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Abundant Sr-rich aragonite in eastern Mediterranean sapropel S1: Diagenetic vs. detrital/biogenic origin

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Abstract

$CaCO_3$ contents in eastern Mediterranean sapropels are generally lower than in the enclosing marl sediments. In sediments of a transect from ~650 to 2100 m water depth at the Sirte continental slope, the opposite feature was observed. Although the increased Sr/Ca ratios observed in these sediments agree with such feature observed in other eastern Mediterranean S1 sediments, their absolute magnitude is much higher. The enhanced Sr/Ca ratio in these sediments is associated with their aragonite content, which for the Sirte transect reaches levels of up to ~40 wt.%. The aragonite content and Sr/Ca ratios in the S1 sediments of this transect decrease with increasing water depth and decrease with distance to the African coast for all eastern Mediterranean cores. In view of the lack of a coherent relationship with sedimentary reduced sulphur contents and porosity, and considering the major amount of aragonite found specifically in the sediments of the Sirte transect, authigenic precipitation can contribute only a limited fraction at most. SEM observation and electron-microprobe analyses showed that the needles and needle clusters are morphologically aragonite, contain the highest Sr/Ca ratio, and are similar to skeleton fragments of the green alga *Halimeda*. Consequently, a detrital/biogenic source is the likely mechanism for the major part of the aragonite enrichments found in S1 sediments. Possibly, offshore-directed surface water flows related to wind stress and/or enhanced run-off (consistent with enhanced precipitation during sapropel S1) may have assisted in the transport of near-coastal aragonitic organisms to more coast-remote areas.

Keywords: Sapropel S1; Eastern Mediterranean; Aragonite; Inorganic geochemistry; Sr/Ca ratio

1. Introduction

The export of carbon occurs both as precipitation of calcium carbonate by pelagic organisms and by photosynthesis and formation of organic carbon (e.g., Jahnke, 1996; Mucci et al., 2000). Generally, only a small proportion of the C_{org} is accumulated on the sea floor, as most of it is converted back to CO_2 in the water column due to bacterial oxidation. Enhanced preservation of C_{org} in the sedimentary record may point to dysoxic or anoxic conditions in the water column (e.g., Arthur and Dean, 1998; Sachs and Repta, 1999) and/or increased productivity (e.g., Calvert and Pedersen, 1992; Rohling and Hilgen, 1991). However, on a global scale, a variable portion of inorganic carbon as $CaCO_3$ reaches the sea floor depending on the saturation state of the water column with respect to calcium carbonate.

The Holocene sediment record of the eastern Mediterranean Sea is characterized by C_{org}-poor sediments (0.1–0.2 wt.%; e.g., van Santvoort et al., 1996, 2002)

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that are interrupted by a distinct interval of C_{org}-rich sediments (>~2 wt.%): the so-called sapropel S1. This sapropel formed at the time of maximum northern hemisphere summer insolation when the intensity of the African monsoon was enhanced (e.g., Rossignol-Strick, 1985). Numerous authors have reported on the humid sapropel intervals in general and the S1 specifically (e.g., Rossignol-Strick, 1983; Gasse, 2000) suggesting a major flooding of water from Africa (Rossignol-Strick et al., 1982). The relatively light ocean surface $\delta^{18}O$ values of *Globigerinoides ruber* (*G. ruber*) during S1 (e.g., Fontugne and Calvert, 1992) as well as the decreased Ti/Al ratio (e.g., Nijenhuis et al., 2001) all support enhanced precipitation. Additionally, Meier et al. (2004) reported a decrease in the halophylic calcareous dinoflagellate species *Lebessphaera urania* deducing that salinity of surface water was definitely decreased being induced by freshwater input.

The C_{org}-poor sediments enclosing the S1 horizon are a consequence of intensive remineralization of C_{org} in a well-oxygenated water column, like that of the present oligotrophic eastern Mediterranean (Béthoux, 1993; Roether and Well, 2001). However, C_{org}-poor and light brown sediments directly overlying the S1 unit are in origin part of the S1. The loss of C_{org} in these sediments is a secondary feature induced by post-depositional oxidation that the upper S1 unit has been experienced since their formation (De Lange et al., 1989; Higgs et al., 1994; Thomson et al., 1995, 1999; van Santvoort et al., 1996). Although the original C_{org} signal is oxidized, it is possible to estimate the full primary S1 horizon as the biogenic Ba that accompanies the settling C_{org} is preserved (Thomson et al., 1995, 1999; van Santvoort et al, 1996). The characteristic geochemical signatures evoked by this post-depositional progressing oxidation front, as the Mn double-peak one of the most conspicuous, have been described in earlier publications (Thomson et al., 1995; van Santvoort et al., 1996; Mercone et al., 2000).

In general, the S1 sediments have a lower total carbonate content than the C_{org}-poor nannofossil marls that enclose them. These generally lower carbonate contents within sapropel sediments has been observed for most sapropels from Pliocene to Holocene. The origin of this difference has been suggested to be due to dilution, dissolution, or dominant opal rather than carbonate production during sapropel formation (van Os et al., 1994; Aksu et al., 1995; Nijenhuis et al., 1996; Schenau et al., 1999; Kemp et al., 2000; Corselli et al., 2002). In contrast, Weldeab et al. (2003) reported an increase in carbonate contents for sapropel S6 sediments and explained this by a favored dominance of non-opportunistic calcareous plankton due to moderate productivity increase.

The general $CaCO_3$ record usually mainly consists of three mineral polymorphs, (i) low-Mg calcite that is generally formed by surface dwelling organisms and commonly the only form that is preserved in deepwater sediments, (ii) aragonite, and (iii) high-Mg calcite. The latter two are generally not typically found in deep-ocean sediments because they tend to dissolve before or after deposition since oceanic deepwater is strongly undersaturated with respect to aragonite and high-Mg calcite (Berner and Honjo, 1981; Fabry and Deuser, 1991). However, eastern Mediterranean sediments do contain these more soluble $CaCO_3$ polymorphs (Rutten, 2001). In open-ocean areas, aragonite and high-Mg calcite are found predominantly in sediments at shallow water depth and/or at low latitudes (Wilkinson and Given, 1986, Tucker and Wright, 1990). The high-Mg calcite found in the marls above and below the S1 unit has been interpreted as diagenetic (Milliman and Müller, 1973; Aksu et al., 1995; Calvert and Fontugne, 2001).

Thomson et al. (2004) found that eastern Mediterranean sapropel S1 shows high Sr/Ca ratios and explained the Sr enrichment by the enrichment of aragonite because samples with the highest aragonite content also had the highest Sr contents. They proposed three potential mechanisms that could lead to higher aragonite contents in S1 sediments: (i) aragonite production in surface waters, (ii) detrital aragonite, and (iii) diagenetic aragonite formation due to sulphate reduction. In view of the good correlation between the amount of sulphur, the Sr/Ca ratio, and the aragonite content, the latter mechanism was suggested as the most likely principal source for the aragonite enrichment. At the same time, they state not to be able to fully exclude a potential detrital source.

The present study particularly investigates Sirte continental slope sediments that have Sr/Ca ratios and aragonite enrichments that are much higher than ever reported for deep eastern Mediterranean sediments. Since a detrital origin of aragonite in S1 sediments has eminent implications considering the paleoclimatic and oceanographic reconstruction of this period, it is important to distinguish between a diagenetic and a detrital/biogenic origin.

2. Methods

The investigated box core transect of BP15 (32.778°N, 19.876°E), BP18 (33.100°N, 19.733°E), and BP10 (33.222°N, 19.767°E) was recovered north-