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Evaluating the Effect of Marine Diagenesis on Late Miocene Pre-Evaporitic Sedimentary Successions of Eastern Mediterranean Sea

Assimina Antonarakou¹, George Kontakiotis¹, Charalampos Vasilatos¹, Eva Besiou¹, Stergios Zarkogiannis¹, Hara Drinia¹, P. Graham Mortyn^{2,3}, Nikolaos Tsaparas¹, Panayota Makri¹, Vasileios Karakitsios¹

¹ Faculty of Geology & Geoenvironment, Department of Historical Geology-Paleontology, National & Kapodistrian University of Athens, Zografou, Greece

² Institute of Environmental Science and Technology (ICTA), Universitat Autònoma de Barcelona (UAB), Edifici Cn - Campus UAB, Bellaterra 08193, Spain

³ Department of Geography, Universitat Autònoma de Barcelona (UAB), Spain

aantonar@geol.uoa.gr

Abstract. The microstructure and geochemical composition of foraminiferal tests are valuable archives for the reconstruction of paleoclimatic and paleoecological changes. In this context, the late Miocene *Globigerinoides obliquus* shells from Faneromeni section (Crete Island) were investigated through Scanning Electron Microscopy (SEM) imaging, Energy Dispersive System (EDS) analysis and X-Ray Diffraction (XRD) spectroscopy in order to evaluate their potential as paleoenvironmental archives in the eastern Mediterranean. Investigation of diagenetic features, in late Miocene sediments from the Faneromeni section, shows that carbonate precipitation and cementation occur in various lithologies, particularly in carbonate-rich portions, such as bioclastic or clayey limestones. We identified 3 different diagenetic stages (early, intermediate, advanced), as a function of taphonomy in the study area. The comparison of microstructural and geochemical characteristics reveals a sequence of preservation states with “glassy” to “frosty” to “chalky” shells, indicative of the progressive diagenetic alteration of late Miocene planktic foraminiferal calcite. The early diagenetic stage occurs during the Tortonian, and consists of intermediates between “glassy” and “frosty” individuals. Around the Tortonian/Messinian (T/M) boundary at the second diagenetic stage, planktonic foraminifera have a clear “frosty” appearance, showing a gradual high-Mg calcite (to dolomite) crystal overgrowth development and dissolution of biogenic calcite. During the late Messinian and progressively through the Messinian Salinity Crisis (MSC), planktonic foraminifera present a “chalky” taphonomy. The additional precipitation of authigenic high-Mg inorganic calcite and dolomite crystals in the exterior of the tests characterizes the advanced diagenetic stage. The measured amount of diagenetic Mg-rich (10-14% molar Mg on average) calcite and/or dolomite coatings is compatible with results obtained on modern eastern Mediterranean core-top sediments. The assessment of such a diagenetic alteration contributes to a more precise reconstruction of sea surface temperatures (SSTs) during the Neogene, such that only when the changing proportions of the texture are accounted for, would geochemical measurements and subsequent paleoenvironmental interpretations be more meaningful. However, further investigations should extend this approach to test the robustness of our findings across a range of taphonomies, ages and burial settings.



1. Introduction

The Late Miocene has attracted recent interest as a potential model system for testing future climate change scenarios [1, 2]. Especially, the Messinian (7.24–5.33 Ma) has been considered as one of the most climatically stable periods of the Cenozoic, characterized by minor long-term cooling and ice growth [3]. However, these long-term trends are punctuated by the Messinian Salinity Crisis (MSC; 5.97–5.33 Ma), which has been attributed to changes in the carbon cycle, ocean circulation, and global sea level variations related to changing ice volume [4-7]. The MSC represents one of the most unique events in the history of the Mediterranean during which the basin experienced a dramatic hydrological and biological crisis induced by a powerful combination of geodynamic and climatic drivers [8-13]. The change of the Mediterranean's connections with both the Atlantic Ocean and the freshwater Paratethyan basins, caused high-amplitude fluctuations in the hydrology of its basins [14, 15] which had a great impact on the subsequent geological history of the Mediterranean area, and on the salinity of the global oceans.

The original definition of the MSC referred to a marked environmental change at the base of the Tripoli diatomite formation close to the base of the Tortonian/Messinian (T/M) boundary (Selli, 1960). As evidenced by the synchronous basin-wide salinity increase [13, 15, 16], restricted conditions started well before the MSC due to the gradual closure of the Betic and Rifian marine corridors (7.35 Ma [17], 7.2 Ma [14], 6.7–6.0 Ma [8], 6.64–6.44 Ma [18]). In the last decade sustained and coordinated efforts focused on understanding the evolution of the Late Miocene Mediterranean-Atlantic gateways and their impact on regional, and global environmental changes [14, 19]. In this context, recent advances in the application of geochemistry-based proxies (e.g. Mg/Ca, Sr/Ca, Ba/Ca, U^{k}_{37} , $\delta^{18}O$, GDGTs, clumped isotopes) offer novel, yet largely underexploited tools in unravelling fundamental climatic parameters like sea surface temperature (SST) and salinity (SSS) for the Mediterranean Sea during the pre-MSC to the Pliocene interval [20-25]. However, the majority of the above proxies suffer from important biases (e.g. burial diagenesis) and ill-constrained limitations (e.g. growth season and habitat offsets of key planktonic organisms) in the Mediterranean realm. Therefore, the full potential of Mediterranean sedimentary sequences as paleoclimate archives remains to be exploited because of problems with SST reconstructions in the Mediterranean Sea using well-calibrated proxies coupled with improvements in analytical instrumentation (e.g. LA-ICPMS, FT-TRA, SIMS), and assessing the diagenetic effect [26-31].

There is increasing awareness of how both the microstructure and geochemistry of fossil foraminiferal tests from deep-sea sediments are modified by post-mortem diagenetic alteration [22, 26, 28, 32-40]. We present the first record of testing the impact of diagenesis on the pre-evaporitic sequence during the time interval preceding the onset of the MSC (7.3-6.7 Ma) based on analysis of the Faneromeni section (Crete Island, eastern Mediterranean). The selected section is stratigraphically continuous in the late Miocene, has planktonic foraminifera present throughout, and most importantly, benefit from excellent stratigraphic control based on astronomically calibrated biostratigraphic events [41-43] and tephra layers [44, 45] and magnetostratigraphy [42]. Moreover, the relatively high sediment porosity and permeability, and carbonate-rich lithologies support their enhanced “diagenetic potential” relative to clay-rich sediments [46]. Furthermore, the observed high-frequency lithological alterations that give rise to rhythmic variations in foraminiferal taphonomy provide an ideal test set of samples to investigate the impact of diagenesis in planktonic foraminiferal calcite routinely employed in paleoceanographic studies. We utilize the wealth of microstructure (Scanning Electron Microscopy; SEM) and geochemistry (Energy Dispersive Spectroscopy; EDS and X-ray powder diffraction; XRD) data generated on species-specific (*Globigerinoides obliquus*) planktonic foraminiferal tests recovered from sampling the Faneromeni sequence.

2. Material and Methods

In the eastern Mediterranean, the Faneromeni section is located on northeastern Crete, and consists of a continuous, pelagic sedimentation covering the T/M transition. Sediment lithologies are predominantly homogeneous and/or laminated marls in alternation with sapropels and limestones. The study time slices (Tortonian and Messinian stages) are characterized by different proportions of calcium carbonate (CaCO_3) and thus inferred calcareous microfossil preservation. Overall, thirty-eight samples were collected in the studied sedimentary interval, and processed following standard procedures. The dried bulk samples were weighed, washed over a 63- μm sieve, oven-dried at 40^oC, and subsequently dry sieved into sub-fractions. The entire residue from each sample was analyzed for biostratigraphy and geochemistry. Representative specimens of *G. obliquus* were selected for SEM/EDS analyses. All specimens were mounted on stubs using carbon conductive adhesive tape and carbon-coated prior to imaging. Scanning electron micrographs were generated using a Jeol JSM 5600 SEM, equipped with an ISIS 300 OXFORD automated energy dispersive X-ray analysis system, at the Faculty of Geology & Geoenvironment (National and Kapodistrian University of Athens; NKUA). Ultra-texture, precipitation of authigenic carbonates and preservation/dissolution of biogenic tests were evaluated using SEM/EDS backscattering images. X-ray powder diffraction (XRD) data were obtained using a Siemens Model 5005 X-ray diffractometer. The operating conditions for both SEM/EDS and XRD analyses were described in Vasilatos & Economou-Eliopoulos [47].

3. Results and Discussion

3.1. Inter-section variability in planktonic foraminiferal taphonomy

The general view is that as carbonate sediments transition from marls to biogenic limestones, they undergo compaction, dissolution, recrystallization, and eventually cementation [46]. At the same time, foraminifera in the sediments undergo dissolution, and develop mineral infillings and/or extensive overgrowths during late stage diagenesis [32, 37]. In addition to burial depth and sediment age, lithology and sedimentation rates also play important roles in controlling the rate of carbonate diagenesis [32, 34, 48]. Modelling experiments have shown that recrystallization is more dependent on the lithological diagenetic potential of the constituent sediments rather than burial depth [49]. Preservation state was determined from the estimated degree of overgrowth, dissolution, and fragmentation of planktonic foraminiferal specimens. A first-order assessment of the down-section preservation from light microscope observations indicate that the best preservation of foraminiferal tests occurs at the Tortonian and close to the T/M boundary, coincident with the hemipelagic clay-rich sediments due to their impermeable nature to prevent interaction of the foraminiferal calcite with surrounding pore waters [32]. In contrast, the most permeable sediments (e.g. limestones) apparently lead to poorer preservation because of greater chemical interaction between foraminiferal calcite and pore waters.

3.2. SEM observations

To investigate micron-scale recrystallization of planktonic foraminiferal calcite not detectable by light microscope, we examined specimens by SEM. The magnification of different parts of the exterior of the tests during SEM analysis provides observations of the microstructural details of *G. obliquus* shells and further increases awareness of how both the microstructure and geochemistry of planktonic foraminiferal tests are modified by post-mortem diagenetic alteration. SEM observations are a powerful tool to trace the degree of diagenetic modifications by identifying the amplitude and time-equivalent distribution of the overgrowth effect, and finally to evaluate its correspondence to the paleoclimate-sensitive geochemical archives. Figure 1 shows images of representative planktonic specimens from the different time slices studied here. Data were generated using monospecific separates of *G. obliquus* from the 250 to 300 μm size fraction to minimize potential interspecies and/or ontogenetic offsets. Whole-specimen images are presented for each time interval showing that all samples show evidence of recrystallization, i.e. specimens are more “frosty” than “glassy” [34], which

is common in deep-sea buried sediments with low clay content. We advocate the use of more specific terminology to describe the different types of diagenetic alteration in terms of foraminiferal appearance, such as introduced by Sexton et al. [34]. The terms “glassy” and “frosty” imply two end-member taphonomies, but as shown here there are progressively developed intermediate stages of preservation in between. Moreover, material that has progressed further through the alteration process could be described as “chalky”.

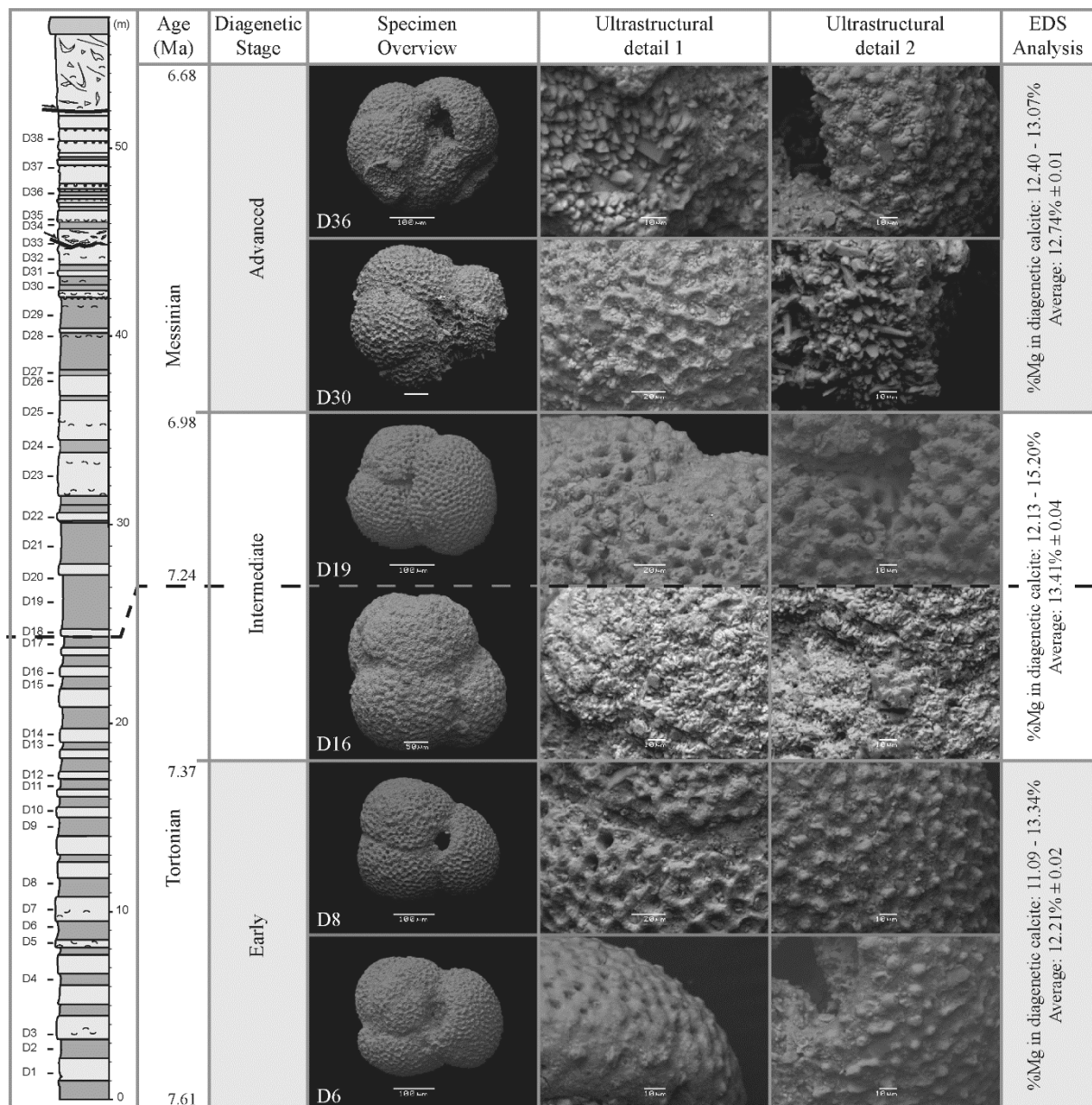


Figure 1. Representative high-resolution SEM backscatter images and relevant mineralogical data indicative of the three diagenetic stages identified in the present study.

All SEM backscatter images show extensive micron-scale rhombohedral cemented overgrowths covering the tests. However, from the base to the top of the section we observed different diagenetic signals, and therefore we identified three distinct diagenetic stages, which are in accordance with recent findings of Antonarakou et al. [36] and Kontakiotis et al. [28] on modern core-top material from the eastern Mediterranean Sea. During the Tortonian, at the first diagenetic stage, foraminifera retain

microstructural features such as wall pores and surface ornamentation. These specimens, although they present an intermediate between “glassy” to “frosty” appearance has undergone diagenetic alteration. The disparity in preservation, which can be considered as an evidence of a complete sequence of intermediates, is illustrated by the fact that the pores of these specimens are generally larger and more clearly defined than those of “frosty” and/or “chalky” individuals from the Messinian time period. Moreover, the apertures of these individuals reveal an absence of the slight infilling of chamber interiors that “frosty” specimens often display. Around the T/M boundary (second diagenetic stage), planktonic foraminifera have a clear “frosty” appearance. Foraminifera altered in this manner show a gradual overgrowth development, which is confirmed by a smooth calcite veneer that covers the outer ridges and sometimes narrows the pores, filling them partially or almost completely. Growth of inorganic calcite crystals during cementation occur across a spectrum of crystal sizes, from micron-scale rhombs of inorganic calcite, or overgrowths to much larger-scale “infilling” of foraminiferal chambers (Figure 1). A second diagenetic process that appears to be evident at this stage is the “peeling” effect. This effect is characterized by removal of the outer surface of the test, obliterating the original pore structure and exposing the earlier wall layers that have less topographic relief [34, 50]. Although this phenomenon possibly occurs during sample washing, here it appears to be due to partial dissolution processes. The above diagenetic processes are not surprising due to the vicinity of the study section to carbonate platforms during that time, which implies similar processes in sediments with precipitation of high-Mg calcite and dissolution of significant proportions of calcite respectively. Thus, overgrowths observed on foraminifer shells are likely related to the precipitation of high-Mg calcite from interstitial waters close to the sediment/water interface. During the late Messinian and progressively through the MSC (third diagenetic stage), planktonic foraminifera present a “chalky” taphonomy. The advanced diagenetic stage also consists of additional precipitation of authigenic high-Mg calcite/dolomite crystals in the exterior of the tests (Figure 1). In these situations, inorganic calcite typically precipitates deep in the sediment column where environmental parameters and the geochemistry of pore fluids are different from those that the foraminifera originally precipitated in.

3.3. Toward constraining the composition and quantifying the extent of foraminiferal diagenetic alteration through mineralogical analyses

To quantify the amount of chemical alteration that has occurred in frosty and chalky specimens, which may be dependent on how texturally recrystallized specimens are, we performed two types of mineralogical analyses. X-Ray diffractometry of washed material revealed the presence of two sets of calcite with different lattice parameters. The first corresponds to calcite usually found in planktonic foraminifera [51], while the second one shows diffraction peaks that are shifted towards higher angles. This is further reinforced by additional EDS-derived data, showing a clear separation between the biogenic (0.55-1.4% molar Mg) and diagenetic (2.6-25.2% molar Mg) calcite. Focused on the Mg-rich calcite phase, most of the data fall within the large range 7.7-15.2% molar Mg, a few even reaching strongly anomalous values as high as 25.2% (mostly during the Messinian). Noticeably, these extreme (and highly scattered) values could be attributed to the presence of high-Mg calcite/dolomite crystals in the exterior of the tests, with the degree of scattering indicative of the extent of their development. The average ~12-13% Mg we estimate in each diagenetic stage far exceeds the highest Mg content that was reported for biologically precipitated foraminiferal calcite. Such a Mg-rich calcite is typical of marine inorganic calcite deposition directly from seawater [31, 35, 52], and is in accordance with the content (10–15% Mg, with a strong maximum abundance at ~13%) of shallow-water and deep-sea carbonate cements in eastern Mediterranean sediments [53].

3.4. Implications for paleoclimate-sensitive geochemical archives

Dissolution of biogenic calcite and re-precipitation of inorganic calcite (overgrowth and recrystallization) at the seafloor and in the sediment column can alter the primary geochemical composition of the foraminiferal test, potentially biasing any resulting SST paleoreconstruction [32, 34, 54]. Especially in highly evaporative (sub)tropical settings (e.g. Mediterranean Sea, Red Sea,

Caribbean Sea), the information on the bulk and/or foraminiferal geochemical composition altered by diagenesis, derived by all types of sediments such as modern core-tops [26, 28, 31, 36, 52] and Neogene down-core [35, 55] or down-section [37-40, 55] deposits, combines the actual biogenic and inorganic calcite signals, and finally biases the isotope composition ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) or elemental ratios (Mg/Ca, Sr/Ca, B/Ca), thus confounding SST and other estimates. Additionally, despite the advances made through culturing experiments to understand parameters related to water column physical/chemical properties, culture studies [56] have similarly shown evidence of high-Mg calcareous overgrowths on both benthic and planktonic foraminifera, but there is still uncertainty about the mechanisms responsible for these inorganic precipitates. Following empirical observations, foraminifera may undergo extensive recrystallization at their recovered burial depth as sediments are lithified and interstitial cement, carbonate infilling, and overgrowths develop [57]. This can be problematic because there is often little discernable change in test morphology visible under light microscopy with increasing recrystallization. Specifically, wall pores and surface ornamentation are often retained, giving the impression that sample material is relatively well preserved. This is particularly true for planktonic foraminifera, one of the main archives on which many paleoceanographic reconstructions and stratigraphic correlations are based, but for which the impacts of diagenesis are still poorly known. We highlight the approach of intensive SEM observations, as a tracer of preservation regime indicative of which foraminifera could be used for additional geochemical investigations to assess the diagenetic effect.

4. Conclusions

SEM observations and EDS/XRD analyses show the post-depositional precipitation of inorganic, Mg-rich (12-13%) calcite on foraminiferal shells. Our results potentially pave the way to better utilize the vast number of Neogene sections hosting “frosty” foraminifera for reconstructing SSTs with greater accuracy. However, although this approach appears to be robust, further work from additional sites in the Mediterranean and/or in a number of similar oceanic settings by matching SEM findings with geochemical signatures would be a valuable contribution to understanding diagenetic alteration, and could further provide consistency in the paleoclimate trends and validate our interpretations.

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