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Morphological recognition of *Globigerinoides ruber* morphotypes and their susceptibility to diagenetic alteration in the eastern Mediterranean Sea

G. Kontakiotis [a,*], A. Antonarakou [a], P.G. Mortyn [b,c], H. Drinia [a], G. Anastasakis [a], S. Zarkogiannis [a], J. Möbius [d]

[a] National & Kapodistrian University of Athens, School of Earth Sciences, Faculty of Geology & Geoenvironment, Department of Historical Geology-Paleontology, Panepistimiopolis, Zografou 15784, Greece
[b] Institute of Environmental Science and Technology (ICTA), Universitat Autònoma de Barcelona (UAB), Edifici Cn - Campus UAB, Bellaterra 08193, Spain
[c] Department of Geography, Universitat Autςnoma de Barcelona (UAB), Spain
[d] Institute of Geology, Hamburg University, Bundesstr. 55, 20146 Hamburg, Germany

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ABSTRACT

Planktonic foraminiferal geochemistry presents a valuable archive for paleoceanographic reconstructions. However in high salinity and carbonate super-saturated settings, precipitation of inorganic calcite onto foraminiferal tests can potentially alter the primary geochemical signal, biasing Mg/Ca ratios and ensuing paleoceanographic reconstructions. Here we utilize test biometrics (specifically related to the compression and elongation of the last chambers) to identify four distinct morphotypes (labelled A-D) of the paleoceanographically important planktonic foraminifer species *Globigerinoides ruber*, and further evaluate their susceptibility to diagenetic alteration from a suite of surface sediments in the eastern Mediterranean Sea. The three distinguished morphotypes (A–C) correspond to previously recognized morphotypes ("Normal", "Platys", "Elongate" respectively) in the Mediterranean Sea, while the remaining (D or "Twin") was designated for the first time. We also compare Scanning Electron Microscopy (SEM) observations performed on four distinguished morphotypes, indicative of potential diagenetic alteration influence. We identified 3 different overgrowth stages (OGA1–OGA3), as a function of geography in the study area. The early diagenesis degrees (involving all the morphotypes) are only geographically distinct along the eastern Mediterranean (increasing to the south), since the morphology does not play a role in the likelihood of diagenetic alteration. Particularly, in the north Aegean Sea, SEM analyses reveal the absence or limited presence of an overgrowth imprint in all recognized morphotypes, while in the central-south Aegean and Levantine Seas they show higher amplitudes of diagenetic overprint supporting the general trend to advanced diagenetic alteration. The semi-enclosed oligotrophic nature and high salinity of this setting, in combination with the different degree of carbonate precipitation and calcite super-saturation between the sub-basins, could be the most plausible explanation for the observed diagenetic stages. The ecological divergence between the morphotypes, determined by different controlling factors (depth habitats, growth optimum/stressed conditions, productivity, stratification, near-/offshore-conditions), in combination with their different test morphologies (related to shell porosity), control directly their distribution pattern. Regardless of the exact mechanism of early diagenetic processes, our results remove one potential source of uncertainty in Mg/Ca-T reconstructions in such highly evaporitive basins of the (sub)tropics, and potentially open the door to the calculation of a multivariate calibration with greater accuracy. However, further investigations should extend this approach to test the robustness of our findings in a number of similar oceanic settings.

1. Introduction

Planktonic foraminiferal Mg/Ca is a widely used tool for paleoceanographic reconstruction. The proxy basis is that bulk Mg/Ca is mainly controlled by calcification temperature (Lea et al., 2000; Dekens et al., 2002; Anand et al., 2003). However, it has been shown that the incorporation of Mg^{2+} into foraminiferal calcite is controlled by more than one environmental parameter (e.g. salinity, and calcite saturation among others (Ferguson et al., 2008; Kisakürek et al., 2008; Mathien-Blard and Bassinot, 2009; Martínez-Botí et al., 2011; Hönisch et al., 2013; Kontakiotis et al., 2016)). Especially in high salinity settings, proxy reliability has been questioned due to complicating diagenetic factors (overgrowth effect) affecting Mg/Ca variability in foraminiferal tests (Hoogakker et al., 2009; Kontakiotis et al., 2011). The information on the bulk foraminiferal geochemical composition altered by diagenesis, derived by both modern core-top (Boussetta et al., 2011; Kontakiotis

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* Corresponding author.
E-mail addresses: gkontak@geol.uoa.gr (G. Kontakiotis), aantonar@geol.uoa.gr (A. Antonarakou), graham.mortyn@uab.es (P.G. Mortyn), cntrinia@geol.uoa.gr (H. Drinia), anastasakis@geol.uoa.gr (G. Anastasakis), sterjios@hotmail.com (S. Zarkogiannis), juergen.moebius@uni-hamburg.de (J. Möbius).

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et al., 2011; Sabbatini et al., 2011) and down-core (Regenberg et al., 2007; Hoogakker et al., 2009) studies from highly evaporative subtropical seas (e.g. Mediterranean Sea, Red Sea, Caribbean Sea), combines the actual biogenic and inorganic calcite signals of planktonic foraminiferal tests and confounds Mg/Ca–Temperature estimates. Additionally, despite the advances made through culturing experiments to understand parameters related to water column physical/chemical properties, culture studies (Raitzsch et al., 2010) have similarly shown evidence of high-Mg overgrowths on both benthic and planktonic foraminifera, but there is still uncertainty about the mechanisms responsible for these inorganic precipitates.

Especially for the Mediterranean Sea, several recent studies (Kontakiotis et al., 2011, 2016; Van Raden et al., 2011; Boussetta et al., 2011; Sabbatini et al., 2011) have highlighted the role of diagenetic overgrowth, beyond T, as influential on Mg/Ca. The study of Van Raden et al. (2011) showed that different species are influenced by diagenesis to different degrees due to their different test morphologies. However, these findings were only available for *Globoborotalia inflata*, a species that is of relatively minor significance to this proxy. Progress on documenting the precipitation of high-Mg calcite overgrowths from different sub-basins (e.g. Adriatic Sea, Aegean Sea, Ionian Sea, Tyrrhenian Sea, Levantine Sea) of the Mediterranean Sea on different species (*Globigerinoides ruber*, *Globigerina bulloides*; typically used for T reconstructions) has recently occurred (Kontakiotis et al., 2011; Boussetta et al., 2011; Sabbatini et al., 2011) due to improvements in analytical instrumentation (e.g. LA-ICPMS, FT-TRA), emphasizing several aspects of the overgrowth effect, such as the mechanism, amplitude, and quantification of the diagenetic alteration and its species-specific potential response.

To assess the diagenesis impact on planktonic foraminiferal calcite in terms of Mg/Ca paleothermometry, and to further elucidate the mechanism causing the observed overgrowths, we present a suite of new Scanning Electron Microscopy (SEM) data in distinct *Globigerinoides ruber* morphotypes from 20 Aegean and Levantine core-tops. The selected species is geographically continuous along the eastern Mediterranean Sea and most importantly, the most susceptible to diagenetic overprint (Boussetta et al., 2011; Kontakiotis et al., 2011, 2016; Sabbatini et al., 2011), and the selected sites benefit from their diagenetic potential (Mg/Ca range: 3.35–21.61 mmol/mol; Kontakiotis et al., 2011) due to a substantial environmental gradient in temperature (T), salinity (S), and calcite saturation state from north to south. For each of the sub-basins (north, central, south Aegean and NW Levantine) we assess: 1) the sensitivity of each analyzed morphotype to the overgrowth effect, 2) the geographic distribution of the observed diagenetic alteration, 3) differences in the Mg/Ca values from each sub-basin, and 4) potential paleoceanographic implications for the trends observed. Moreover, by focusing on the morphotype evaluation of *G. ruber* (w), especially with the definition and designation of morphotype "Twin" for the first time, our study also provides an extensive perspective on the taxonomic concept for this species, although there is a little information currently available for this application in the Mediterranean Sea (Type Ia, Ib, IIa, IIb; Aurahs et al., 2009, 2011, and Type Normal, Platys, Elongate; Numberger et al., 2009). Additionally, the assessment of the intra-specific diagenetic alteration, based on the direct comparison of the overgrowth effect on subspecies (morphotype) level, contributes to a much better knowledge of their ecological differentiation. This evidence corroborates already existing differences between *G. ruber* morphotypes in their stable isotope compositions or Mg/Ca geochemistry (Wang, 2000; Löwemark et al., 2005; Steinke et al., 2005; Antonarakou et al., 2015; Henehan et al., 2015), and it further contributes to a more precise reconstruction of SSTs, such that only when the changing proportions of morphotypes are accounted for, would geochemical measurements and subsequent paleoenvironmental interpretations be more meaningful.

2. Environmental drivers

The Aegean Sea communicates with the Black Sea through the Straits of Bosporus and Dardanelles, and with the open eastern Mediterranean (Levantine Sea) through several larger and deeper straits between Peloponnesus, the Islands of Crete and Rhodes and south-western Turkey (Fig. 1a, b). It is separated into three main sub-basins: the north, central and the south Aegean. These basins have significantly different water column characteristics, which are controlled by the exchange of water masses within the Levantine and Black Seas and by the climate contrasts between more humid conditions in the north and semi-arid conditions in the south, respectively (Lykousis et al., 2002). The surface water mass in the Aegean forms a counter-clockwise gyre, which is complicated by mesoscale cyclonic and anticyclonic eddies resulting from interaction processes, especially in the south Aegean Sea (Karageorgis et al., 2008). Due to the large excess of evaporation over precipitation and the fact that the Aegean Sea is almost completely isolated from the Atlantic, unusually large N-S-trending T (17.0–23.0 °C) and S (35.3–39.5 psu) gradients exist for such a small geographic area, with the cooler and fresher waters in the north (Fig. 1a, b). This characteristic is important for locally assessing the relationship between T and Mg/Ca. The strong T-S contrast registered between the north and south Aegean basins confirms the southern trend towards an oligotrophy gradient in the eastern Mediterranean Sea. The estimated annual production was 29.8 g C m^{-2} y^{-1} in the north Aegean and 15.2 g C m^{-2} y^{-1} in the south Aegean Sea (Lykousis et al., 2002). However, although the concentrations of nutrients and oxygen are relatively similar in both basins (with a N/P ratio of about 21) significant differences exist in their distribution and regeneration, influenced by the Black Sea water fluxes in the north and the exchange of Levantine water masses through the Cretan Straits in south.

3. Material and methods

3.1. Sampling strategy and site selection

Although the issue of diagenetic bias on Mg/Ca thermometry from this region has been documented (Boussetta et al., 2011; Kontakiotis et al., 2011, 2016; Sabbatini et al., 2011), we still lack detailed understanding of its extent for key planktonic foraminiferal species. Here we use 20 core-top samples from the study of Kontakiotis et al. (2011) and complement them with detailed SEM investigations. High-resolution SEM analyses were performed at the Department of Historical Geology and Paleontology at the National and Kapodistrian University of Athens with a Jeol JSM 6360 SEM. We have specifically targeted the tropical spinose planktonic species *G. ruber*, because it is a) one of the most important sources of information on surface ocean properties and the most dominant species in the eastern Mediterranean (Pujol and Vergnaud-Grazzini, 1995; Triantaphyllou et al., 2009; Kontakiotis, 2016), b) the most common species used for the calibration of the Mg/Ca tracer (e.g. Lea et al., 2000; Dekens et al., 2002; Kisakürek et al., 2008; Herzberg and Schmidt, 2013) and c) the species most susceptible to diagenesis (Boussetta et al., 2011; Kontakiotis et al., 2011, 2016; Sabbatini et al., 2011).

The sampling locations are carefully selected based on the major circulation features in representative Aegean sub-basins as well as the Levantine Intermediate Water (LIW) and Black Sea influences. The selection of sampling locations with deliberate duplication at some latitudes was designed to gauge the robustness of any separation between the diagenetic stages. The analyzed modern core-tops from the eastern Mediterranean are strategically positioned to check the sensitivity of environmental parameters and consequently to assess the vulnerability of each morphotype to early diagenetic processes, as well as to pinpoint the mechanism causing the overgrowths. Mean annual T and S values of the eastern Mediterranean water masses at each core location were used from the World Ocean Atlas (Locarnini et al., 2013; Zweng et al.,