A LATE QUATERNARY STRATIGRAPHIC FRAMEWORK FOR EASTERN MEDITERRANEAN SAPROPEL S1 BASED ON AMS ¹⁴C DATES AND STABLE OXYGEN ISOTOPES

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ABSTRACT. Detailed stable oxygen isotope analyses coupled with AMS ¹⁴C measurements on an eastern Mediterranean sapropel S1 sequence indicate that adverse bottom conditions persisted for ca 8000 years. AMS dates on additional sequences show that complete bottom anoxia lasted for 300-800 years. The S1 event is not synchronous throughout the eastern Mediterranean, but started earlier in the deeper parts of the basin.

INTRODUCTION

Deep-sea cores raised from the eastern Mediterranean Sea often contain dark-colored organic rich intervals, the so-called sapropels. During the last 400,000 years, 12 such layers were deposited, numbered in stratigraphic order S12-S1 (Cita *et al* 1977). The youngest sapropel S1 is of basal Holocene age, deposited at 9000-7000 BP, corresponding to the Flandrian transgression (Cita *et al* 1982) and to isotopic Stage 1 of Emiliani (1955) and later authors. The driving mechanism for sapropel formation is the occurrence of a low salinity surface layer, causing density stratification resulting in bottom anoxia. A complete sapropel sequence consists of gray protosapropel (PS), indicative of increasing near-bottom oxygen deficiency, black sapropel proper, signaling complete bottom anoxia, and of a brown/reddish laminated oxidized layer. This upper part of the sequence is often considered indicative of a return to oxic conditions.

Explanations for the provenience of the low-salinity surface have been sought in excessive runoff of major rivers such as the Nile and the Po (Rossignol-Strick *et al* 1982) or alternatively, overflow of the Black Sea (Olausson 1961; Ryan 1972; Thunell, Williams & Kennett 1977) or changes in the precipitation/evaporation balance. Increased productivity was proposed to be the driving mechanism by Calvert (1983). Anastasakis and Stanley (1986) present a good overview of current theories.

We present here a detailed chronostratigraphic framework for the sapropel S1 event in boxcore T87/26B taken in the southern part of the Ionian Basin (Fig 1), based on oxygen isotope stratigraphy and AMS measurements on planktonic foraminifera and pteropods. We consider the duration of the event and the status of the "oxidized layer." We investigate the supposed synchroneity of sapropel S1 in the eastern Mediterranean Basin in additional widely spaced box cores from the Ionian and Levantine Basins.

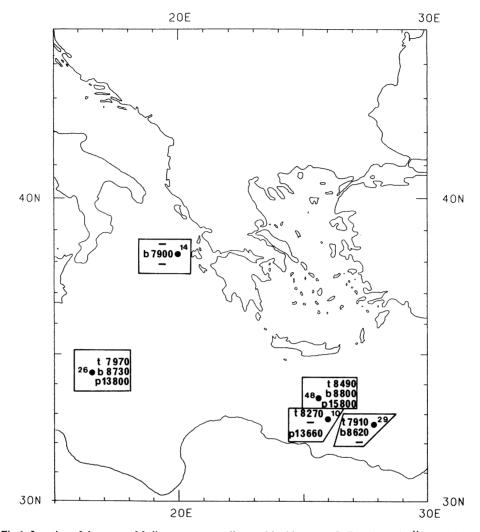


Fig 1. Location of the eastern Mediterranean cores discussed in this paper. Indicated are the ¹⁴C ages for the most important lithologic boundaries in each core. P = base protosapropel S1; B = base sapropel S1; T = top sapropel S1.

Eastern Mediterranean deep-sea core samples discussed in the text						
Station no.	Lat	Long	Depth (m)	Recovery (cm)		
T87/14B*	38°34′N	19°54′E	1999	42		
T87/26B	34°44′N	16°48′E	2415	48		
T83/10B	33°25′N	26°26′E	2445	36		
T83/48P**	33°50′N	25°59′E	2724	186		
T83/29B	33°38′N	28°26′E	3295	35		

	ТА	BLE 1	l				
Eastern Mediterranean	deep-sea	core	samples	discussed	in	the	text

*B = box core

**P = piston core

MATERIAL AND METHODS

The material we describe here derives from 4 box cores and 1 piston core collected in the eastern Mediterranean during Cruises T83 and T87 of the R/V Tyro. Sample locations, water depth and core recovery are shown in Table 1 and Figure 1. Only Cores T83/48P and T87/26B yielded a sapropelic sequence which could be fully sampled; too shallow penetration of Cores T87/14B and T83/29B resulted in the absence of the protosapropel base, whereas either base or top were too fine-grained to allow handpicking of foraminifera in Cores T83/10B and T87/14B. For the AMS measurements, planktonic foraminifera and/or pteropods were picked from the washed residues of the remaining samples. Preparation of the calcitic/aragonitic tests followed standard procedures (Hut, Ostlund & van der Borg 1986). During times of (proto)sapropel deposition, the input of relatively young terrestrial organic matter into the marine realm will lower the reservoir age drastically. As this process is difficult to quantify, we decided not to correct for reservoir age.

Core T87/26, 51cm long, was sampled in detail; 41 samples were taken, averaging 1.2cm intervals. Oxygen isotope analyses were carried out on the $250-400\mu$ m fraction of the surfacedwelling planktonic foraminifer, *Globigerinoides ruber*. Measurements were performed offline on a Finnigan Mat 251 mass spectrometer. The standard deviation of an internal standard during the period of measurements is 0.05%.

We made detailed micropaleontological studies on this core, and will present the results elsewhere along with geochemical data (Troelstra, Ganssen & Klaver, ms in preparation).

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Core T87/26B is 51cm long and presents a typical sapropel S1 sequence, schematically drawn in Figure 2. Based on the characteristic gray color of the sediment, the complete 36–51cm section was described onboard as "proto-sapropel"; however, x-ray photography shows a vague boundary at 43cm which other authors might consider the proper base of the protosapropel. The laminated sapropel (29–36cm) has sharply defined boundaries and is overlain by the oxidized layer, consisting of a brown/white laminated section and a wavy manganese-rich part with an indistinct upper boundary.

We treated 13 samples from this core for organic carbon content; the graph in Figure 2 shows a distinct increase during the upper part of the protosapropel and in the sapropel proper, values exceeding the 2% necessary for sapropel designation (Kidd, Cita & Ryan 1978). We sampled all lithologic boundaries for AMS ¹⁴C analysis and took additional samples at regular intervals or where we observed important shifts in the δ^{18} O curve. Results are given in Figure 2.

The duration of the S1 event depends very much on the position of the protosapropel base. To evaluate whether this level is located at 51 (or even lower; not recovered) or at 43 cm, other cores (T83/48P and T83/10B) containing a distinct protosapropel were also sampled for AMS dating. They revealed ages of 15,800 and 13,660 BP, respectively, indicating that our onboard description of core T87/26B was correct, and that the base of the core at 51cm is part of the protosapropel. Table 2 shows the basal protosapropelic ages and basal/top sapropelic ages obtained on these additional sequences.

The stable isotope curve (Fig 2) has an amplitude of nearly 3‰. We interpret this as caused mainly by salinity fluctuations (Ganssen & Troelstra 1987). Between 13,800 and 10,900 BP, a gradual decrease of the values of ca 0.5‰ can be observed. However, the onset of glacial melting (Termination 1A) normally centered near 13,000 BP (Berger 1990) and reflecting the first step of deglaciation, is not seen in this interval. A clear shift of nearly 1‰ to lower values is recorded

shortly after 10,900 BP, between 42 and 41cm core depth, possibly reflecting the final stage of Termination 1A, associated with the Pleistocene/Holocene transition. Unfortunately, sediments in the core are not older than 13,800 BP. Hence, we cannot prove possibly older deglaciation steps.

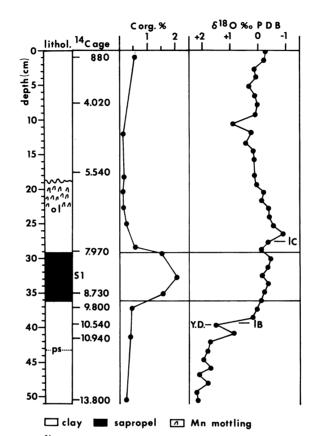


Fig 2. Simplified lithology, ¹⁴C age, organic carbon content and oxygen isotope data of eastern Mediterranean core T87/26B. ¹⁴C dates in years BP. Isotope data from *Globigerinoides ruber*. PS = protosapropel; OL = oxidized layer; Terminations 1B and 1C and the Younger Dryas cold spell (Y D) are also indicated.

Between 10,700 and 10,500 BP, the Younger Dryas period is clearly reflected, followed immediately by the second pulse of deglaciation (Termination 1B), ending at 10,000 BP and representing the earliest Holocene. At this point, the low-salinity layer was firmly established, but it took another 1000 years before true sapropelic sediments started to accumulate. Shortly after 8000 BP, another shift to lower values (28-26cm) is recorded, here interpreted as the third and last pulse of deglaciation, Termination 1C.

Between 26 and 18cm, a gradual increase of 1‰ is seen, reflecting the gradual return to normal Mediterranean salinities between ca 7000 and 5800 BP. Isotopic variations in the upper 15cm of the core may reflect minor late Holocene salinity/temperature fluctuations.

Combined AMS ¹⁴C dates and oxygen isotope values thus provide a firm chronostratigraphic framework for Core T87/26B.

Station	UtC	Position in		δ ¹³ C**			
no.	no.*	core (cm)	Т	уре	%0	Age BP [†]	
T87/14B	672	40	BS‡	Forams	0.63	7900 ± 130	
T87/26B	1231	0-2	ooze	Forams		880 ± 50	
	1232	7-8	ooze	Forams		4020 ± 70	
	1233	17-18	ooze	Forams		5540 ± 80	
	809	28.5-29.5	TS [‡]	Orbulina	1.89	7970 ± 110	
	805	34.5-35.5	BS	Pteropods	0.65	8730 ± 150	
	807	36.5-37.5	TPS	Forams	1.61	9800 ± 130	
	1234	39-40	ooze	Forams		$10,540 \pm 100$	
	808	41-42	BPS*	Forams	1.08	$10,940 \pm 150$	
	806	50-51	?BPS	Forams	1.60	$13,800 \pm 300$	
T83/10B	813	22-23	TS	Forams/pter	1	8270 ± 200	
	812	35-36	BPS	pteropods	1	$13,660 \pm 190$	
T83/48P	713	32-33	TS	Forams	1.17	8490 ± 160	
	712	40-41	BS	Forams	1.23	8800 ± 200	
	711	57-58	BPS	Forams	1	$15,800 \pm 200$	
T83/29B	811	23-24	TS	Orbulina	1.52	7910 ± 110	
	810	27-28	BS	Orbulina	1	8620 ± 130	

 TABLE 2

 Inferred AMS dates of samples discussed in the text

*Utrecht Laboratory

** δ^{13} C values measured at the Geology Department, Utrecht

[†]Age in years Before Present from ¹⁴C activity after normalization to $\delta 13 = -25\%$. No correction applied for reservoir age.

^{*}BS = Base sapropel S1

[#]TS = Top sapropel S1

TPS = Top protosapropel S1

*BPS = Base protosapropel S1

DISCUSSION

Up till now, datings on eastern Mediterranean sapropel S1 sequences were mainly made with the conventional (organic carbon) ¹⁴C method involving large samples. Because of the limited amount of material retrieved by box- and piston-coring, this often involved substantial quantities of a sapropel sequence, thus limiting an accurate determination of the various steps leading to bottom anoxia and the subsequent return to oxic conditions. This accounts for the general age for S1 of 9000–7000 BP accepted by most authors.

Through our data, we can substantiate that conditions leading up to sapropel formation started ca 14,000 BP in Cores 10B and 26B and even earlier, ca 16,000 BP, in core T83/48P. The same picture arises from the onset of bottom anoxia, the base of the sapropel. Ages become progressively younger with decreasing water depth (Table 2). This is in conflict with Anastasakis and Stanley (1986), who postulate that the S1 sequence is time transgressive, having started earlier in the eastern Levantine basin. In our opinion, the local bottom topography mainly determines the age of the onset of anoxic conditions, with older ages occurring in the deeper parts of the basin.

It is clear from Figure 1 that age differences also exist for the top of the sapropel. It is obvious, however, that conditions leading up to bottom anoxia lasted considerably longer (5000-7000 yrs) than the anoxic event itself, which lasted only 300-800 years.

Another question is whether the "oxidized layer" truly represents the return of oxic conditions. If we analyze the oxygen isotope curve, it appears that the influence of a low-salinity surface layer is still noticeable up to the 19cm level, eg, to the top of the Mn mottled section, which, by extrapolation of the age of 5540 BP at 17–18cm, has an age approximating 6000 BP. The laminated nature of the oxidized layer and its microfaunal content (Troelstra, Ganssen & Klaver, ms) further substantiate that this section still belongs to the sapropelic "abnormal" conditions. The peculiar brown/reddish color of the sediments is due to the upward migration and oxidation of Fe/Mn (Troelstra, Ganssen & Klaver, ms).

Adverse bottom conditions caused by density stratification in Core 26B (and consequently in the other cores) thus lasted for ca 8000 years, from 13,800-6000 BP. The same conclusion was tentatively reached by Anastasakis and Stanley (1986) by extrapolation of conventional ¹⁴C results, but is here substantiated by firm data. Even longer adverse conditions, starting ca 16,000 years BP are observed in Core 48P, taken on the sill between the presently anoxic Tyro Basin and the adjacent Kretheus Basin (Troelstra 1987).

CONCLUSION

It is clear that the onset of sapropel formation is caused by a complex interplay of parameters involving the following:

1. Melting of the ice caps on the Northern Hemisphere and the subsequent introduction of glacial meltwater in the Mediterranean starting ca 16,000 BP followed by re-introduction of isotopically lighter Atlantic water into the Mediterranean ca 14,000 BP (Vergnaud-Grazzini, Deveaux & Znaidi 1986; Buckley & Johnson 1988). Both factors influence the start of protosapropel deposition.

2. A further establishment of the low-salinity surface layer following the Younger Dryas "cold spell," centered ca 10,500 BP (Fig 2).

3. High runoff of the Nile River and increased precipitation from 9000 BP (Richie, Eyles & Haynes 1985) causing complete density stratification of the water column and leading to complete bottom anoxia.

4. Return to oxic conditions at 6000 BP, caused by the disappearance of the low-salinity surface. Aridification of northeastern Africa (Richie, Eyles & Haynes 1985) resulted in low river runoff (low sedimentation rates in the upper part of the core) and related low input of organic matter into the marine realm (very low benthic foraminiferal numbers). Around this time, the present Nile regime was established (Adamson *et al* 1980).

Our study proves the potential of multidisciplined high-resolution core studies. Berger (1990) states that termination 1C is hardly ever recorded in deep-sea cores, but this is obviously caused by a too-wide sample interval. The clear record of the Younger Dryas cold spell is also due to the continuous sampling procedure.

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REFERENCES

Adamson, DA, Gasse, F, Street, FA and Williams, MAJ 1980 Late Quaternary history of the Nile. Nature 288: 50-55.

Anastasakis, GC and Stanley, DJ 1986 Uppermost sapropel, eastern Mediterranean: Paleoceanography and Stagnation. National Geographic Research 2(2): 179-197.

Berger, WH 1990 The Younger Dryas cold spell, a quest for causes. Global and Planetary Change, in press.

Buckley, HA and Johnson LR 1988 Late Pleistocene to Recent sediment deposition in the central and western Mediterranean. *Deep-Sea Research* 35(5): 749-766.

Calvert, SE 1983 Geochemistry of Pleistocene sapropels from the eastern Mediterranean. Oceanologica Acta 6: 255-267.

- Cita, MB, Vergnaud-Grazzini, C, Robert, C, Chamley, H, Ciaranfi, N and D'Onofrio, S 1977 Paleoclimatic record of a long deep-sea core from the eastern Mediterranean. *Quaternary Research* 8: 205-235.
- Cita, MB, Broglia, C, Malinverno, A, Spezzibottiani, G, Tomadin, L and Violanti, D 1982 Late Quaternary pelagic sedimentation on the southern Calabrian Ridge and western Mediterranean Ridge, eastern Mediterranean. Marine Micropaleontology 7: 135-162.

Emiliani, C 1955 Pleistocene temperatures. Journal of Geology 63: 538-578.

- Ganssen, GM and Troelstra, SR 1987 Paleoenvironmental changes from stable isotopes in planktonic foraminifera from eastern Mediterranean sapropels. *Marine Geology* 75: 221-230.
- Hut, G, Ostlund, HG and van der Borg, K 1986 Fast and complete CO₂-to-graphite conversion for ¹⁴C Accelerator Mass Spectrometry. In Stuiver, M and Kra, RS, eds, Internatl ¹⁴C conf, 12th, Proc. Radiocarbon 28(2A): 186–190.
- Kidd, RB, Cita, MB and Ryan, WBF 1978 The stratigraphy of eastern Mediterranean sapropel sequences recovered by DSDP Leg 42A and their paleoenvironmental significance. In Hsü, KS and Montadert, L, eds, Initial Reports Deep Sea Drilling Project 42: 421-443.

Olausson, E 1961 Studies of deep sea cores. Reports of the Swedish Deep-Sea Expedition 1947-1948 8: 337-391.

- Richie, JC, Eyles, CH and Haynes, CV 1985 Sediment and pollen evidence for an early to mid-Holocene humid period in the eastern Sahara. *Nature* 314: 352-355.
- Rossignol-Strick, M, Nesteroff, W, Olive, P and Vergnaud-Grazzini, C 1982 After the deluge: Mediterranean stagnation and sapropel formation. *Nature* 295: 105-110.
- Ryan, WBF 1972 Stratigraphy of Late Quaternary sediments in the eastern Mediterranean. In Stanley, DJ, ed, The Mediterranean Sea: A natural sedimentation laboratory: 149–169. Stroudsburg, Pennsylvania, Dowden, Hutchinson and Ross.
- Thunell, RC, Williams, DF and Kennett, JP 1977 Late Quaternary paleoclimatology, stratigraphy and sapropel history in the eastern Mediterranean deep-sea sediments. *Marine Micropaleontology* 2: 371-388.
- Troelstra, SR 1987 Late Quaternary sedimentation in the Tyro and Kretheus Basins, southeast of Crete. Marine Geology 75: 77-91.
- Troelstra, SR, Ganssen, GM and Klaver, GT (ms) High resolution analysis of eastern Mediterranean sapropel S1; chronostratigraphy, stable oxygen isotopes and geochemistry. In preparation.
- Vergnaud-Grazzini, C, Deveaux, M and Znaidi, J 1986 Stable isotope "anomalies" in Mediterranean Pleistocene records. Marine Micropaleontology 10: 35-69.