



Geochemical evidence for high-resolution variations during deposition of the Holocene S1 sapropel on the Cretan Ridge, Eastern Mediterranean

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ABSTRACT

Major and minor element distributions and solid phase phosphorus contents were measured in a sediment core from the Cretan Ridge that contains the Holocene S1 sapropel. Micro-XRF ultra-high resolution analysis reveals multiple Mn peaks in the oxidized upper portion of the sapropel, which implies either a non-steady-state upward remobilization of Mn or not constant downward diffusion of bottom water oxygen. Sequential extraction allowed the identification of different phosphorus phases. Detrital phosphorus increases in the sapropel layer, suggesting enhanced delivery from land during sapropel deposition. Higher organic carbon to organic phosphorus ratios in the sapropel indicate enhanced regeneration of phosphorus relative to carbon under low-oxygen conditions. Fourier analysis on the ultra-high resolution XRF data reveals frequencies that are provisionally assigned to millennial to decennial solar cycles. Although these cycles have been reported from several continental and marine archives, they have never been documented from Sapropel S1 in the Eastern Mediterranean.

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1. Introduction

The Eastern Mediterranean Sea is characterized by the occurrence of organic matter-rich layers, termed sapropels. According to the original definition by Kidd et al. (1978), sapropels are well-delimited layers within open marine sediments, with thickness >1 cm and organic carbon content >2%. The relatively high organic carbon content of a sapropel is due to the combination of enhanced supply and limited degradation of organic matter at the sediment–water boundary, which is water-depth dependent (Murat and Got, 2000). Thereby, the difference between the organic carbon content of a sapropel and that of the surrounding sediments seems to be a more suitable parameter to define these layers (Murat, 1991; Ariztegui et al., 2000).

Among the various processes that have been invoked to explain sapropel formation (see Rohling, 1994 for a review), the “stagnation/anoxia” and the “increased productivity” models are the most discussed. According to the stagnation/anoxia model, anoxic bottom conditions are caused by a strong stratification of the water column that prevents vertical mixing and oxygen supply to the bottom waters. Different explanations have been proposed for the origin of this stratification: 1) Eurasian ice-sheet melt water entering the Mediterranean Sea (Olausson, 1961; Ryan, 1972; Aksu et al., 1995);

2) increased Nile river runoff linked to the periodic enhancement of the African–Asian monsoons (Rossignol-Strick 1983, 1985); 3) increased rainfalls and river discharge along the northern part of the Eastern Mediterranean Sea (Cramp et al., 1988; Rohling and Hilgen, 1991).

In the “increased productivity” model, sapropel deposition is linked to enhanced organic matter flux (Calvert, 1983; Calvert et al., 1992), since the present production of organic matter in the eastern Mediterranean cannot account for the high values of organic carbon (TOC) characterizing these layers (Calvert, 1983).

According to other authors (Castradori, 1993; Rohling, 1994; Emeis et al., 1998; Emeis et al., 2000), an increase of nutrient input via river runoff could have caused enhanced primary production and also promoted the stratification of the water column, coupling the two models. A significant increase of productivity at times of sapropel deposition is also revealed by paleo-productivity proxies, as Ba and marine barite concentration (e.g., Thomson et al., 1995, 1999; Martinez-Ruiz et al., 2000, 2003; Gallego-Torres et al., 2007). Enhanced productivity has also been explained with a radical change in the Mediterranean Sea circulation, from the modern anti-estuarine to an estuarine circulation (Sarmiento et al., 1988; Howell and Thunell, 1992). Results of recent modeling studies on thermohaline circulation suggest that a weakening of the present-day anti-estuarine circulation can lead to the deposition of enough organic carbon to account, at least, for the formation of the youngest sapropel S1 (Myers et al., 2000; Stratford et al., 2000). Uncertainties still exist regarding the

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extension of the anoxic/dysoxic layer in the water column; this layer has been described as a large water mass extending below the mixed layer (Murat and Got, 2000; Stratford et al., 2000), as well as an “anoxic blanket” above the sediment/water interface (Casford et al., 2003). More recently, Bianchi et al. (2006) suggest that a modified thermohaline circulation supplying oxygen only to the first 500 m of the water column may be responsible for the development of an anoxic blanket at the sea-floor, when coupled with higher productivity in the euphotic zone.

Regardless of the mechanism that led to their formation, sapropel occurrence is cyclic and is thought to be linked to minima in the precession cycle, corresponding to Northern Hemisphere summer insolation maxima, with a periodicity of about 21 kyr (Rossignol-Strick, 1983, 1985; Hilgen, 1991; Lourens et al., 1996).

In this research, we present a high-resolution geochemical study of sapropel S1, since any change in environmental or climatic conditions is reflected in major and minor element abundances (e.g., Wehausen and Brumsack, 1998). Furthermore, because our proxy data offer a very detailed and continuous record, the identification of high-order cyclicities is attempted.

2. Materials and methods

Gravity core SIN97-01GC was collected on the morphological high between Crete and the Peloponnese (35°49′07″ N, 22°42′02″ E; water depth 933 m) during the 15/97 cruise of R/V *Urania* (Fig. 1). Sampling for this study was limited to the uppermost part of the core (section 1; 0.0–68.0 cm bsf), since it contains a thick sapropel S1 overlaid by a few centimeters-thick oxidized interval, both interbedded in a hemipelagic muddy succession.

Sediment samples of 0.5 cm thickness for geochemical analyses were taken along the core at 3 cm spacing; a contiguous sampling was also performed at any change in sediment type or color. Sediments were then dried at room temperature and split into sub-samples. An aliquot of the material was gently ground in an agate mortar and passed through a sediment sieve (<125 µm), with the minimal extent of grinding necessary to achieve this size.

Table 1

Results of AMS ^{14}C dating on planktonic foraminifers. Calibration using OxCal 3.10 (Bronk Ramsey, 2005)

Lab code	Depth (cm)	Material	^{14}C age	Calibrated age
			(yr BP)	(yr BP)
ETH-34228	1.0–2.0	Mixed planktonic foram	1050±55	610±70
ETH-34229	22.0–22.5	<i>Globigerinoides ruber</i>	6165±80	6570±180
ETH-34230	44.5–45.5	<i>Globigerinoides ruber</i>	11910±110	13405±235
ETH-34231	67.5–68.0	<i>Globigerinoides ruber</i>	17200±160	19925±375

A reservoir effect of 400 years was subtracted.

2.1. Organic matter

Organic matter characterization was performed at the University of Neuchâtel on about 80 mg of ground and sieved sediment with a Rock-Eval 6, using the standard whole rock pyrolysis method (Espitalié et al., 1986).

2.2. Phosphorus

Phosphorus was extracted from the dried sediment after grinding to <125 µm. A 5-step sequential extraction technique was used to distinguish among different phosphorus sedimentary phases (SEDEX method; Ruttenberg, 1992; Tamburini et al., 2002). Solid phases were progressively dissolved by using a series of extractants, each chosen in order to extract phosphorus associated with well defined sedimentary components: (1) loosely-bound P adsorbed on mineral surfaces, (2) iron and manganese oxy-hydroxides (referred in the text as CDB-P), (3) authigenic apatite, (4) detrital material (igneous, metamorphic and “aged” authigenic apatite), and (5) organic matter. The obtained sample solutions were diluted in milli-Q water and a color developing agent was added to the solutions following the ascorbic acid method for phosphate (Eaton et al., 1995). All the concentrations were then measured using a Perkin Elmer UV/Vis Spectrophotometer Lambda 10 at the GEA lab (University of Neuchâtel).

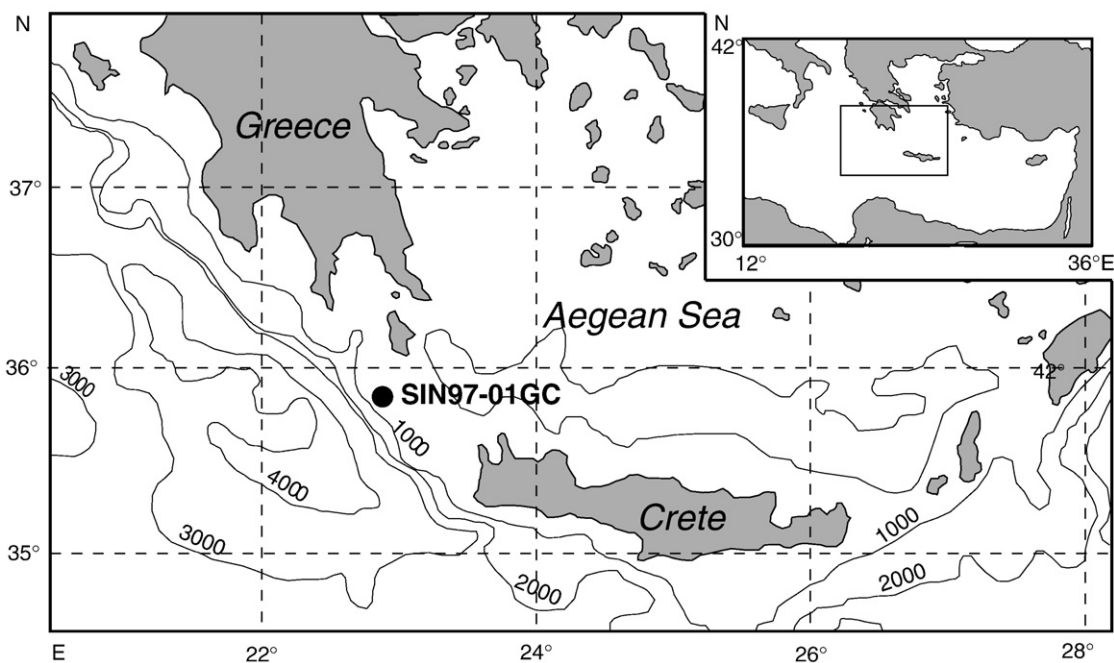


Fig. 1. Location map of core SIN97-01GC.

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