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Mg/Ca-paleothermometry in the western Mediterranean Sea on planktonic foraminifer species *Globigerina bulloides*: Constraints and implications

Le paléothermomètre Mg/Ca appliqué à l'espèce de foraminifère planctonique Globigerina bulloides *en Méditerranée occidentale : contraintes et implications*

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ABSTRACT

We generated a high-resolution $SST_{Mg/Ca}$ record for the surface-dwelling planktonic foraminifera *Globigerina bulloides* from the core MD99-2346 collected in the Gulf of Lion, and compared it to that obtained using modern analogue techniques applied to fossil foraminiferal assemblages (SST_{MAT}). The two temperature records display similar patterns during the last 28,000 years but the $SST_{Mg/Ca}$ estimates are several degrees warmer (∼ +4 °C) than $SST_{MAT.}$ The temperature shift between $SST_{Mg/Ca}$ and SST_{MAT} remained relatively constant over time. This seems to exclude a bias on the Mg/Ca record associated with salinity or secondary Mg-rich calcite encrustation on the foraminiferal tests during early diagenesis. Therefore, anomalously high Mg/Ca suggests either: (1) the empirical equation for *G. bulloides* of Elderfield and Ganssen (2000) is incorrect; or (2) there is a specific Mediterranean genotypes of *G. bulloides* for which a specific Mg/Ca-temperature calibration is needed.

RÉSUMÉ

Nous avons reconstitué l'évolution des températures de surface le long de la carotte MD99-2346, prélevée dans le Golfe du Lion, à l'aide de deux paléothermomètres : la mesure du rapport Mg/Ca des tests du foraminifère planctonique *Globigerina bulloides*, et la méthode des plus proches analogues, appliquée aux assemblages de foraminifères planctoniques. Les résultats montrent une co-variance entre les deux courbes de température pendant les derniers 28 000 ans. Les températures basées sur les mesures du rapport Mg/Ca sont cependant systématiquement plus chaudes que celles obtenues par les associations de foraminifères et l'écart entre les deux courbes est resté constant (∼ +4 °C) au cours du temps. Cette constance semble exclure un biais sur les mesures du rapport Mg/Ca associé à la salinité ou au dépôt d'une calcite riche en Mg, lors de la diagenèse précoce. Dès lors, les $SST_{Mg/Ca}$ anormalement élevées suggèrent : (1) que la calibration disponible pour l'espèce *G. bulloides* en océan Atlantique est erronée ; ou (2) qu'il existe en

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Méditerranée une sous-espèce endémique pour laquelle il faut développer une calibration spécifique en raison d'un effet vital sur l'incorporation du Mg.

1. Introduction

Among the various proxies developed to reconstruct past sea surface temperatures (SST), the Mg/Ca measured on planktonic foraminifera has been given much attention these recent years (Anand et al., 2003; Barker et al., 2005; de Garidel Thoron et al., 2005; Eggins et al., 2003; Elderfield and Ganssen, 2000; Levi et al., 2007; Mashiotta et al., 1999). An advantage of this method is that the same biotic carrier can be used for both Mg/Ca and oxygen isotope analyses, which makes it possible to estimate seawater $\delta^{18}O$, a proxy for salinity. Nevertheless, recent studies pointed out several potential biases that may affect the incorporation of Mg in foraminiferal tests or its preservation during early diagenesis. Regarding the incorporation of Mg into foraminiferal calcite, previous works have addressed the potential effects of seawater carbonate ion concentration (Barker and Elderfield, 2002; Bijma et al., 1998; Spero et al., 1997) and salinity (Ferguson et al., 2008; Kisakürek et al., 2008; Lea et al., 1999; Mathien-Blard and Bassinot, 2009). The Mg/Ca ratio of foraminifera can be also modified in the surface sediment either by partial dissolution of Mg-rich shell components in waters under-saturated with respect to calcite (Brown and Elderfield, 1996; Dekens et al., 2002; Regenberg et al., 2009) or by the overgrowth of Mg-rich, secondary-calcite likely formed near the sediment–seawater interface, in areas where interstitial waters are super-saturated with respect to $CaCO_3$ (Boussetta et al., 2011).

Given the modern temperature range of the surface waters in the Mediterranean Sea, foraminiferal Mg/Ca values measured on core top sediments are higher than what can be expected from the recent Mg/Ca-isotopic temperature empirical calibrations based on open-ocean sediment traps (Anand et al., 2003) or core tops (Elderfield and Ganssen, 2000). Recently, Ferguson et al. (2008) have attributed such anomalously high values to the higher salinities in the Mediterranean Sea compared with the Atlantic Ocean. The highest values have been observed on *Globigerinoides ruber* from the eastern Mediterranean basin (Levantine basin). In this area, Mg/Ca values are not only high, but also display a very large scattering, which cannot be explained by a temperature or a salinity effect (Boussetta et al., 2011). SEM observations and X-ray diffractometry analyses exhibit clearly a post-depositional precipitation of inorganic, Mg-rich (10–12%) calcite on foraminiferal shells. This inorganic calcite coating is considerably less pronounced in the western Mediterranean basin than in the eastern basin, where diagenetic calcite can represent up to 21% of the total volume of calcite for *G. ruber* (Boussetta et al., 2011).

In the western Mediterranean Sea, the planktonic foraminifer *G. bulloides* is abundant and the geochemistry of its test could be used to reconstruct past changes in surface water conditions. However, the small, modern sea surface temperature (SST) gradient (~4 °C) (Stephens et al., 2002) in this area does not allow us to develop an accurate calibration of the Mg/Ca thermometer based on *G. bulloides* specimens picked from surface sediments. In order to better constrain the incorporation of Mg into foraminiferal tests over a wider temperature range, we generated a high-resolution Mg/Ca record of *G. bulloides* picked from core MD99-2346 collected in the Gulf of Lion and which covers the last 28,000 years. This Mg/Ca record was compared to temperatures inferred using a modern analogue technique applied to fossil foraminiferal assemblages. In the western Mediterranean basin, it has been shown that sea surface temperature (SST) reconstructions using foraminiferal associations are generally obtained with low dissimilarity coefficient indicating reliable estimates (Kallel et al., 1997b, 2004; Melki et al., 2009). Conditions are, however, different during the Last Glacial Maximum when fossil assemblages have no good modern analogues particularly in the eastern Mediterranean Sea. This comparison study has been completed by the data obtained on seven Mediterranean core tops.

2. Material and methods

2.1. Study material

Mg/Ca analyses were performed on *G. bulloides* retrieved from well-preserved core tops spanning the western Mediterranean Sea (Boussetta et al., 2011) and along the core MD99-2346 (42°02.61′N, 4°09.04′E, 2100 m of water depth, 10.61 m long; Fig. 1) collected in the Gulf of Lion. The MD99-2346 core, which is 10.63 m long, is well dated using accelerator mass spectrometry (AMS) ^{14}C dating. The age model of core MD99-2346, for the last 28 kyr, has been established using AMS ^{14}C dates from 13 planktonic foraminifera levels (Melki et al., 2009). For this core, in addition to micropaleontological analysis, which have been used for reconstructions of past sea surface temperatures (SST), the oxygen stable isotope analyses measured on the *G. bulloides* ($\delta^{18}O$) are available (Melki et al., 2009).

2.2. Oxygen isotopic analyses

Oxygen isotopic ($\delta^{18}O$) measurements were performed on *G. bulloides* specimens along the core MD99-2346 and on the available western Mediterranean core tops. About six foraminifer tests (60 μg) per sample were picked from the 200–250 μm size fraction for each oxygen isotopic measurement. Shells were ultrasonically cleaned in a methanol bath to remove clays and other impurities. They were roasted under vacuum at 380 °C during 45 min to eliminate organic matter. Samples were analyzed with a Finnigan Δ+ mass spectrometer. All results are expressed as $\delta^{18}O$ in ‰ versus PDB via the calibration with respect to

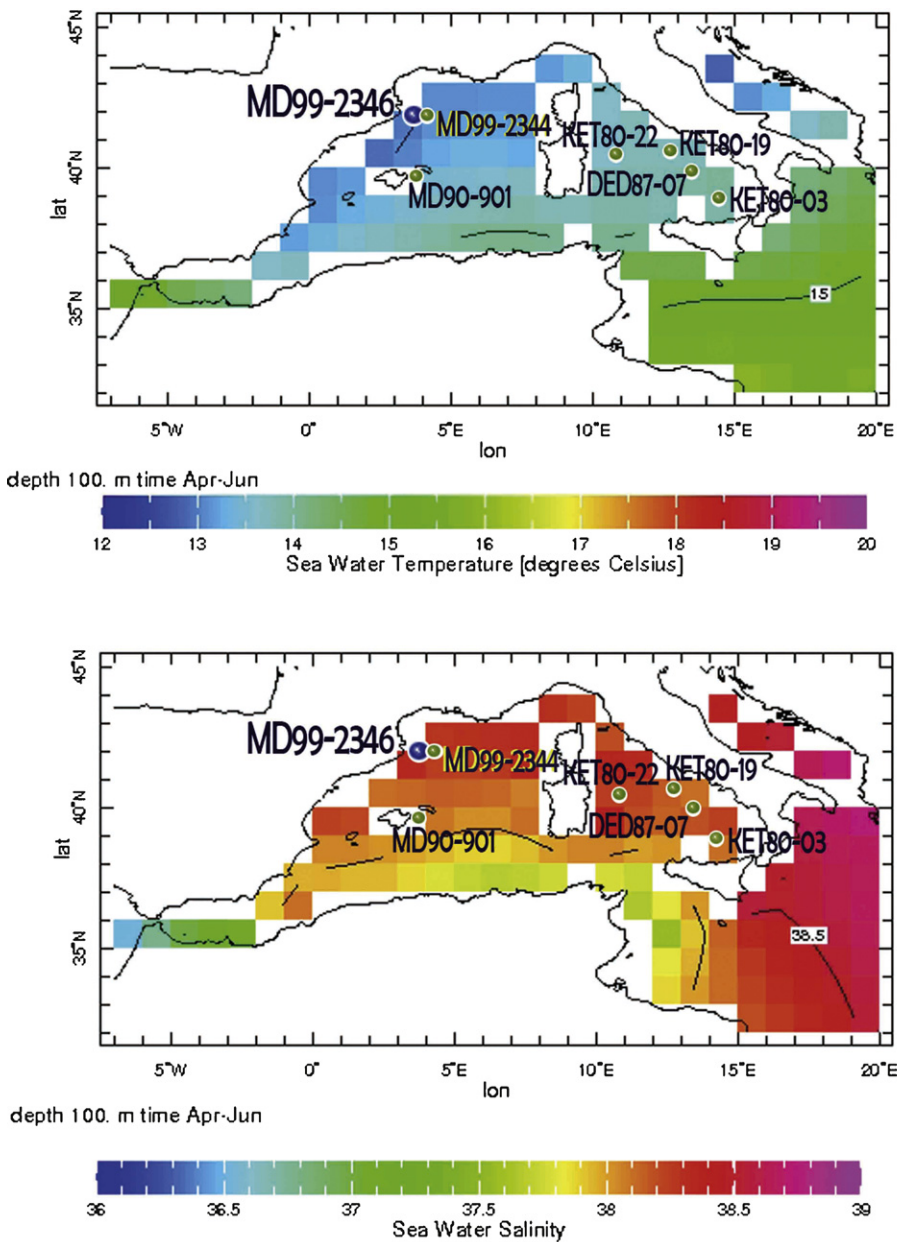

Fig. 1. Maps of the water salinity (psu) and temperature (°C) of the western Mediterranean Sea at the appropriate depth habitat of the planktonic foraminifera *Globigerina bulloides*. Location of the core tops (green circles) and of core MD99-2346 (blue circle) are shown.

Fig. 1. Cartes des salinités (psu) et des températures (°C) des eaux de la Méditerranée occidentale, à la profondeur appropriée d'habitat du foraminifère planctonique *Globigerina bulloides*. Sont montrées également, les localisations des sommets de carotte (cercles verts) et de la carotte MD99-2346 (cercle bleu).

the international standards NBS-19 and NBS-18. The analytical reproducibility as determined from replicate measurements of an internal standard is $\pm$ 0.05% (1σ).

2.3. Mg/Ca analyses

About 20–30 specimens of *G. bulloides* per sample were used from the 200–250 μm size fraction for each Mg/Ca measurement. These shells were gently crushed to open the chambers. Prior to analysis, samples were cleaned following the procedure of Barker et al. (2003), which includes several ultrasonic treatments in water then ethanol to remove adhesive clays, and then a reaction with hydrogen peroxide treatment 1% at 100 °C to remove any organic matter. A very slight acid leaching with 0.001 M nitric acid was finally applied to eliminate contaminants adsorbed on foraminiferal tests. Analyses were performed on a Varian Vista Pro Inductively Coupled

Plasma Atomic Emission Spectrometer (ICP-AES) at the Laboratoire des sciences du climat et de l'environnement (LSCE), a member of an interlaboratory comparison study of calibration standards for foraminiferal Mg/Ca thermometry (Greaves et al., 2008), following the method of de Villiers et al. (2002). The mean external reproducibility of a standard solution of Mg/Ca = 5.23 $mmol.mol^{-1}$ $\pm 0.5\%$ (RSD).

On average, clay minerals contain between 1 and 10 weight % Mg (Deer et al., 1992). Clay contamination may cause, therefore, a significant bias in foraminifer Mg/Ca ratios. Barker et al. (2003) showed that the covariances of Fe/Ca and Mg/Ca, as well as Fe/Mg values exceeding 0.1 $mol.mol^{-1}$ are indicators of clay contamination. All our cleaned samples showed a Fe/Mg ratio smaller than 0.1 $mol.mol^{-1}$, and neither Fe/Ca nor Al/Ca correlate with Mg/Ca.

This clearly shows the efficiency of the cleaning procedure in removing silicate contaminants.

2.4. Sea surface temperature reconstruction using the modern analogue technique

Sea surface temperature reconstructions were performed using foraminiferal assemblages along the core MD99-2346 based on the modern analogue technique (Hutson, 1980; Overpeck et al., 1985; Prell, 1985; Prentice, 1980), Fig. 1. This technique is used to compare fossil planktonic foraminiferal samples to a modern reference database and to identify, for each fossil association, the ten best modern analogues. The mean degree of similarity between each fossil assemblage and the corresponding ten best modern analogues is measured by a dissimilarity coefficient. The SST estimates are considered reliable when this coefficient is lower than 0.25 (Prell, 1985). Above this threshold value, SST estimates have to be considered with caution. The reference database used for the present study has been first developed by Kallel et al. (1997a) and then improved by Hayes et al. (2005) and corresponds to 274 core-top sediments, 145 from the Mediterranean Sea and 129 from the North Atlantic Ocean. In the Mediterranean Sea, it has been found that modern analogues of foraminiferal fossil assemblages are found in the Mediterranean Sea itself during warm periods of the Upper Quaternary. However, during glacial periods, the best modern analogues originate mainly from the North Atlantic (Essallami et al., 2007; Kallel et al., 1997b, 2000; Melki et al., 2009).

2.5. Sea surface salinity reconstruction

By combining SST estimates derived from foraminifera using modern analogue technique and the foraminiferal $\delta^{18}O$ values, we reconstructed the Gulf of Lion surface salinity record (Fig. 1) following the method introduced by Duplessy et al. (1991) and Kallel et al. (1997a). Taking into account the SST estimates, the $\delta^{18}O$ surface water variations were calculated by solving the paleotemperature equation (Shackleton, 1974).

In the Mediterranean Sea, surface water $\delta^{18}O$ (δ_w) changes reflect both changes in the $\delta^{18}O$ value of the incoming Atlantic water and variations of the local freshwater budget (Precipitation plus continental Runoff minus Evaporation, $P + R - E$) of the Mediterranean basin (Kallel et al., 1997b). The effect of continental ice volume variations on global seawater $\delta^{18}O$ is assumed to be equal to the sea-level curve of Lambeck and Chapell (2001) multiplied by a constant coefficient of 1.1‰/130 m from Waelbroeck et al. (2002). As the Mediterranean Sea is linked to the North Atlantic Ocean through the Straits of Gibraltar, we suppose that the effect of continental ice volume variations was recorded in a similar manner in the two areas. We therefore estimated the local Mediterranean Sea surface $\delta^{18}O_{sw}$ variations with respect to the modern situation as the difference between calculated and modern seawater $\delta^{18}O_{sw}$, corrected for the global effect: $\delta^{18}O_{anomaly}$ = calculated $\delta^{18}O_{sw}$ − [modern $\delta^{18}O_{sw}$ + global $\delta^{18}O$signal].

To convert the $\delta^{18}O$ anomaly to a salinity anomaly, we used the modern seawater $\delta^{18}O_{sw}$-salinity relationship for the western Mediterranean Sea (1‰ change in local salinity will result in 0.41‰ change in local $\delta^{18}O_{sw}$; Kallel et al., 1997a).

Core MD99-2346 exhibits four strong negative salinity anomalies (Fig. 3) during H2, H1, the Younger Dryas and the Middle Holocene period between about 10,000 and 4,000 yrs B.P. (3.5, 3.3, 1.7 and 1‰ respectively). The Gulf of Lion salinity decrease events are similar to those observed in other Mediterranean cores recovered in the Alboran Sea (Cacho et al., 1999), in the Tyrrhenian Sea (Kallel et al., 1997b, Paterne et al., 1999) and in the Sicilian–Tunisian Strait (Essallami et al., 2007).

To understand better the origin of these salinity changes, Melki et al. (2009) compared them with those obtained from the core SU81-18 recovered in the North Atlantic Ocean off Portugal (Duplessy et al., 1992, 1993). They found that the first three events were associated with a similar salinity decrease of the incoming Atlantic water entering the Mediterranean Sea in the upper part of the Gibraltar Strait, but the western Mediterranean freshwater balance was not affected at these epochs. The basin acted as today as a concentration basin ($P + R < E$), whereas the Holocene event, absent in the North Atlantic Ocean, was found to be of local origin. It indicates an increase of precipitation over the whole Mediterranean region.

Consequently, the effect of the deglaciation melt water in the Gulf of Lion was mainly transferred from the North Atlantic via the Gibraltar Strait, whereas the Alpine glaciers contribution in the last deglaciation could have been potentially significant only for the northern Mediterranean sites (Stocchi et al., 2005). It was restricted to the Adriatic Sea and the Gulf of Genoa (Lambeck et al., 2004).

3. Results

3.1. Data of surface sediments

Values of $\delta^{18}O_{foraminifera}$ measured on *G. bulloides* from the Mediterranean core tops (Fig. 1) and their corresponding calcification temperatures (Tiso) are summarized in Table 1. The isotopic temperature (Tiso) was calculated

Table 1
Hydrologic parameters at the location of core tops and geochemical data obtained on *Globigerina bulloides*. Values of $\delta^{18}O_f$ were measured on *G. bulloides*, and the isotopic temperature (T_{iso}) was calculated using an equation from Shackleton (1974). Values of Mg/Ca were measured on *G. bulloides*, and the corresponding temperatures ($SST_{Mg/Ca}$) were calculated based on calibration from Elderfield and Ganssen (2000) for *G. bulloides*. April-May SST and April-May-June SST are extracted from Atlas (Levitus and Boyer, 1994).

Tableau 1
Paramètres hydrologiques à l'emplacement des sommets de carottes et données géochimiques obtenues sur *Globigerina bulloides*. Les valeurs de $\delta^{18}O_f$ sont mesurées pour le foraminifère planctonique *G. bulloides*, et les températures isotopiques ont été estimées à partir de l'équation des paléotempératures de Shackleton (1974). Les rapports Mg/Ca sont mesurés sur *G. bulloides* et les températures correspondantes ($SST_{Mg/Ca}$) ont été déduites à l'aide de l'équation de calibration d'Elderfield et Ganssen (Elderfield and Ganssen, 2000) pour *G. bulloïdes*. Les températures d'avril-mai et d'avril-mai-juin ont été estimées à partir d'un atlas océanographique (Levitus et Boyer, 1994).

Core	Mg/Ca (mmol/mol)	$\delta^{18}O_f$ (PDB)	Tiso (°C)	April-May SST (°C)	April-May-June SST (°C)	$SST_{Mg/Ca}$ (°C)
MD90-901	4.0	1.18	16.3	16.2	17.7	19.9
MD99-2344	5.3	1.14	17.3	13.9	15.6	23.1
MD99-2346	4.8	1.29	16.5	14.7	16.4	22.0
KET 80-22	5.1	1.36	16.4	16.0	17.7	22.7
DED 87-07	4.3	1.06	17.4	16.5	18.1	20.7
KET80-03	4.6	1.46	17.7	16.5	18.2	21.4
KET80-19	4.9	1.14	15	16.6	18.2	22.3

using the paleotemperature equation of Shackleton (1974) by combining these $\delta^{18}O_f$ measurements with the oxygen isotopic ratio of seawater ($\delta^{18}O_{sw}$) extracted from a gridded atlas (LeGrande and Schmidt, 2006) at the appropriate location of each core. Results for Mg/Ca measured on *G. bulloides* are also shown in Table 1. The Mg/Ca of *G. bulloides* were converted to temperatures ($SST_{Mg/Ca}$) based on Elderfield and Ganssen (2000) ($Mg/Ca = 0.81\ e^{0.081T}$) empirical equation for *G. bulloides*. Using this Mg/Ca-temperature empirical calibration results in surface temperatures ($SST_{Mg/Ca}$) that are systematically higher than the isotopic temperatures (Tiso).

3.2. Modern analogue technique: selection of season and results

Under modern conditions, *G. bulloides* develops preferentially during the spring bloom in the Mediterranean Sea (Pujol and Vergnaud-Grazzini, 1995). This is demonstrated, for instance, by the strong correlation over all the Mediterranean Sea, between modern April-May SSTs (Levitus, 1982) and isotopic temperatures estimated using $\delta^{18}O$ values of *G. bulloides* (Kallel et al., 1997a).

However, if we focus only on data from the western Mediterranean Sea, particularly in the Gulf of Lion (Table 1), we note that isotopic temperatures estimated using $\delta^{18}O$ values of *G. bulloides* from core tops average ~ 16.5 °C, and are, therefore, ~ 2 °C warmer than April-May SST (Atlas WOA5). In this area, the planktonic spring bloom is mainly linked to the start of the vertical stratification of the water column associated with the water warming after winter overturning. As the vertical winter overturning is particularly intense in the Gulf of Lion, it is likely that the stratification and development of *G. bulloides* spread over a longer period and/or start later than in the other areas of the Mediterranean Sea. Thus, in the Gulf of Lion, the best correlation with the isotopic temperatures estimated using $\delta^{18}O$ values of *G. bulloides* is obtained with the mean spring (April, May, June) SST, and not with April-May SST.

Past April-May-June SST (SST_{MAT}) were estimated along the core MD99-2346 from the counts of planktonic foraminifera published by Melki et al. (2009), using the modern analogue technique. These temperatures estimates are shown in Fig. 2A. The dissimilarity coefficients associated with this SST reconstruction are generally lower than 0.25 except for the Last Glacial Maximum (Fig. 2B; between 21.09 and 18.07 cal kyr BP.) when they can reach 0.3 (Fig. 2C). All estimates were obtained with low standard deviations (not exceeding 1.25 °C).

3.3. SST Mg/Ca record along the core MD99-2346

The high-resolution $SST_{Mg/Ca}$ record for the last 28 kyr, can be compared to that obtained using modern analogue technique applied to fossil foraminiferal assemblages (SST_{MAT}) (Fig. 2A). Records display similar patterns. In both cases, the last glaciation is colder than the Upper Holocene by about 7 °C and the post-glacial warming of the Bollïng/Alleröd (B/A), which began at about 14.7 cal kyr BP., was interrupted by a climatic deterioration and an abrupt cooling at the same epoch as the European and North Atlantic Younger Dryas (YD) between about 12.8 and 11.5 kyr BP. (Bard et al., 1987; Duplessy et al., 1991; Rasmussen et al., 2006). This pattern of temperature change is similar to that observed in other Mediterranean areas such as the Alboran Sea, the Tyrrhenian Sea, the Sicilian-Tunisian Strait and the eastern Mediterranean basin (Cacho et al., 1999; Emeis et al., 2000, 2003; Essallami et al., 2007; Kallel et al., 1997b; Paterne et al., 1999).

Significant differences between the two records of the Gulf of Lion are observed, however, during the Younger Dryas and the Lower Holocene. The YD cooling phase is shorter in the Mg/Ca record (of 12.93 at 11.49 kyr BP.) than in the modern analogue technique record (of 13.45 to 11.49 kyr BP.). The timing of the $SST_{Mg/Ca}$ cooling is more consistent with that defined in the North Atlantic for the Younger Dryas (12.8 to 11.7 kyr BP.; Bard et al., 2000;

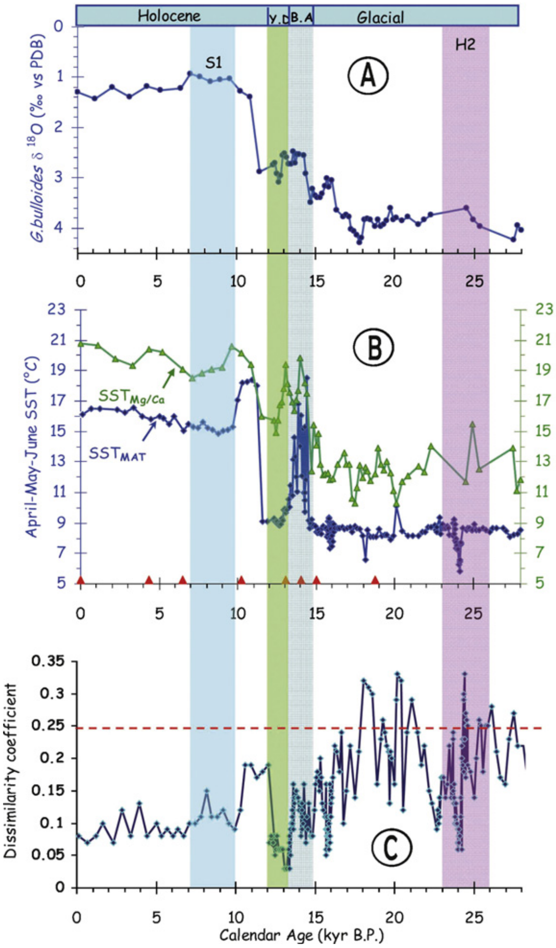

Fig. 2. Climatic records of core MD99-2646: (A) Oxygen isotope composition of *Globigerina bulloides*; (B) Sea surface temperatures (SSTs) obtained by the use of Mg/Ca ratios in *G. bulloides* (green curve), and planktonic foraminifera assemblages for April–May-June (in blue); (C) dissimilarity coefficient for temperatures generated using modern analogue technique. Levels reported in red were analyzed by XRD.

Fig. 2. Enregistrements climatiques de la carotte MD99-2346: (A) Composition isotopique de l'oxygène de *Globigerina bulloides;* (B) Paléotempératures de surface estimées par la mesure du rapport Mg/Ca du foraminifère planctonique *G. bulloides* (courbe verte) et par la technique des analogues actuels (MAT) pour Avril-Mai-Juin (en bleu); (C) coefficients de dissimilarité qui contrôlent la fiabilité des estimations de paléotempératures par la technique des analogues actuels. Les niveaux signalés en rouge ont été analysés par DRX.

Heinrich, 1988; Rasmussen et al., 2006). Moreover, the foraminiferal record indicated that SSTs were higher at the beginning of the Holocene than the Upper Holocene SSTs by about 2 to 3 °C. Such a structure is not as marked on the Mg/Ca record.

More importantly, Fig. 2A clearly indicates that while the structures of two temperature records are broadly similar; the $SST_{Mg/Ca}$ estimates are, however, several degrees warmer than SST_{MAT}. The shift is constant during the last glaciation and Holocene but changes significantly through time during the last deglaciation. This is probably due to the offset of the biological responses with respect to hydrological changes in temperature. Thus, in order to determine the average offset between the two temperature records, we suggest to retrieve the deglaciation interval, and we calculated the mean differences for the interval 0–8 kyr BP. (Holocene) and 15–25 kyr BP. (glacial period). Over the Holocene, the temperature offset is about 3.8 °C, and is +4 °C for the glacial period.

4. Discussion

4.1. Mg enrichment in G. bulloides from core MD99-2346: potential effect of early diagenesis processes

A recent work pointed out that anomalously high Mg/Ca ratios measured by conventional ICP-AES analysis of planktonic foraminifers from the Mediterranean Sea (and in particular in the eastern basin) are mainly related to the presence of early diagenesis, high Mg-calcite overgrowths (10–12%) (Boussetta et al., 2011; Hoogakker et al., 2009; van Raden et al., 2011). However, along the core MD99-2346, an interpretation of the XRD profiles, deconvoluted using the IGOR® software, did not reveal any measurable amount of Mg-rich calcite on *G. bulloides* shells. If it exists, in trace amounts, it is below the XRD detection-limit (Sabbatini et al., 2011). Nevertheless, the deposition of secondary inorganic calcite containing 10–12% of Mg, even in small quantities, has the potential to change noticeably Mg/Ca values obtained on whole planktonic shells (which contain only a few mmol mol-1 Mg/Ca; Sexton et al. (2006)).

In the eastern Mediterranean basin, where the diagenetic coating appears to be generally more important, Boussetta (2011) showed that there is considerable local variability in its amount even at the sample scale. Unpublished data, dealing with the evolution of the diagenetic coating along a core recovered in the Levantine basin, show that the amount of diagenetic calcite also varies over time (Boussetta, 2011, PhD thesis). Such variability in the Mg-rich calcite encrustation, both spatial and temporal, is not compatible with the relative constancy, within the rather stable time period of the Holocene and the LGM, of the temperature shift between $SST_{Mg/Ca}$ and SST_{MAT} that we note in the core MD99-2346. We can therefore reasonably conclude that the presence of a diagenetic coating cannot account for this systematic Mg enrichment observed in core MD99-2346.

4.2. Can a salinity bias explain G. bulloides high Mg/Ca values?

The Mediterranean Sea is a semi-enclosed basin showing a strong salinity gradient from west (~36 psu near the Strait of Gibraltar) to east (~40 psu) (Boyer et al., 2002; Lascaratos et al., 1999). These salinities are higher than the average for the World Ocean. Recently, several studies have emphasized the potential role of high salinity as a bias on Mg/Ca thermometry, with sensitivities ranging from 4 ± 3% Mg/Ca per psu unit observed in culture studies (Kisakürek et al., 2008; Lea et al., 1999; Nürnberg et al., 1996) up to 15–59% per psu suggested by field studies on Mediterranean core top samples (Ferguson et al., 2008).

In order to evaluate the possibility that Mg/Ca temperature anomalies from the western Mediterranean Sea are affected by surface salinity, we reconstructed the Gulf of Lion surface salinity record, by combining SST estimates derived from foraminifera using modern analogue technique and the foraminiferal $\delta^{18}O$ values, following the method introduced by Duplessy et al. (1991) and Kallel et al. (1997a). Then, these salinities are compared with the potential shift (ΔT) between Mg/Ca temperatures ($SST_{Mg/Ca}$) and inferred temperatures using modern analogue technique (SST_{MAT}).

As can be seen (Fig. 3), the surface salinity record obtained from core MD99-2346 reveals large-scale fluctuations that are neither correlated with Mg/Ca temperatures nor with the shift (ΔT) between $SST_{Mg/Ca}$ and SST_{MAT}. This is particularly visible during the cold periods synchronous to the Heinrich events 2 and 1, during the Younger Dryas and during the Lower to the Middle Holocene. Abrupt and strong salinity decrease events of 2 to 3‰ are observed during these periods (Melki et al., 2009) and they are not reflected by corresponding changes in Mg/Ca temperatures or in the shift relative to SST_{MAT}.

To confirm the hypothesis that salinity does not play any dominant role in the Mg uptake into Mediterranean foraminiferal tests, we looked if a salinity effect can be detected from Mg/Ca measured in *G. bulloides* core tops samples (Boussetta et al., 2011) and from plankton tows (van Raden et al., 2011) recovered from the western Mediterranean Sea.

In the western Mediterranean basin, SEM observations and X-Ray Diffractometry Analyses indicate that the post-mortem calcite overgrowth is minor (Boussetta et al., 2011) and that the most of this calcite being likely removed during the chemical cleaning for Mg/Ca analyses (Sabbatini et al., 2011).

For these samples we estimated the difference (Δ Mg/Ca) between the measured Mg/Ca ratio ($Mg/Ca_{measured}$) and that expected (Mg/Ca_T) from the calibration of Elderfield and Ganssen (2000), by the use of estimated temperatures from oxygen isotope composition of *G. bulloides*. The residuals (Δ Mg/Ca) were then compared with salinity changes (Fig. 4). This figure clearly shows that there is no significant correlation between salinity and plankton tow or core top sample Δ Mg/Ca supporting our conclusion that the Mg/Ca enrichment of *G. bulloides* along core MD99-2346 cannot be explained by salinity.

4.3. *Mg/Ca thermometry in the western Mediterranean Sea: is there a specific vital effect for the incorporation of Mg into G. bulloides calcite?*

The Mg/Ca-temperature calibration for *G. bulloides* that we used in this study has been established by Elderfield and Ganssen (2000) using surface sediment material from open ocean, particularly the North Atlantic Ocean on a latitudinal transect, from, 30° to 60°N at about 25°W. It should be noted that Elderfield and Ganssen (2000) have removed from their database several *G. bulloides* Mg/Ca values, which appeared "unusually high" compared to values obtained in the same surface temperature conditions on other planktonic foraminiferal species. These authors observed that Mg-enriched samples of *G. bulloides* are mainly found on shallower core tops, but they do not provide a clear explanation about why only the *G. bulloides* species appears to show such anomalous Mg/Ca values. We believe that the existence of anomalously high *G. bulloides* Mg/Ca ratios clearly suggest the problem of developing a Mg/Ca thermometry on this species, although — at this stage — no clear explanation exists about its cause.

This Mg enrichment seems, therefore, to be a signal acquired during the development of *G. bulloides* and not at the sediment surface. This interpretation is supported by the data obtained by van Raden et al. (2011) showing that the high Mg/Ca values also characterize *G. bulloides* shells

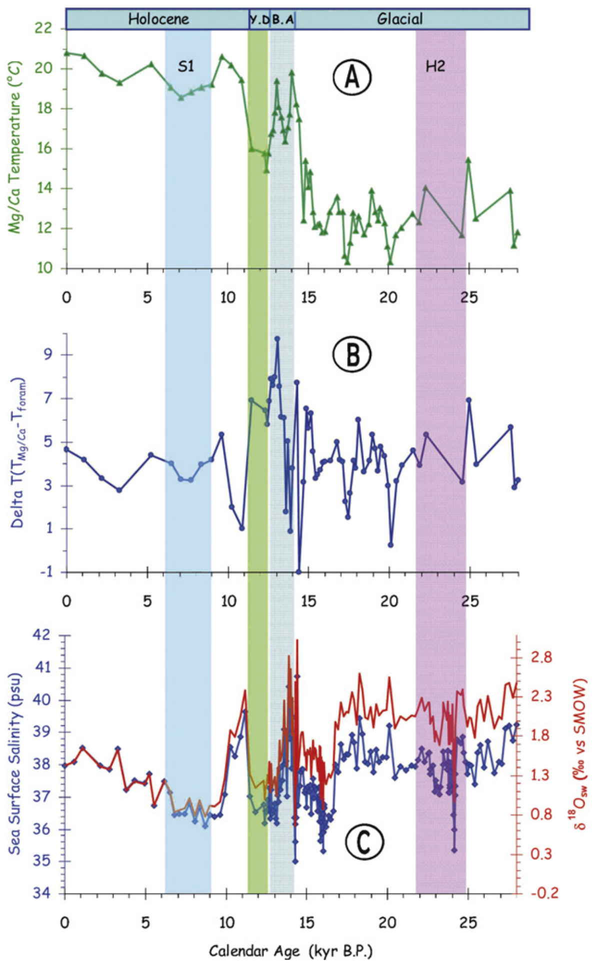

Fig. 3. Climatic records of core MD99-2646 against age: (A) Mg/Ca temperature; (B) comparison of the difference (ΔT) between $SST_{Mg/Ca}$ and $SST_{April\text{-}May\text{-}June}$ (B) Sea surface salinity and $\delta^{18}O_{water}$ calculated from the SST estimates derived from foraminifera using modern analogue technique and the foraminiferal $\delta^{18}O$ values, following the method introduced by Duplessy et al. (1991) and Kallel et al. (1997a).

Fig. 3. Enregistrements climatiques en fonction de l'âge de la carotte MD99-2646: (A) tempér atures Mg/Ca; (B) écarts (ΔT) entre les températures Mg/Ca et les températures des plus proches analogues; (C) paléosalinités et $\delta^{18}O_{eau}$ reconstitués en combinant le $\delta^{18}O$ du foraminifère planctonique *G. bulloides* et les estimations des températures par la technique des Analogues Actuels, selon la méthode introduite par Duplessy et al. (1991) et Kallel et al. (1997a).

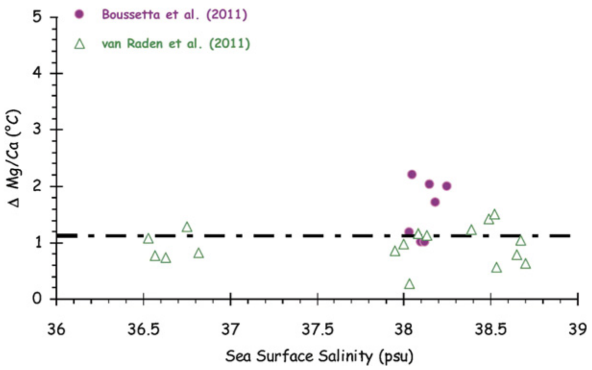

Fig. 4. Difference (Δ Mg/Ca) between the Mg/Ca ratios measured in *G. bulloides* from core tops (Boussetta et al., 2011) and plankton tow samples (van Raden et al., 2011) of the western Mediterranean Sea and the value expected from the calibration of Elderfield and Ganssen (2000) versus Mediterranean surface water salinity. Salinities were estimated by averaging World Ocean Atlas 2005 data (Antonov et al., 2006).

Fig. 4. Différence (Δ Mg/Ca) entre le rapport Mg/Ca mesuré sur *G.bulloides* des sommets de carottes (Boussetta et al., 2011) et des pièges à sédiments (van Raden et al., 2011) de la Méditerranée occidentale et celui prédit par l'équation de calibration d'Elderfield et Ganssen (Elderfield and Ganssen, 2000) en fonction de la salinité de surface de la Méditerranée. Les salinités observées des eaux de surface sont alors estimées à partir des données de l'Atlas océanographique WOAD05 (Antonov et al., 2006).

retrieved from plankton tows in the western Mediterranean. The high calcite saturation state of Mediterranean surface waters cannot explain this Mg enrichment. Culture experiments on planktonic foraminifera, including *G. bulloides*, have shown that less Mg rather than more Mg is incorporated into the tests during calcification at higher saturation states (Kisakürek et al., 2008; Lea et al., 1999; Russell et al., 2004).

Two hypotheses will have to be tested in the future, but unfortunately it cannot be done with the currently available data set:

1. is the empirical equation obtained by Elderfield and Ganssen (2000) incorrect because it should have taken into account the *G. bulloides* Mg/Ca values considered by these authors as "abnormally" high?;
2. is the Mediterranean *G. bulloides* associated to a particular genotype that has developed a specific process of biomineralization characterized by high Mg uptake (vital effect)?

Darling et al. (2003) demonstrate, in the Santa Barbara Channel (Pacific Ocean), that the same genotype of *G. bulloides* (type IId) occurs in all the changing hydrographic regimes associated with this region throughout the annual cycle with the exception of January, when they recorded the additional presence of the high-latitude *G. bulloides* type IIa. On the other hand, it has been shown that different morphotypes of *G. ruber*, which are most likely representative of different genotypes have distinct Mg/Ca (Steinke et al., 2005). Consequently, genotype difference, if it exists, between *G. bulloides* individuals used in the Atlantic calibration and those analysed in the Mediterranean Sea might be responsible for the observed anomalously high Mg/Ca in the Mediterranean Sea.

Deciphering the origin of this consistent Mg enrichment of *G. bulloides* shells in the Mediterranean Sea requires further investigations, based on modern material.

5. Conclusions

1. Measurement of Mg/Ca ratios of the surface-dwelling planktonic foraminifera *G. bulloides* along the core MD99-2346 have allowed us, using the Atlantic calibration of Elderfield and Ganssen (2000), to reconstruct the sea surface temperatures (SST) in the Gulf of Lion during the last 28,000 years.
2. The comparison between Mg/Ca temperatures ($SST_{Mg/Ca}$) record obtained for *G. bulloides* along the core MD99-2346 with that inferred using modern analogue technique, applied to fossil foraminiferal assemblages in the same core, shows a striking similarity but also emphasizes that the $SST_{Mg/Ca}$ estimates are several degrees warmer than SST_{MAT} during the last 28,000 years. The shift is constant during the last glaciation and Holocene but changes significantly through time during the last deglaciation. This is probably due to the offset of the biological responses with respect to hydrological changes in temperature.
3. The high Mg-calcite diagenetic coating (10–12%), which appears to be *generally important* in the eastern Mediterranean basin, cannot account for the anomalously high Mg/Ca ratios and the constant shift (ΔT) between the two palaotemperature records ($SST_{Mg/Ca}$ and SST_{MAT}).
4. Comparisons of Mg/Ca data obtained on *G. bulloides* from core top and plankton tow samples as well as along the core MD99-2346 with modern and paleosalinities of the western Mediterranean Sea exclude any surface salinity effect on the Mg uptake into *G. bulloides* tests.
5. We must therefore consider that either the empirical equation for *G. bulloides* of Elderfield and Ganssen (2000) is incorrect or there is a specific Mediterranean genotypes of *G. bulloides* for which a specific Mg/Ca-temperature calibration is needed. Further studies are required to confirm these two hypotheses.

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