.

The variations in  $\delta^{18}\text{O}_w$  recorded by the three species are very similar (figure 5c), showing the same asymmetry between 245 and 200 ka as the  $\delta^{18}\text{O}$  record. Also the abrupt decrease at 175 ka followed by a gradual recovery to heavier values is observed in the  $\delta^{18}\text{O}_w$  values.

The carbon isotope records of the three species are fairly parallel over time (figure 5d). The heaviest values are shown by *Globigerinoides ruber*, ranging between 0.18 and 0.96 ‰. This is followed by *Neogloboquadrina pachyderma*  $\delta^{13}\text{C}$ , with values between -0.77 and +0.77 ‰. The lightest carbon isotope values are recorded by *Globigerina bulloides* (from -2 to 0 ‰). The general trend consists of a gradual increase from the beginning of substage 7.5 to the beginning of substage 7.4, a pronounced decrease during the second half of 7.4, then another gradual increase until the end of substage 7.2 and a final decreasing trend during substage 7.1 which finishes with heavier values to the very end of substage 7.1. During stage 6 the *Globigerina bulloides* record shows decreasing  $\delta^{13}\text{C}$  values until around 175 ka, where  $\delta^{13}\text{C}$  stabilizes.

Estimates of past water salinity derived from paired  $\delta^{18}\text{O}$  and Mg/Ca analyses infer considerable uncertainties related to the methods [Rohling, 1999; Rohling et al., 2007]. However, they can be used in relative terms, interpreting increasing and decreasing trends. As it is observed in figure 5c, the most saline values coincide with the heaviest isotope records.

## 6. Discussion

### 6.1 Paleotemperature estimates

Each species records the temperature variations of the water mass in which it thrives. Hence, the warmest water mass is the one in which *Globigerinoides ruber* (white) lives, and it corresponds to the summer mixed layer [Pujol and Vergnaud-Grazzini, 1995; Rohling et al., 2004]. Our data suggest that Alboran Sea surface waters may have been occasionally warmer at the beginning of substages 7.5 and 7.3 than at present (red line in figure 5a). The amplitude of the temperature changes recorded by *Globigerinoides ruber* is very broad, up to 8 °C from the warmest to the coldest values, although it is likely to be even broader, since this species was absent during most of the cold periods. This broad amplitude is due to the fact that the summer mixed layer is very thin, and hence any runoff event or heating anomaly would have great impact as compared with other thicker water masses. The maxima of *Globigerinoides ruber* calcification temperatures are located just after the Northern Hemisphere summer insolation maxima with a lag of 1-4 ka, coinciding with the interglacial maxima. Moreover, the *Globigerinoides ruber* SST record is roughly parallel to the sea-level and hence ice-volume curve [Shackleton, 2000]. This pattern suggests that a greater ice-volume at northern latitudes during lowstand periods had a significant influence on Mediterranean summer surface water temperatures. A possible mechanism are outbursts colder winds to the Mediterranean region in late spring and early summer as it has often been observed today.

*Globigerina bulloides* shows much less variability than *Globigerinoides ruber*, although the general trends are similar. The water mass recorded by *Globigerina bulloides* is

assumed to be a mixture between the late spring/early summer surface layer and deeper waters upwelled during those months at 50-100 water-depth [Pujol and Vergnaud-Grazzini, 1995; Barcena et al., 2004; Hernández-Almeida et al., 2005]. In this record, the most remarkable feature is the narrow temperature amplitude: around 5 °C of difference between the coldest and the warmest samples within stage 7. However, several substages in stage 7 are not well defined (7.3, 7.2 and 7.1), probably because *Globigerina bulloides* is a stenotopic species [Skinner and Elderfield, 2005], which means greater habitat selectivity. Another hypothesis for this stability could be the displacement of upwelling situations to warmer months during substage 7.2.

The large gradient between the temperatures recorded by *Globigerinoides ruber* and *Globigerina bulloides* can be related to seasonality. The highest gradients occurred when seasonality was stronger, just after the Northern Hemisphere summer insolation maxima. This temperature gradient gradually diminished until the end of the warm substages, when it reached its minimum values; that is, when sea surface temperatures in May and at the end of the summer were very similar. During periods with enhanced seasonality, a warmer summer mixed layer could have resulted in strong stratification over a prolonged period of time throughout the year, whereas a colder summer layer during weaker seasonality periods would have resulted in a less pronounced stratification for a short period of the year.

*Neogloboquadrina pachyderma* (right coiling) inhabits the lower surface layer (between 50 and 150 m), although it can be influenced by intermediate Mediterranean waters [Pujol and Vergnaud-Grazzini, 1995]. Accordingly, it reflects the coldest temperatures. Although Mediterranean waters are seasonally homogeneous in terms of temperature

below 150 m of water-depth, at millennial scale their temperature may change by more than 5 °C between stadials and interstadials [Cacho et al., 2006]. This millennial variability may reflect winter climate variations in the area of intermediate water formation in the Eastern Mediterranean as suggested Rohling et al. [2002] for the Holocene or it could be the imprint of a possible secondary unknown factor that could be controlling Mg/Ca ratio in this species apart from the calcification temperature.

## 6.2 Isotopic characterization

The differences observed in the *Globigerinoides ruber*  $\delta^{18}\text{O}$  record with respect to the other species are due to the thermal effect. When this component is subtracted from the  $\delta^{18}\text{O}$  values, the resulting *Globigerinoides ruber*  $\delta^{18}\text{O}_w$  resembles that of the other two species (figure 5c). This pattern supports the interpretation that the *Globigerinoides ruber* calcification temperature based on the shell Mg/Ca ratio reflects the evolution of the summer mixed layer along the time studied. We consider that the differences between the absolute  $\delta^{18}\text{O}_w$  values obtained from the different species analysed are mainly due to their specific deviations from equilibrium. However, the unusual fresh signal recorded by *Neogloboquadrina pachyderma* could be related with the calibration equation applied to this species, since the lower limit of the temperature range from the living cultures (9-19 °C) used for the calibration was a pair of degrees lower than the lowest temperatures ever recorded in the Alboran Sea at 150 m of water depth. In addition, salinity variations are parallel to those seen for the  $\delta^{18}\text{O}_w$  record (inverted salinity scale), and the absolute values are mainly influenced by the mentioned specific deviations from equilibrium.



The  $\delta^{18}\text{O}_w$  values and the salinity of Mediterranean waters would have also been affected by changes in sea level and the residence time of water masses in the Mediterranean Sea. Residence time is determined by the rate of water exchange through the Strait of Gibraltar, controlled by global sea level changes (figure 5e). Longer residence times during lowstands would have enhanced both  $\delta^{18}\text{O}_w$  and salinity, since when the sea level was at its minimum water exchange through the Strait of Gibraltar was reduced, and consequently Mediterranean waters were subjected to a negative hydrological balance for a longer period of time, thus effecting higher salinities and hence, heavier  $\delta^{18}\text{O}_w$  values. By contrast, during highstands the salinity and oxygen isotope values of Mediterranean waters decreased as Atlantic-Mediterranean water exchange increased.

The lightest oxygen isotope values were reached during special events, such as during the deposition of the organic-rich layers defined at around 245 and 195 ka, during the warm substages 7.5 and 7.1 [Comas et al., 1996]. A source of light-oxygen isotope water is needed to explain the low  $\delta^{18}\text{O}_w$  values observed within these layers, which seem to be equivalent to the Eastern Mediterranean sapropels S7 and S9 [Capotondi and Vigliotti, 1999]. The input of ice-melting waters to the basin or large river discharges during wetter periods may have been responsible for these negative oxygen isotope anomalies. The geochemical data suggest that river discharges increased during these periods [Gonzalez-Mora et al. submitted]. As expected, this anomaly is more pronounced in *Globigerinoides ruber* (w): the most superficial species. The very low salinities recorded during these events suggest the occurrence of salinity stratification during these organic-rich layers. It is remarkable that in substage 7.5, the thermal stratification recorded by the *Globigerinoides ruber* temperature maximum peak does

not coincide with the salinity stratification prevailing during the formation of ORL11 and 12. However, in substage 7.1, thermal stratification does coincide with the salinity minimum. In light of the amplitude of the  $\delta^{18}\text{O}_w$  decrease, it seems that the most pronounced organic-rich layers are ORL11 and 12 (at around 244 ka), whereas the ORL9 was less important.

Centered at around 220 ka, decreases in salinity and  $\delta^{18}\text{O}_w$  are also found, but these decreases do not coincide with any previously defined organic-rich layer. Unlike what was observed in the ORLs, this isotope anomaly is accompanied by very low sea surface temperatures, together with slight increases in  $\text{C}_{37:4}$  [Martrat et al., 2004] and *Neogloboquadrina pachyderma* (left coiling) [Gonzalez-Mora et al. submitted], and may be considered a Heinrich-like event [Gonzalez-Mora et al. submitted]. According to previous findings [Cacho et al., 1999; Sierro et al., 2005], these very low sea surface salinities and temperatures seem to be related to the input of iceberg meltwaters from the North Atlantic into the Mediterranean Sea. *Globigerinoides ruber* shows the most pronounced decrease in  $\delta^{18}\text{O}_w$  values, since the most superficial waters would have been more affected by such meltwaters. However, these changes are also seen in *Neogloboquadrina pachyderma* (r.c), which suggests that these isotopic variations reached at least the first 150 m of water-depth. During this event, stratification of the basin probably occurred due to the existence of upper water masses with very low salinity.

The fourth prominent  $\delta^{18}\text{O}_w$  minimum appears at around 175 ka, close in time to the Northern Hemisphere summer insolation maximum. This event is also characterized by low sea surface temperature, and oxygen isotope waters, spanning between 175 and 165

ka, it is not recorded in cores from the Atlantic Ocean. However, these significant light-oxygen isotope values have been observed in other parts of the Mediterranean region, suggesting an internal source [Sierro et al. submitted]. Furthermore, this period is related to the formation of sapropel 6 in the Eastern Mediterranean, in which rainfall was very high [Ayalon et al., 2002; Bard et al., 2002], and the geochemical data (Si, Al, and Ca) from the same core in the Alboran Sea suggest increasing river discharge during this period. However, this  $\delta^{18}\text{O}_w$  decrease might be also partially caused by the sea level increase that took place during the same interval, which would favour the Atlantic-Mediterranean water exchange.

The  $\delta^{13}\text{C}$  values recorded by the three species follow a very similar pattern (figure 5d). The absolute differences between species are partially due to their vital effects and the isotopic disequilibria, and also, due to the ecological preferences of each species. The heaviest values are recorded by *Globigerinoides ruber* (w) because this species lives in the stratified summer mixed layer, especially during autumn, when most of nutrients have been consumed, and therefore water  $^{12}\text{C}$  has decreased. On the other hand, *Neogloboquadrina pachyderma* (r.c.) and *Globigerina bulloides* are influenced by the intermediate water signal. *Neogloboquadrina pachyderma* (r.c.) especially develops in winter, when water mixing is enhanced, and *Globigerina bulloides* colonizes the areas in which intermediate and deeper waters upwell. In the Mediterranean Sea, intermediate waters are depleted in  $\delta^{13}\text{C}$  compared to surface waters (Pierre, 1999), and this signal is reproduced by the *Neogloboquadrina pachyderma* (r.c.) and *Globigerina bulloides*  $\delta^{13}\text{C}$  records. However, there is a significant offset between both species due to the important isotopic disequilibrium inherent to *Globigerina bulloides*, which causes very light shell  $\delta^{13}\text{C}$  values compared to the water  $\delta^{13}\text{C}$  signal (F.J. Sierro, personal communication).

The common pattern observed in the three species suggests that the entire Mediterranean basin had quasi-homogeneous  $\delta^{13}\text{C}$  values for all times studied. The general increasing carbon isotope trend from the beginning of the warm substages to the end of the cold ones observed in *Neogloboquadrina pachyderma* (r.c.) and *Globigerina bulloides* reproduces the intermediate-water basin-wide  $\delta^{13}\text{C}$  trends over time. Intense mixing in the areas of deep water formation, especially in the Levantine basin, where most of the intermediate water is formed, can result in heavier carbon isotope values throughout the basin. However, the *Globigerinoides ruber* (w) fluctuations during MIS7 are partially affected by the intermediate water signal due to the upwelling of this water mass during several months around the year, but those fluctuations are also responding to changes in the rate of nutrient utilization throughout time.

Regarding the formation of organic-rich layers, there is no evidence in the carbon isotope data of changes in the nutrient availability/utilization ratio, implying the absence of significant variations in surface productivity during those periods. Moreover, no changes in the intermediate-water basin-wide  $\delta^{13}\text{C}$  are observed according to the *Neogloboquadrina pachyderma* (r.c.) and *Globigerina bulloides* records. During the possible Heinrich-like event at 220 ka, a basin-wide  $\delta^{13}\text{C}$  significant decrease seems to have occurred. This could be related to weaker mixing in the areas of deep water formation.

### **6.3 Sr/Ca**

It has been suggested that dissolution lowers the shell Sr/Ca ratio in some planktonic foraminifer species [Brown and Elderfield, 1996]. The comparison of the fragmentation

index and the shell Sr/Ca ratio of the three species shows that dissolution was not the main factor controlling the major downcore Sr variations in shells. However, some of the high-frequency changes could have been caused by differential dissolution.

Several experiments with living foraminifers have shown that environmental parameters affect shell Sr incorporation [Bender et al., 1975; Carpenter and Lohmann, 1992]. In some species, the shell Sr/Ca ratio increases with increasing temperature, salinity, and pH, probably reflecting an effect of the calcification rate on Sr incorporation. If temperature were the primary factor controlling downcore shell Sr/Ca variations, the foraminifer shell Sr/Ca ratio should be lower during colder intervals. However, the three species show higher Sr/Ca ratios during the cold substages, which means that temperature cannot have exerted a strong control in shell Sr/Ca. Experiments conducted with living planktonic foraminifers indicate that increases in pH and salinity lead to higher shell Sr/Ca ratios, with about 0.6–1.1% per 0.1 pH unit and a 0.6% Sr/Ca increase per 1 unit increase in salinity [Lea et al., 1999]. Since during glacial stages pH was slightly higher [Sanyal et al., 1995], it is likely that the water pH also increased during the cold substages (approximately +0.1 pH units) [Martin et al., 1999]. On the other hand, salinity in the Alboran Sea could increase 2-3 salinity units during cold substages. Therefore, both parameters could affect Sr/Ca low-frequency variations although they could only account for variations of less than 3%. Nevertheless, our Sr/Ca record shows variations of up to 8% in *Neogloboquadrina pachyderma* (r.c.); 7% in *Globigerina bulloides*, and 6% in *Globigerinoides ruber* (w). This means that other factors must have been involved in the low-frequency shell Sr/Ca oscillations documented by the three species.

Thus, variations in the Sr/Ca ratios of the three species could partially be explained in terms of seawater Sr/Ca changes as previously suggested by Martin et al. [1999] and Elderfield et al. [2000]. These global glacial-interglacial fluctuations have been linked to the weathering of Sr from aragonitic shelf sediments during low sea level stands [Stoll and Schrag, 1998], although such models suggest a glacial Sr/Ca increase of 1-3%, which is lower than the variations obtained here. Moreover, the Sr/Ca changes (both the increases and the decreases) in the foraminifer shells were rapid during stage 7, which is unexpected considering the long residence times of Sr and Ca in the oceans. Shelf Sr weathering cannot account for such rapid increases in seawater Sr/Ca ratios. Martin et al. [1999] also recorded rapid and important shell Sr/Ca fluctuations in different species of foraminifers (up to 5%) from the Atlantic and the Pacific oceans over the last 300 ka, and suggested increases in both shelf carbonate deposition and the deglacial river flux as the mechanisms that resulted in significant rapid changes in the cycling of both Sr and Ca. This may also explain our results.

The previous Sr/Ca ratio study based on different planktonic species made by Elderfield et al. [2000] reported fairly different patterns for the same three species. The authors suggested that factors other than Sr/Ca seawater changes may have been involved. By contrast, in our study the general trend of the three species is very similar and seems to be mainly controlled by Sr/Ca changes in the ocean, whereas the other parameters seem to be less important. However, there is one significant difference between the three records. The *Neogloboquadrina pachyderma* (r.c) and *Globigerinoides ruber* (w) records have the same absolute values, whereas the *Globigerina bulloides* values are slightly lower and maintain a constant offset with respect to the others over time. The

reason for this could be physiological mechanisms, since no evidence of variable preservation of species has been observed in this core.

If these changes in ocean Sr/Ca ratio at glacial/interglacial timescales are confirmed by some other studies, glacial paleotemperature reconstructions based on corals should be revised since coralline Sr/Ca paleothermometry assumes that mean ocean Sr/Ca is constant on short timescales.

## **7. Conclusions**

The present record confirms the usefulness of Mg/Ca paleothermometry applied to planktonic species in order to characterize different water masses.

The planktonic foraminifer species *Neogloboquadrina pachyderma* (r.c), *Globigerinoides ruber* (w) and *Globigerina bulloides* have maintained their modern habitat in the Alboran Sea during the last 250 ka.

Geochemical features suggest that there was enhanced seasonality, with a significant thermal stratification of the water column in the Alboran Sea at the beginning of the warm substages. This gradually changed to weaker seasonality and thermal stratification during the cold substages.

Long-term oxygen isotope and salinity variations are controlled by global ice-volume changes and their consequent variations in the residence time of Mediterranean water. When sea level was low, the residence time was presumably longer and hence this invoked an increase in the  $\delta^{18}\text{O}_w$  and salinity.

The organic-rich layers formed during the interval studied are characterized by stratification of the basin due to the very low salinity of the upper water masses. Surface productivity did not undergo significant changes during these periods.

During the possible Heinrich-like event recorded at 220 ka, another episode of water stratification seems to have occurred, since the upper water masses show very low salinities. The carbon isotope record suggests weaker mixing in the Mediterranean areas of deep water formation during this event.

Very light oxygen isotope values are found between 160 and 170 ka, not seen in the Atlantic Ocean, thus suggesting an internal Mediterranean origin for this event. It is conceivable that this episode may have been related to the increase in monsoonal rainfall over the Mediterranean region, which would have caused the formation of sapropel 6 in the Eastern Mediterranean. A global sea level increase during this interval might also contribute to this  $\delta^{18}\text{O}_w$  decrease.

The Sr/Ca ratios measured in shells from different planktonic foraminifer species from the Alboran Sea suggest that its variations are mainly related to Sr/Ca glacial/interglacial changes in the ocean. Variations in oceanic pH, temperature or salinity can only explain half of the observed fluctuations. Furthermore, the similar trends observed in the three species confirm that ocean Sr/Ca variations are one of the main factors controlling the Sr/Ca ratios in their shells.



The importance of the possible changes in ocean Sr/Ca ratio at short timescales is that coral-derived paleotemperature reconstructions should be recalculated, since the assumption that ocean Sr/Ca was constant could not be true, and therefore, this method would have underestimated sea surface temperature during glacial times.

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## Figure captions

Figure 1. Location of ODP site 977 (36° 01.907'N, 1° 57.319'W) in the Alboran Sea, Southern Spain, Western Mediterranean. Arrows indicate the surface circulation pattern [Heburn and La Violette, 1990].

Figure 2. Mg/Ca scatter plot against fragmentation index (*G. ruber* (white), *G. bulloides* and *N. pachyderma* (right coiling)), showing a lack of correlation between both values and hence suggesting no significant effect of dissolution on the Mg/Ca measurements.

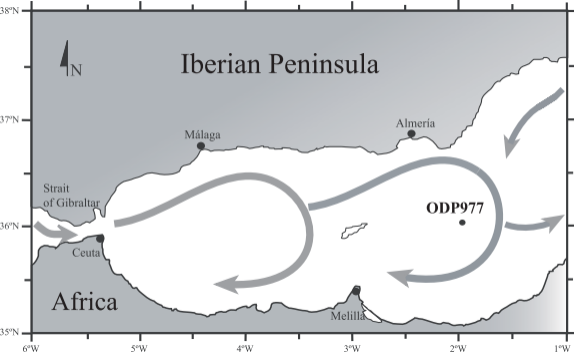
Figure 3. Scatter plot of Fe/Ca, Mn/Ca and Al/Ca against Mg/Ca, showing no covariance between these elements (*G. ruber* (white), *G. bulloides* and *N. pachyderma* (right coiling)).

Figure 4. Mg/Ca results (mmol/mol) in the three species, *G. ruber* (white) (red), *G. bulloides* (green) and *N. pachyderma* (right coiling) (blue).

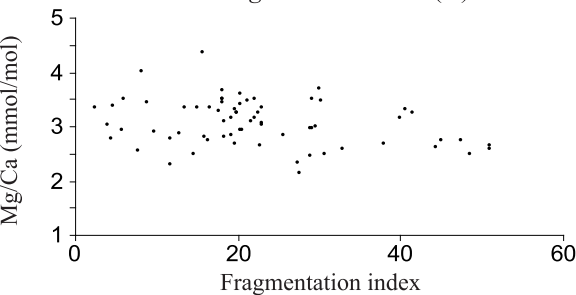
Figure 5. Calcification temperature estimates (a) as compared with the  $\delta^{18}\text{O}$  (b) and  $\delta^{13}\text{C}$  (d) records for *G. ruber* (white) (red), *G. bulloides* (green) and *N. pachyderma* (right coiling) (blue), the reconstructed surface  $\delta^{18}\text{O}_w$  (c) derived from Mg/Ca temperature estimates and salinity (c) based on the equation by Pierre [1999]. Also, the sea level curve after Shackleton [2000] and the Northern Hemisphere maximum insolation curve (65°N) have been represented (d) for comparison (HE: Heinrich-like event; ORL: organic rich layer). The calibration equations used were: von Langen et al. [2005] equation for *N. pachyderma* (r.c.); Elderfield and Ganssen [2000] specific equation for *G. bulloides*; and Anand et al. [2003] equation (constant A assumed, 250-350  $\mu\text{m}$ ) for

*G. ruber* (w). The straight lines in graphic a indicate the modern sea temperatures for the different water masses in the Alboran Sea.

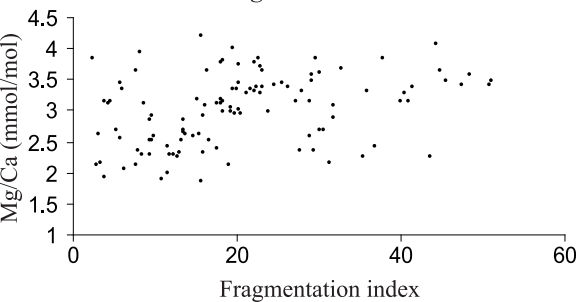
Figure 6. Evolution of the Sr/Ca ratio (mmol/mol) in shells from *G. ruber* (white) (red), *G. bulloides* (green) and *N. pachyderma* (right coiling) (blue) between 250 and 160 ka.



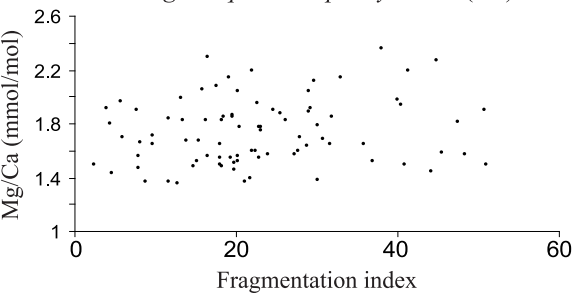
*Globigerinoides ruber* (w)



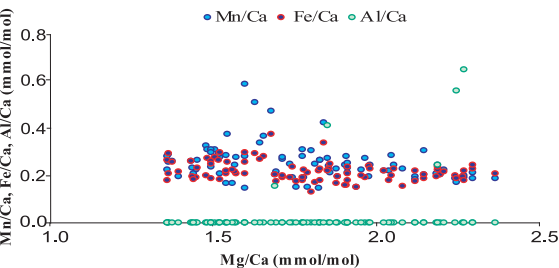
*Globigerina bulloides*



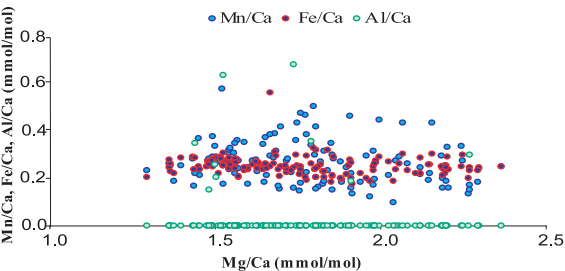
*Neogloboquadrina pachyderma* (r.c.)



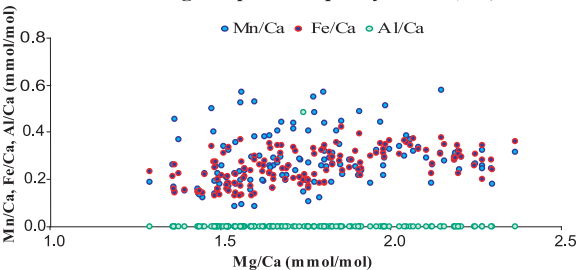
*Globigerinoides ruber* (w)

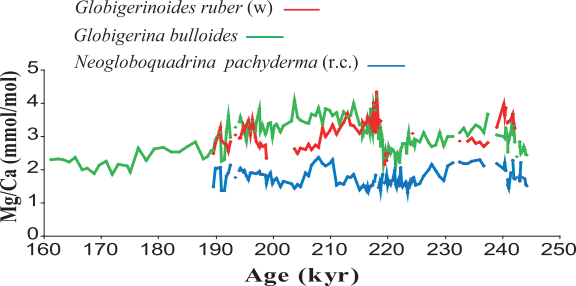


*Globigerina bulloides*

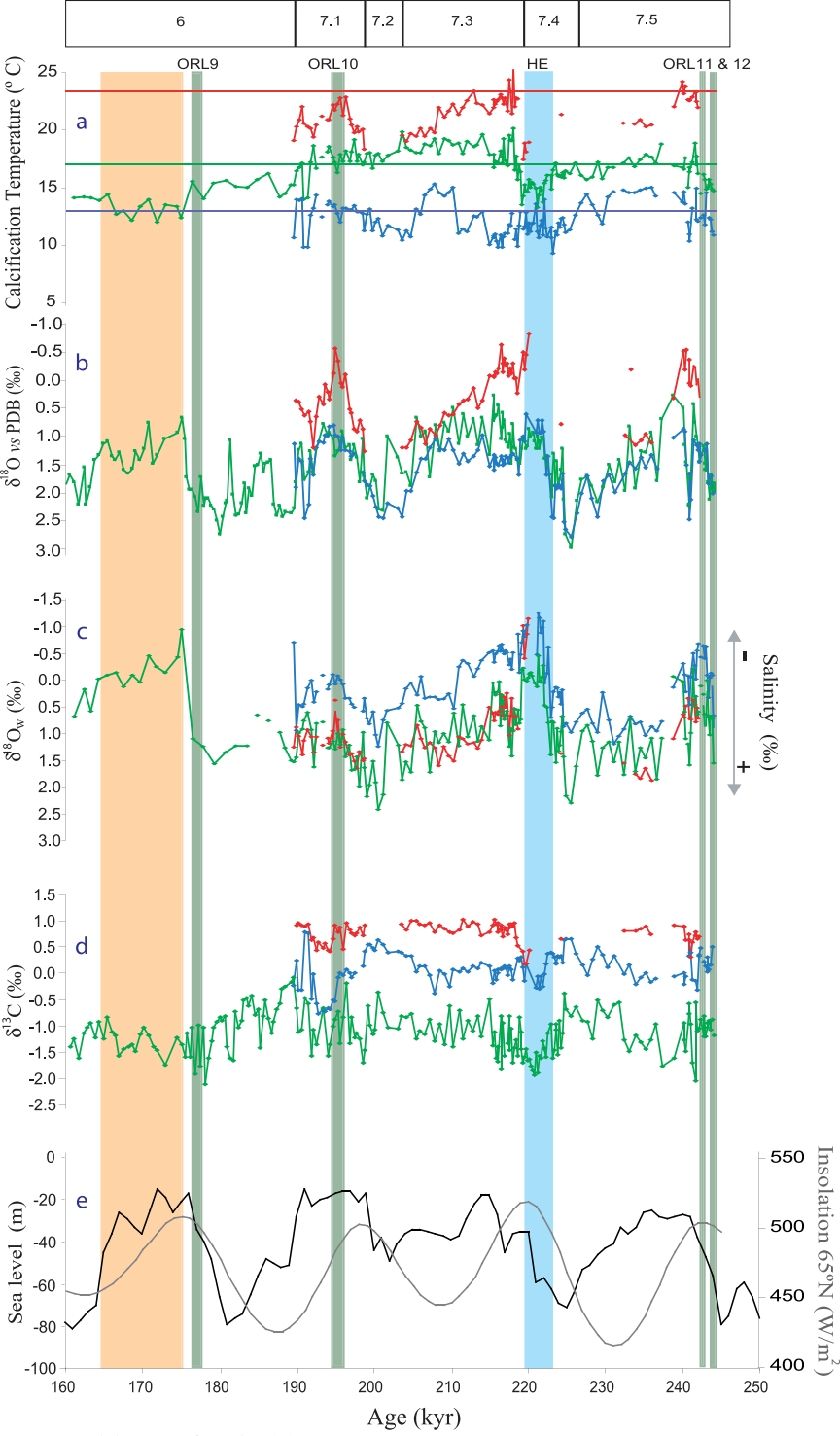


*Neogloboquadrina pachyderma* (r.c.)





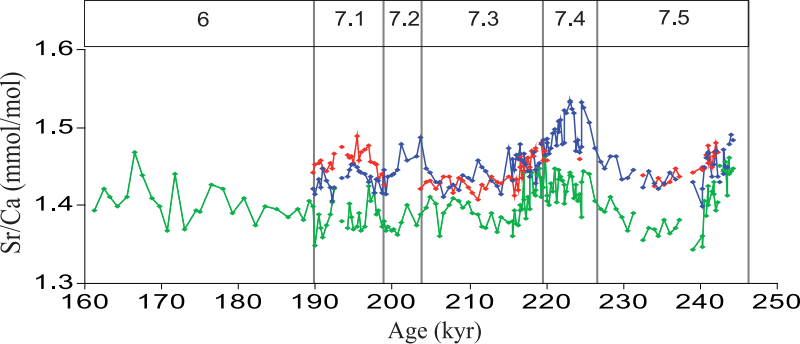




*Globigerinoides ruber* (w) —

*Globigerina bulloides* —

*Neogloboquadrina pachyderma* (r.c.) —



*Globigerinoides ruber* (w) —

*Globigerina bulloides* —

*Neogloboquadrina pachyderma* (r.c.) —