DIAGENETIC TRENDS IN THE PLEISTOCENE CALCAREOUS RIDGES, MERSA MATRUH AREA, EGYPT

By
HANAFY HOLAIL
Department of Geology, Faculty of Science
University of Qatar, Doha, Qatar

Abstract

Ooids are a major constituent of the Pleistocene carbonates along the northwestern coastal ridges of Egypt. For a detailed diagenetic study of the rocks, the Mersa Matruh area was selected. Petrographic examination shows that the rocks are partly consolidated ooid grainstones with low-Mg calcite cement in granular voids.

δ18O, δ13C, and Sr values were determined on whole rock samples, on the manually separated ooids and calcite cements. Oxygen
Pleistocene calcareous ridges, Egypt

isotopic and Sr values for the whole rock (+0.5%o PDB; 9,300 ppm) are consistent with data on limestones of the same age. In contrast, oxygen isotopic values for ooids (average +0.5%o PDB) are heavier relative to values for low-Mg calcite cement (average -1.4%o PDB) and Sr contents are higher for ooids (10,000 ppm). In addition, δ13C values are identical for the whole rock and ooids (average +4.5%o PDB) and heavier relative to δ13C values of the calcite cements (ranging from +4.1 to +3.8%o PDB). These data may suggest that calcite cements are formed in non-diluted pore-water under relatively high rock/water ratios.

INTRODUCTION

Studies of diagenesis of Quaternary carbonate rocks have yielded an immense amount of information and understanding of meteoric diagenetic processes (Halley and Harris, 1979; Allan and Matthews, 1982; Budd, 1988; Budd and Land, 1990; Salier and Moore, 1991). These studies and others have the obvious advantages of monitoring pore-water chemistry and combining this with detailed petrographic, chemical and mineralogical analyses.

The Pleistocene calcareous ridges along the northwestern coastal zone of Egypt have been extensively investigated in terms of their distribution, sedimentology, origin and diagenesis (Hilmy, 1951; Shukri et al., 1956; Butzer, 1960; El-Shazly et al., 1964; Selim, 1974; Hassoub, 1980; Anwar et al., 1981). However, little attention has been given to the water/rock interaction relationships which potentially control dissolution of carbonate grains (ooids) and precipitation of low-Mg calcite cements.

The present study integrates Sr and stable isotope data with the petrographic observations of samples collected from two calcareous ridges located in the Mersa Matruh area. These elucidated the fabric, timing, mineralogy, and chemistry of fluids responsible for ooids formation, and the subsequent meteoric diagenesis of the carbonate rocks.

GEOLOGICAL SETTING

The Mersa Matruh area, locate in the northwestern coastal zone of Egypt (Fig. 1), has a uniform topographic relief with Pleistocene calcareous ridges parallel to the coast and separated by flat-bottomed depressions. Ridges sediments are composed predominantly of well-sorted, medium-grained aragonitic ooids sands. Their internal geometry and sedimentary structures are characteristics of wind-formed-dune deposits. Several meters of horizontal stratification adjoining cross-stratification inclined up to 32° and convex towards the top are present.

In the study area, there are three calcareous ridges of late Lower to Middle Pleistocene in age (Zeuner, 1952, Shukri et al., 1956). Samples were collected from the first (coastal, younger ridge) and second (inland, older ridges). Sediments in both ridges show texturally distinct ooids and cements, as well as whole-rock geochemistry, and Sr and stable isotope data. Some of these data may suggest that calcite cements are formed in non-diluted pore-water under relatively high rock/water ratios.

Fig. 1: Generalized geologic map of Mersa Matruh area, Egypt.

MATERIAL AND METHODS

In order to investigate the possible interaction of meteoric water with the oolitic calcareous rocks, a sampling scheme was chosen which traverses ridges and extends laterally from coastline towards table land (old ridge). Forty representative samples from both ridges were collected for microfabric, petrographic and geochemical analyses.

Polished thin-sections were prepared and examined by standard optical microscopy and cathodoluminescent petrography. Chips and polished thin-sections (etched by 50% glacial acetic acid) of selected samples were coated with a thin layer of gold and examined with the scanning electron microscope. Sample powder was X-rayed to ensure mineral purity prior to chemical and isotopic analyses. Strontium contents for the same powders were determined by atomic absorption spectrophotometry.

Texturally distinct ooids and cements, as well as whole rocks, were sampled for oxygen and carbon isotope analysis. Ooids and cements of twenty samples (ten from each ridge) were manually separated under a binocular microscope. Sample powder was then roasted under vacuum for 1h at 380°C for the cements and at 100°C for the whole rock and ooids. The difference in roasting temperature is to eliminate any possibility of conversion of aragonite to calcite. After
roasting, samples were treated with anhydrous phosphoric acid at 50°C in an in-line extraction system connected to the inlet of a VG 602 E Micromass ratio mass spectrometer. Isotope enrichments are corrected for $^{17}O$ contributions and are reported relative to the PDB carbonate standard (Craig, 1957). Precision of analysis was 0.09‰ for oxygen and 0.07‰ for carbon based on daily analysis of NBS-20 analyzed as an unknown carbonate powder.

RESULTS AND DISCUSSION

Carbonate mineralogy

In the whole rock samples, aragonite and low-Mg calcite are the only carbonate minerals detected in measurable amounts (Fig. 2). The aragonite contents of the coastal ridge range from 99% to 94%, with the lowest values in the inland ridge (Fig. 3). Moreover, all ooids are composed of aragonite, and the cement consists of low-Mg calcite.

Petrography

In the Mersa Matruh area, an important lithic feature is the variable preservation of primary ooids fabric from the coastal to the inland ridges. In the coastal ridge, well developed ooids are easily identified; whereas, samples from the adjacent inland ridge exhibit a partial loss of the primary ooids fabric. More striking is the variation of calcite cement (Fig. 4). The amount of calcite cement, as determined by X-ray diffraction, ranges from 15% to 26% in the inland ridge; whereas, the coastal ridge contains ~ 5% (Fig. 3).

Compositonally, modern ooids may consist of low-Mg calcite, high-Mg calcite, and aragonite with more than one phase commonly occurring within an individual cortex (Land et al., 1979; Medwedeff and Wilkinson, 1983). However normal marine ooids are composed of aragonite (Newell et al., 1960; Purdy, 1963; Friedman et al., 1973); calcite ooids are much less abundant in modern environments (Popp and Wilkinson, 1983). Mechanisms invoked to explain the mineralogy of ooids are highly dependent on Mg/Ca ratio, hydrodynamic parameters (Given and Wilkinson, 1985), and the tectonically induced changes in $PCO_2$ (Mackanzie And Pigott, 1981). The Mg/Ca ratios of seawater during Pleistocene time were favoring formation of aragonitic ooids (Given and Wilkinson, 1985).
Pleistocene calcareous ridges, Egypt

Fig. 4: SEM photomicrographs of the Pleistocene carbonate rocks. Samples were sectioned, polished, and etched by 50% glacial acetic acid. A- Coastal ridge. B- Inland Ridge. The amount of cement in the inland ridge is more than that in the coastal ridge.

Geochemistry

Strontium

Strontium contents of the Pleistocene calcareous ridges are positively correlated with the aragonite content (Fig.6). The concentration of Sr in calcite cements can be related to the composition of the precipitating solution through the partition coefficient (D)

\[(\text{Sr}/\text{Ca})_{\text{calcite}} = D_{\text{Sr}} \times (\text{Sr}/\text{Ca})_{\text{fluid}}\]

The partition coefficients for Sr in calcite vary according to temperature, ion concentrations, and rate of precipitation (Lorens, 1981; Pingitore and Eastman, 1986; Morse and Bender, 1990). Calculated partition coefficients for Sr in calcite range from 0.03 (Lorens, 1981) to 0.14 (Kinsman, 1969); whereas, a partition coefficient of 0.055 is probably a reasonable estimate for precipitation of Sr into low-Mg calcite cement in natural near-surface system (Budd and Land, 1990).

In the present study, the high Sr contents of the aragonitic ooids (0.200 to 10,000 ppm; Table 1) are consistent with the Sr contents of modern aragonitic ooids from Bahama and Baffin Bay (Halley and Harris, 1979, Land et al., 1979). These high Sr values are in accord with the theoretical prediction for marine aragonitic ooids, and indicate their direct precipitation from ambient seawater.

The low-Mg calcite has significantly higher Sr contents (4,000 to 6,000 ppm) than those of most meteoric calcite cements. In view of the value of $D_{\text{Sr, calcite}}$, it is unlikely that the low-Mg calcite cement retained ~ 50% of Sr contents in the aragonitic ooids. The observed Sr concentrations are high enough even to be comparable to the equilibrium value for marine water calcite. Utilizing the partition coefficient of Kinsman (1969), calcite in equilibrium with seawater should contain about 1100 ppm Sr. The concentration of Sr in meteoric calcite depends mostly on the Sr partition coefficient and its concentration in the meteoric water. Meteoric water which is commonly considered in the transformation of metastable CaCO$_3$ (aragonite and/or high-Mg calcite) to low-Mg calcite, is generally low in Sr content. Due to this fact and that the Sr partition coefficient is  $D_{\text{Sr, calcite}}$ <1, the meteoric calcite should show low concentrations of Sr. Budd and Land (1990) and Saller and Moore (1991) found very high Sr concentrations (600 to 3,700 ppm) in meteoric calcite cements precipitated in the Holocene and Pleistocene aragonitic ooids. Given the fact that aragonite dissolution is the dominant source of aqueous Sr, a large quantity of aragonitic ooids must have been dissolved into the aqueous system to account for the enhanced concentration of Sr in the low-Mg calcite cements of the Pleistocene calcareous ridges.

Stable oxygen and carbon isotopes

In order to infer cementation conditions in the Pleistocene calcareous ridges, the oxygen and carbon isotopic composition of the whole rocks, ooids (aragonite), and cements (low-Mg calcite) have been determined (Fig 7). These isotopic data can be explained by the general model for early near surface meteoric diagenesis (Land, 1970; Wagner, 1983; James and Choquette, 1984).

Results of oxygen and carbon stable isotope analyses are summarized in Table 1. Stable oxygen isotope ratios are generally enriched in the whole rocks (+0.6 to +0.5% PDB) and the ooids (+0.6 to +0.3% PDB) and depleted in the calcite cements. The Coastal ridge calcite cements $\delta^{18}O$ values (average -1.0% PDB) are more enriched than those of the inland ridge (average -1.7% PDB). So the transition from the coastal ridge into the inland ridge is marked by a pronounced 0.7 per mil shift in $\delta^{18}O$ of the calcite cement towards the more depleted. The $\delta^{13}C$ values of the whole rocks and ooids are identical for both ridges (average +4.5% PDB) and are close to their calcite cement values (+4.1 to +3.8% PDB).

The $\delta^{18}O$ values of carbonate rocks are sensitive indicators of alteration (Brand and Veizer, 1981). The studied ooids show a limited range of $\delta^{18}O$ values from -0.6 to +0.3% PDB. The values are similar to modern ooids and suggest that the present isotopic compositions can reflect equilibrium with marine water. In contrast, the calcite cements have noticeably lower $\delta^{18}O$ values (-1.0 to -1.7% PDB, Table 1). These low $\delta^{18}O$
Fig. 5: SEM photomicrographs of cementation and dissolution features. A - Well rounded ooid with visible nuclei, concentric laminae and calcite cement. B - Enlargement of low-Mg-calcite cement crystals. C - Partly dissolved ooid nuclei, the interparticle pores are partially filled with calcite cement spar. D - Calcite cement crystals are oriented perpendicular to the ooid surface. E - SEM photomicrograph of strongly etched ooid showing individual aragonite lamina. F - Microboring dissolution in ooid cortex.
values are most likely the result of alteration by meteoric water. In north Jamaica, diagenetic calcite formed in the Pleistocene marine sediments are in isotopic equilibrium with unevaporated meteoric water with \( \delta^{18}O \) values between -3.2 and -2.3‰ (Land and Epstein, 1970). In the study area, evaporation is significant, therefore slightly evaporated meteoric water, enriched in \( \delta^{18}O \) could precipitate calcite cements different from the meteoric calcite. This indicates that precipitation of low-Mg calcite cements was induced by evolution of \( \text{CO}_2 \) from the dissolution of aragonitic ooids. This evolution was, in turn, influenced by the degree of evaporation which occurred in the near-surface environment.

It is significant that a straight mixing line can be constructed between the \( \delta^{18}O \) values of aragonitic ooids (marine end member) and those of low-Mg calcite cements (meteoric end member). The whole rock \( \delta^{18}O \) values of the studied carbonates would be the weighted average of the \( \delta^{18}O \) values of the primary marine ooids and \( \delta^{18}O \) values of the calcite cements. Therefore, the \( \delta^{18}O \) values of the whole rock should fall on the mixing line between the values of the two end members (Figs. 8, 9 and 10). However, the \( \delta^{18}O \) values were shifted away from the mixing line. This might indicate the presence of more than two end members, a fact which is not clearly confirmed by the petrographic examination of the rocks.

The \( \delta^{18}O \) values of the whole rock for both ridges are identical (Table 1) and display no systematic variations within each ridge. This indicates that the conventional whole rock analysis can not be applied successfully to provide such variations and trends of alteration by meteoric water.

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**Table 1**

Average aragonitic content, oxygen and carbon isotopic compositions, and Sr elemental data of samples from the Pleistocene calcareous ridges.

<table>
<thead>
<tr>
<th></th>
<th>n</th>
<th>Aragonite %</th>
<th>( \delta^{18}O ) (PDB)</th>
<th>( \delta^{13}C ) (PDB)</th>
<th>Sr (PPM)</th>
</tr>
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<tbody>
<tr>
<td>Coastal</td>
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<td></td>
<td></td>
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<tr>
<td>Ridge</td>
<td></td>
<td></td>
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</tr>
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<td>(1)</td>
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<td>97</td>
<td>+0.6</td>
<td>+4.6</td>
<td>9320</td>
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<tr>
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<td>98</td>
<td>+0.6</td>
<td>+4.5</td>
<td>10010</td>
</tr>
<tr>
<td>Cements</td>
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<td>10</td>
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<td>+4.1</td>
<td>5970</td>
</tr>
<tr>
<td>Inland</td>
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<td></td>
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<tr>
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<td>11</td>
<td>-1.7</td>
<td>+3.8</td>
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The \( \delta^{18}O \) values of marine aragonitic ooids (+0.3‰ PDB) were used to calculate ambient water temperature using Grossman and Ku's equation (1986), assuming present-day seawater values of \( \delta^{18}O \) (SMOW):

\[
T(\degree C) = 20.6 - 4.34 (\delta^{18}O_A - \delta W)
\]

where \( \delta^{18}O_A \) is the measured oxygen isotopic ratio of the aragonitic ooids relatives to PDB; and \( \delta W \) is the oxygen isotope ratio of the ambient seawater relative to SMOW. This calculation gives an ambient temperature of \(-20\degree C\) at the time of ooid formation.
CONCLUSIONS

The petrographic observations together with Sr and stable isotope data of rocks from the Pleistocene calcareous ridges present evidences for an early near-surface meteoric diagenesis. The diagenetic features within these rocks shows indications of early aragonitic ooids dissolution and a distinctive phase of low-Mg calcite cementation. There is no evidence of recrystallization by crystal boundary migration or replacement during the transformation process.

The stable isotopic data and Sr contents may suggest that the calcite cements were formed in non-diluted pore-water and at relatively high rock-water ratios. The aragonite ooids dissolution must account for the high Sr concentration and enrichment of $^{18}$O and $^{13}$C of pore-water which formed the calcite cements. Meanwhile, the oxygen reservoir might have been influenced by evaporation (enriched $^{18}$O) which occurred in the near surface environment.

The $^{13}$C values of the aragonite ooids (+4.5%o PDB) are similar to those of low-Mg calcite cements (+4.1 to 3.8%o PDB). This suggests a localized transformation in a system that was closed with respect to carbon with no introduction of carbon from a non-aragonite source. Carbon from organic respiration still would affect the carbon isotopic signature.

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REFERENCES


