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# Deposition of sapropel S1 sediments in oxic pelagic and anoxic brine environments in the eastern Mediterranean: differences in diagenesis and preservation

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#### Abstract

Sediments from a boxcore in the previously anoxic brine-filled Poseidon Basin, eastern Mediterranean, have been studied and compared to sediments deposited in a 'normal' eastern Mediterranean environment. The boxcore can be divided into three main sedimentary intervals based on AMS-radiocarbon ages, foraminiferal and geochemical zonations. From the base of the core upwards these are: (1) 12.3–31.2 cm, organic-rich sediments redeposited from within the brine; (2) 6.6–12.3 cm, sediment containing a 'cold' foraminifera fauna redeposited from above the brine into the basin while the brine was still present; (3) 0-6.6 cm, oxic pelagic sediment accumulated since the reoxygenation of Poseidon Basin which occurred  $\sim 1800$  yrs BP. Near the base of the latter unit, a Mn-oxide peak has formed and it marks the present boundary between oxic and suboxic environments. A progressive downward oxidation front, which is usually found in 'normal' sapropel S1 sediments, has never formed in Poseidon Basin sediments. This has resulted in the preservation of the relationship between organic carbon and organic-related trace elements, e.g. Se, in the organic-rich sediments of Poseidon Basin, whereas such a relationship has been obliterated in 'normal' sapropel S1 sediments. On the basis of the carbonate content as well as the Sr/Ca ratio, preservation of carbonates appears to be better in the brine sapropel sediments of BC15 than it is in 'normal' sapropel S1 sediments. The high opal content of BC15 shows that biogenic opal is also much better preserved. The overall lower C<sub>org</sub>/Ba ratio in BC15 suggests a better preservation of barite relative to that of organic carbon in shallow brine sediments, but is as yet inconclusive for the organic carbon preservation potential of brine relative to 'normal' unoxidised sediments. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: sapropel; diagenesis; preservation; brines; eastern Mediterranean

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# 1. Introduction

A common feature in eastern Mediterranean sediments is the occurrence of marked intervals enriched in organic matter (sapropels). Sapropels were originally defined by Kidd et al. (1978) as "discrete layers, greater than 1 cm in thickness, set in open marine pelagic sediment and containing greater than 2% organic carbon." Visually detected 'sapropels' do not always contain that amount of organic carbon. We have, therefore, adopted the more liberal definition of Van Santvoort et al. (1996), who define sapropels as distinct sediment layers with a organic carbon content that is significantly higher than that of the surrounding hemipelagic sediment and being deposited in an open marine environment. The youngest sapropel has been labelled S1 (Cita et al., 1977) and has been deposited between 5000 and 9000 years ago (Troelstra et al., 1991; Thomson et al., 1995; Van Santvoort et al., 1996). This sapropel is being subjected to diagenesis because of the diffusion of oxygen into its uppermost reaches, thus oxidizing organic matter and giving rise to extensive remobilisation of redox-sensitive metals (De Lange et al., 1989; Pruysers et al., 1993; Higgs et al., 1994; Thomson et al., 1995; Van Santvoort et al., 1996). Burn-down of the sapropel occurs when the oxygen flux into the sediment is larger than the upward flux of reduced species that can be oxidised (Van Santvoort et al., 1996). As a consequence, this excess oxygen is used in the oxidation of the previously anoxic sapropelic sediments. Oxidation of the youngest sapropel develops distinct metal profiles, not only above, but also within the sapropel. This results in a change of the total composition of the initial, now oxidised, sapropel sediment as well as of the remaining, unoxidised, sapropel (Higgs et al., 1994; Thomson et al., 1995; Van Santvoort et al., 1996).

In recent years, some brine-filled basins with persisting anoxic conditions, e.g. Tyro, Bannock, Urania, Atalante and Discovery (Jongsma et al., 1983; De Lange and Ten Haven, 1983; Scientific staff of Cruise Bannock 1984-12, 1985; MEDRIFF Consortium, 1995) have been discovered in the eastern Mediterranean. Two previously brine-filled basins, Kretheus and Poseidon, have been found in the Tyro Basin area (Fig. 1). Completely anoxic sediments have been reported for Tyro Basin (e.g. Troelstra, 1987), whereas a small oxic layer has been found lying on top of an anoxic sequence in the Kretheus Basin (Troelstra, 1987) and Poseidon Basin. Organic matter is thought to be preserved better in anoxic brine basins, containing 2 mM H<sub>2</sub>S (Luther et al., 1990), than it is in oxic, pelagic sediments, although Calvert and Pedersen (1992) have argued that organic carbon preservation in anoxic environments is not significantly different from that in oxic sediments. The occurrence of perfectly preserved radiolarians and of sulphate reduction in anoxic brine sediments but not in contemporaneous 'normal' pelagic sediments in the eastern Mediterranean suggests that biogenic silica and reactive organic matter are preferentially preserved in these brine sediments, assuming similar inputs to these two basin types (Björklund and De Ruiter, 1987; Troelstra, 1987; Aghib, 1996; Henneke et al., 1997). In this study, we compare new data on brine sediments with those on 'normal' hemipelagic sediments from the same region and time interval, namely Holocene eastern Mediterranean sediments which include the S1 sapropel. We thereby use a multi-disciplinary approach, i.e. geochemical, micropalaeontological and radiometric methods. This will permit us to establish potential changes from initial deposition to present-day recovery, hence preservation vs. removal mechanisms. Whereas the present-day sapropel S1 has undergone severe changes in composition due to its burn-down, our new data on S1-aged sediments indicate no alteration of the initial composition.

## 2. Material and methods

# 2.1. Sediment

During the 1991 MD69-Marflux cruise with R.V. *Marion Dufresne* boxcore BC15 (33°51.4'N, 26°05.5'E) was collected in the Poseidon Basin at 3232 m water depth (Fig. 1). The recovered sediment column of 31.2 cm consists of hemipelagic, pteropod-rich mud (unit 1, 0–5.4 cm) overlying a dark-brown zone (unit 2, 5.4–6.6 cm), a creambrownish layer (unit 3, 6.6–8.7 cm) and a coarse foraminiferal ooze (unit 4, 8.7–12.3 cm). The sediment below 12.3 cm (unit 5) is heterogeneous in colour (dark grey/black–green/brown; Fig. 2A).



Fig. 1. The Tyro Basin area and its location with respect to Crete. The location of BC15 is marked.

## 2.2. Sampling and chemical analysis

Pore water was extracted from one of the BC15 subcores following a shipboard routine (De Lange, 1992a). After two years of cold storage at 4°C another subcore was divided into 3 mm thick slices. One half of each slice was dried at 50°C and finely ground in an agate mortar, whereas the second half was kept for micropalaeontological studies (see below). Of each dried sample, 250 mg were digested in a mixture of hydrofluoric, nitric, and perchloric acids, and the digest was subsequently vaporised to dryness in Teflon bombs. Final solutions were made in 1 M HCl and were analysed with an inductively coupled plasma atomic emission spectrometer (ICP/AES; ARL 34000) for Al, Ba, Ca, Fe, Mn, Sr, Ti and Zr. The quality of the analyses was monitored by the inclusion of in-house and international standards and precisions were always better than 2%. In addition, remeasurement (ICP/AES; Perkin Elmer Optima 3000) of some samples of this study and of Van Santvoort et al. (1996) in the same batch gave the same numbers for Ba. Consequently, observed differences (Fig. 8A) cannot be related to possible instrumental or measurement artifacts between the two series. In the same digest Se was measured by hydride generation AAS using a Perkin Elmer 3100 AAS in combination with a Perkin Elmer FIAS mercury/hydride chemifold and an XYZ autosampler.

The organic carbon content of dried samples was determined by first decalcifying the samples with 1 M HCl, then by oxidising the sample at 900°C in a CuO oven and separating the evolved  $CO_2$  cryogenically in a closed system. The pressure of the  $CO_2$ -gas in a fixed volume at room temperature



Fig. 2. (A) Core description and radiocarbon ages of BC15. Numbers indicate the zones as described in the text (core description): I = top; 2 = Mn-rich layer (dark-brown); 3 = cream-brownish layer; 4 = foraminiferal ooze;  $5 = \text{heterogeneous organic-rich layer. (B) Organic carbon vs. depth profile in BC15. (C) CaCO<sub>3</sub> vs. depth profile in BC15. (D) Sr/Ca ratio vs. depth profile in BC15. (E) Amount of foraminifera per cm<sup>3</sup> vs. depth in BC15. Note the three different linear scales.$ 

is a measure for the organic carbon content of the sample. Included standards give a reproducibility better than 6%.

Total opal contents were measured using the automated leaching method described by Müller and Schneider (1993), and its reproducibility is better than 10%.

After appropriate dilution, the squeezed pore waters were analysed in Utrecht for  $Mn^{2+}$  and  $Fe^{2+}$ using a Perkin Elmer 4100 ZL Zeeman AAS. All samples were measured in triplicate. Reproducibility was better than 4% for Mn and better than 8% for Fe.

A sequential extraction was performed to determine the speciation of manganese and iron phases. This procedure consisted of eight steps: 250 mg of dried and ground sediment were subsequently extracted with: (1) 25 ml of a 1 M MgCl<sub>2</sub> solution (pH 8; absorbed ions; Ruttenberg, 1992); (2) 25 ml 2 M NH<sub>4</sub>Cl (2× pH 9, 2× pH 8, 2× pH 7.5, 3× pH 7, respectively; carbonates; De Lange, 1992b; De Lange et al., 1994); (3) 25 ml of an ascorbic acid/sodium bicarbonate/sodium citrate solution (pH  $\sim$ 8; amorphous oxides; Kostka and Luther, 1994); (4) 25 ml 1 M NaAc pH 6 followed by 25 ml of 1 M NaAc pH 5 (remaining carbonates); (5) 25 ml of dithionite solution (pH 4.8; crystalline oxides; Kostka and Luther, 1994); (6) 20 ml of 20% HF (silicates; Lord, 1982; Pruysers et al., 1993); (7) 25 ml of concentrated HNO<sub>3</sub> (pyrite and other reduced phases; Lord, 1982; Pruysers et al., 1993); (8) 20 ml of a HF/HNO<sub>3</sub>/HClO<sub>4</sub> mixture (residual phases; Lord, 1982; Pruysers et al., 1993). After each extraction the sediment was rinsed with distilled water. The extractants from steps (6) to (8) were each vaporised to dryness and the residue was subsequently dissolved in 1 M HCl. All solutions were analysed with ICP/AES (Perkin Elmer Optima 3000). The quality of the measurements was monitored by blanks and in-house standards. Reproducibility for Ca, Fe and Mn was better than 2%.

After drying at 50°C, the samples for micropalaeontological analysis were weighed, then washed and sieved over mesh widths of 63, 150 and 595  $\mu$ m. Sieve residues were weighed and the 150–595- $\mu$ m size fraction for each sample was split into suitable aliquots containing about 200 planktonic foraminiferal specimens. These were identified and counted, and we here present results in rela-

tive abundances (%) with respect to total planktonic foraminifera.

<sup>14</sup>C Accelerator Mass Spectrometry (AMS) dating was performed on handpicked foraminifera at the AMS-facility in Utrecht (the Netherlands). Experimental procedures follow Van der Borg et al. (1997).

#### 3. Results

#### 3.1. Radiocarbon dating

Seven samples have been dated using AMS-radiocarbon (Fig. 2A; Table 1). The samples at 0.45 and 3.75 cm give ages of 437 and 1337  $^{14}C_{nc}$  yrs (uncorrected for the reservoir age), respectively, implying an average sedimentation rate of 3.67 cm/ka for the top of the core. The sapropelic sediments and the for a rather uniform  ${}^{14}C_{nc}$  age of 6170 to 6490 years. These ages fall in the range of 5000 to 9000 years reported for the most recent sapropel (S1) (Troelstra et al., 1991; Thomson et al., 1995; Van Santvoort et al., 1996). The ages in the Mn-peak (1100 <sup>14</sup>C<sub>nc</sub> yrs) and the interval between the foraminiferal ooze and the Mn-peak (7640  $^{14}C_{nc}$ yrs) deviate from the other ages in that the first appears too young and the latter too old. Due to the low amount of foraminifera (see below), only a few could be picked for the age determination in these samples (Table 1). Consequently, the extremely low sample sizes for these samples have resulted in a relatively large standard deviation, and in an extreme sensitivity to sampling artifacts. This will be discussed later.

#### 3.2. Biogenic components

Benthic foraminifera are absent in BC15. The planktonic foraminiferal fauna of BC15 is rather homogeneous when compared to results from similar high-resolution investigations (Fig. 3; Rasmussen, 1991; Jorissen et al., 1993; Rohling et al., 1997; De Rijk et al., 1998; Hayes et al., 1998). Only in the upper 12.3 cm can some variability be observed in the planktonic fauna. The fauna between 12.3 cm and the beginning of the Mn-enriched layer (6.6 cm) shows increased abundances of colder water species such as *T. quinqueloba*, *G. scitula*, and right-



Fig. 3. Relative percentages of foraminifera vs. depth in BC15. Indicated zonations are identical to those in Fig. 2.

Sample code	Depth	Notes	UtC-No. <sup>a</sup>	Weight	$^{14}C$ age	$\delta^{13}C^{b}$
	(cm)			(mg C)	(yrs BP $\pm 1\sigma$ )	(‰)
AA09129	0.3–0.6	oxic sed.	4557	0.95	$437 \pm 47$	1.0
AA09140	3.6-3.9	oxic sed.	5676	0.80	$1337 \pm 42$	0.3
AA09147-AA09149	5.7-6.6	Mn-peak	4558	0.02	$1100 \pm 300$	n.a.
AA09154	7.8-8.1		5677	0.03	$7640 \pm 280$	n.a.
AA09159	9.3–9.6	foram ooze	4559	0.88	$6170 \pm 45$	0.9
AA09198	21.0-21.3	sapropel	4560	0.73	$6490 \pm 70$	0.7
AA09227	29.9-30.2	sapropel	4561	0.34	$6190 \pm 50$	0.3

Table 1	
AMS-14C ages (uncorrected years), and associated information, of some samples from BC1.	5

<sup>a</sup> Laboratory number (UtC-xxxx) reference Utrecht AMS-facility.

<sup>b</sup> Relative to PDB; n.a. = not available due to extremely small sample size.

coiled *N. pachyderma*, while the warm subtropical SPRUDTS-group is at a low and a sharp drop occurs in *G. ruber* (Fig. 3). The upper part of this interval is characterised by extremely low abundances of foraminifera compared to the rest of the boxcore (Fig. 2E).

Elevated organic carbon contents are found below 12.3 cm, whereas the organic carbon values increase with depth within the foraminiferal ooze (Fig. 2B). Following the definition of Van Santvoort et al. (1996), the sediment below 12.3 cm is considered to be sapropelic. Barium and selenium (Fig. 4) are elevated in this part compared to the upper 12.3 cm and seem to closely follow the organic carbon content (cf. Fig. 2).

The CaCO<sub>3</sub> content (Fig. 2C) was calculated from the total Ca concentration. This is valid because 99% of total Ca is extracted in the carbonate steps of the sequential extraction. A sediment trap study in the eastern Mediterranean has shown that most carbonate is biogenically derived (Rutten et al., submitted). The calculated CaCO<sub>3</sub> content, therefore, is a representation of biogenic carbonate. The carbonate content in the top 8.7 cm varies between 40 and 45 wt%, which is comparable to that found in sediments of the same age and similar depth of a nearby oxic core (T 83-48; Ten Haven et al., 1987). The foraminiferal ooze contains an enhanced amount of carbonates, namely up to  $\sim 60\%$ . The sapropelic sediment has a slightly varying carbonate content of  $\sim$ 45%. When comparing Fig. 2C and 2E, it is obvious that the CaCO<sub>3</sub> content does not correlate with the amount of foraminifera. A recent sediment trap study in the eastern Mediterranean has shown that coccolithophores, and not foraminifera, are the major contributors to the present-day carbonate flux (Ziveri et al., submitted).

Abundant radiolarians and other biogenic siliceous remains are observed in the sapropelic sediments below 12.3 cm in BC15, but are absent in the sediment above it. The opal content was also chemically determined for some samples (after Müller and Schneider, 1993; results in Table 2).

# 3.3. Titanium and zirconium

Variation in the terrestrial composition is recorded by Ti/Al and Zr/Al ratios (Fig. 4C). In the sapropel (unit 5) these ratios are constant, whereas a strong variation occurs in units 3 and 4.

#### 3.4. Manganese and iron

A sharp Mn-peak is found between 5.4 and 6.6 cm with values up to 2 wt% (Fig. 5). The Mn-speciation was determined using a sequential extraction (Table 3). Mn-(oxyhydr)oxides (from here on referred to as Mn-oxides) are mainly present in and above the Mn-enriched band, whereas some pyrite-bound Mn is found in the organic-rich part of the sediment below this band. Mn incorporated into carbonates is found throughout the sediment, but concentrations are conspicuously higher below the Mn-band (Table 3). Dissolved Mn<sup>2+</sup> is absent in and above the Mn-peak, whereas concentrations rapidly increase below the Mn-peak (Fig. 5).

Results from the sequential extractions show that Fe-oxides are mainly present in the top 8.7 cm,



Fig. 4. (A) Ba vs. depth in BC15. (B) Se vs. depth in BC15. (C) Ti/Al and Zr/Al vs. depth in BC15.

Table 2	
Opal content of some	samples from BC15

Sample code	Depth (cm)	Visible	Measured opal (wt%)		
AA09137	2.7-3.0	no	0.5		
AA09165	11.1-11.4	no	2.4		
AA09179	15.3-15.6	yes	2.2		
AA09191	18.9-19.2	yes	3.4		
AA09197	20.7-21.0	yes	6.3		
AA09221	28.1 - 28.4	yes	2.6		

'Visible' indicates whether biogenic silica was observed, or not, during the micropalaeontological studies. 'Measured opal' indicates the chemically determined total opal content (after Müller and Schneider, 1993).

whereas pyrite (FeS<sub>2</sub>) is present below this depth (Fig. 6). A small Fe-oxide enrichment is recorded on top of the foraminiferal ooze. Porewater Fe<sup>2+</sup> remains below 1  $\mu$ M, which is in contrast to the concentration usually found in and below the 'normal' eastern Mediterranean sapropel S1 (concentrations up to 15  $\mu$ M, Van Santvoort et al., 1996).

## 4. Discussion

Biogenic silica is usually absent in eastern Mediterranean sediments. However, it can be found



Fig. 5. Solid phase Mn (dots) and pore water  $Mn^{2+}$  (circles) vs. depth in BC15.

in high concentrations in brine sediments (Björklund and De Ruiter, 1987; Troelstra, 1987; Aghib, 1996). Opal only occurs below the foraminiferal ooze in BC15, implying the initial deposition of this organic-

Table 3	
Speciation of Mn in BC15 as determined by the sequential extraction	

Sample code	Depth (cm)	Mn-carb (ppm)	Mn-ox (ppm)	Mn-pyr (ppm)	Mn-tot <sup>a</sup> (ppm)	Recovery <sup>b</sup> (%)
AA09132	1.2–1.5	180	1382	1	1847	93
AA09137	2.7-3.0	139	1985	1	1949	116
AA09146	5.4-5.7	78	5346	1	5927	94
AA09152	7.2-7.5	338	111	1	690	86
AA09156	8.4-8.7	392	61	2	654	92
AA09160	9.6–9.9	507	101	25	754	100
AA09164	10.8-11.1	481	100	36	773	91
AA09172	13.2-13.5	370	94	79	674	101
AA09178	15.0-15.3	396	87	68	733	100
AA09183	16.5-16.8	439	101	73	809	98
AA09190	18.6-18.9	333	70	94	649	98
AA09198	21.0-21.3	481	85	76	821	97
AA09204	22.8-23.1	402	81	70	719	98
AA09207	23.7-24.0	398	90	88	740	97
AA09212	25.2-25.5	334	73	50	634	94
AA09221	28.1-28.4	538	93	80	941	95
AA09226	29.6-29.9	404	78	94	729	99
AA09230	30.9–31.2	406	91	66	746	96

Mn in carbonates was calculated from the sum of steps 1, 2 and 4; Mn in oxides from the sum of steps 3 and 5; Mn in pyrite by taking Mn recovered in step 7 (see Section 2). Only the fractions relevant to the discussion in this paper have been included. Furthermore, the Mn-tot column only gives the values for the eighteen extracted samples; all values are included in Fig. 5. It should be noted that the speciation of sample AA09146 is indicative of the Mn-peak.

<sup>a</sup> Total-Mn as measured in the total digestion. <sup>b</sup> Sum of all seq. extr. steps divided by total-Mn  $\times$  100%.



Fig. 6. Fe-speciation as determined by the sequential extraction. (A) Fe-oxides vs. depth in BC15. Fe in oxides was determined by summation of steps 3 and 5. (B) Fe-pyrite vs. depth in BC15. Fe in pyrite are the values measured in step 7. See Section 2 for the description of the sequential extraction steps.

rich sediment in a brine environment. The measured opal content of 2.2 to 6.3 wt% for the sapropelic sediments falls in the same range as that for sediments of the anoxic brine-filled Bannock Basin (Aghib, 1996). In contrast, the upper 12.3 cm appear to have been deposited initially in normal oxygenated

bottom water conditions. Furthermore, faunal assemblages of the sediment from the Mn-peak (5.4–6.6 cm) up to the top of BC15 indicate normal pelagic sedimentation.

# 5. Sequence and time of deposition of sediment intervals

#### 5.1. Reservoir age correction

Extrapolation of the two <sup>14</sup>C ages in unit 1 to the sediment-water interface using a constant sedimentation rate of 3.67 cm/ka results in a reservoir age of 314 yrs. This calculation is valid because of the complete recovery of the top sediment and the absence of benthic foraminifera and bioturbation marks. The calculated reservoir age for the eastern Mediterranean is 86 yrs younger than the open ocean average of 400 yrs measured by Stuiver et al. (1986) and Bard (1988). Stuiver et al. (1986) also report differences in the reservoir age for different regions, including the western Mediterranean, for which they found a deviation from the open ocean average of  $-135 \pm 85$  yrs. Our value for the eastern Mediterranean (-86 yrs) falls in the same range as the one reported for the western Mediterranean basin. The lower reservoir age for the Mediterranean might be explained by a smaller turn-over time for the present-day Mediterranean compared to the major ocean basins (Kremling and Petersen, 1981). Therefore, we use the age of 314 yrs to correct the  ${}^{14}C_{nc}$  ages for the reservoir effect, giving  ${}^{14}C_c$  ages.

#### 5.2. Redox boundaries

The redox conditions in the boxcore can be inferred from the pore water  $Mn^{2+}$  profile. The boundary between oxic and suboxic sediments is defined as the depth where dissolved  $Mn^{2+}$  increases rapidly (e.g. Froelich et al., 1979; Van Santvoort et al., 1996).  $Mn^{2+}$  is highly immobile in oxic environments, because it is oxidised and subsequently trapped into insoluble oxides, whereas concentrations rapidly increase in sub- and anoxic sediments due to the instability of Mn-oxides and the higher solubility product of Mn-carbonates compared to Mn-oxides (Middelburg et al., 1987). The present position of the oxic/suboxic boundary is, therefore, located at the depth of the Mn-peak (Fig. 5). This is further substantiated by the Mn-speciation in the boxcore. Mn-oxides are mainly present in and above the Mn-peak, whereas Mn incorporated into carbonates is evidently higher in the sediment below the Mn-peak (Table 3). The pore water  $Mn^{2+}$  profile confirms such upward diffusion, oxidation and precipitation at the level of the Mn-peak.

## 5.3. Timing of the Mn-oxide peak

The time that would be needed to accumulate the Mn-peak by upward diffusion of Mn<sup>2+</sup> can be calculated by using the solid phase and pore water Mn concentrations according to the same procedure and parameters as Pruysers et al. (1993). The calculated time of 1600 years is only 200 years less than the ending of anoxic conditions in the Poseidon Basin, based on the Cl-diffusion profile (1800 years, Van Santvoort and De Lange, 1996). When extrapolating the inferred sedimentation rate of 3.67 cm/ka from the top down to the Mn-peak, the age of the peak lies between 1471 (top of Mn-peak) and 1798  $^{14}C_c$  yrs (bottom). These ages are in conflict with the <sup>14</sup>C date recorded in the Mn-peak ( $\sim 800^{-14}C_c$ yrs, corrected for reservoir age). This age is, however, based on a very small amount of foraminifera (Fig. 2E, Table 1), thereby sensitive to contamination during sampling of the boxcore and considered not reliable; due to the upward extrusion of the boxcore and the not-complete removal of the outer rims of each slice, some contamination might have occurred by the inclusion of younger foraminifera in older slices. This hardly influences <sup>14</sup>C dating when having large amounts of foraminifera, but might be important when foraminifera numbers are low, such as in the Mn-layer (Fig. 2E). The amount of Mn in the Mn-peak can therefore be explained by the oxidation of upward diffusing Mn<sup>2+</sup> and the subsequent precipitation of Mn-oxides alone. In addition, results seem to agree that the border between units 2 (Mnpeak) and 3 marks the end of sediment deposition within the anoxic brine around 1800 yrs BP. Consequently, the sediment from the Mn-peak up to the sediment-water interface indicate 'normal' pelagic deposition.

# 5.4. Timing of the sediment below the Mn-oxide peak

The uniform faunal assemblage, the fairly constant ages and the occurrence of opal indicate that the sapropelic sediments (unit 5) consist of a slump generated and deposited within the brine. This is further substantiated by constant Ti/Al and Zr/Al profiles (Fig. 4C). These ratios are considered to be an indicator for the relative presence of heavy minerals in comparison to clay minerals. The heavy mineral fraction mainly resides in the coarser fraction (Schmitz, 1987; Shimmield, 1992). Uniform Ti/Al and Zr/Al ratios, as in the sapropelic unit, therefore indicate a uniform grain size distribution, thereby also pointing to redeposited sediment. These ratios fall in the same range as those recorded in the S1 sapropel in 'normal' sediments (unpublished results). Because no grain size fractionation has occurred and the ratios are of the same magnitude, it is valid to compare this unit with sapropels in 'normal' eastern Mediterranean sediments.

The explanation of the origin of the sediments from 6.6 to 12.3 cm in BC15 is not straightforward. Biostratigraphy may hold some clues, as a 'cool' planktonic foraminiferal fauna occurs in this interval. Three intervals of several centuries duration have been reported with similar 'cool' faunas in Holocene sequences in the Adriatic and Aegean seas: one around 7000 yrs BP, one around 6300 yrs BP, and one following the Santorini eruption/explosion (Rohling et al., 1997; Hayes et al., 1998; De Rijk et al., 1998). The latter has recently been dated at 3356 years BP (Bruins and Van der Plicht, 1996). The oldest of these three periods is faunistically different from units 3 and 4 in BC15, in that it commonly contains high abundances of pink coloured morphotypes of G. ruber, which, in contrast, are scarce in the interval of 6.6-12.3 cm in BC15. The faunal compositions of the middle (around 6300 yrs BP) and youngest periods with 'cool' faunas are more similar to that in units 3 and 4 of BC15. Because of the occurrence of normal pelagic sediment with an age up to 1800 <sup>14</sup>C<sub>c</sub> yrs overlying these units in BC15, it is more likely that the original sediment was deposited during the latest 'cooling', i.e. the one following the Santorini explosion. The visible absence of opal and a relatively low organic carbon content suggest a source outside the brine basin. The slump might, therefore, have been separated at the seawater-brine interface (Rimoldi et al., 1996), resulting in a foraminifera-rich lower interval (unit 4) and a foraminifera-poor upper interval (unit 3). The measured opal content in the lower foraminiferal ooze together with an upward decreasing organic carbon content indicates some mixing with the upper part of the sapropel in the brine during redeposition. The <sup>14</sup>C dating, however, suggests a much older time of deposition. This might be explained by the commonly reported resedimentation/reworking processes which occur in brine basins, giving rise to the finding of old nannofossil species, even of Pliocene and Miocene ages (Erba et al., 1987; Parisi et al., 1987), and thereby increasing the apparent age of the sediment.

# 5.5. Deposition summary

The sapropelic interval (unit 5) consists of a slump of organic-rich sediments generated and redeposited within the brine. This was followed by redeposition of sediments from outside the brine basin (units 3 and 4), whereby the brine structure caused a density-induced separation of the sediment. The base of unit 4 seems to have mixed with the upper part of unit 5. Both slumps (units 3–4 and unit 5) might have been caused by tectonic activity ultimately leading to the oxygenation of the Poseidon Basin, 1800 yrs BP. After this oxygenation, normal pelagic sediments, a manganese oxide peak was formed.

# 6. Diagenesis in Poseidon Basin sediment versus 'normal' pelagic eastern Mediterranean sediment

# 6.1. Mn and Fe in normal pelagic eastern Mediterranean sediments

In 'normal' eastern Mediterranean sediments, a downward-moving oxidation front exists on top of sapropel S1 (De Lange et al., 1989; Higgs et al., 1994; Thomson et al., 1995; Van Santvoort et al., 1996). Oxygen is not completely utilised at the sediment–water interface, diffusing into the sediment thereby oxidizing previously anoxic, sapropelic, sediments. This type of diagenesis is non-steady-state, resulting in the so-called 'double-manganese-peak' feature. The upper peak is thought to be deposited either hydrogenetically or by a fixation mechanism upon reoxygenation of the eastern Mediterranean deep water (Higgs et al., 1994; Van Santvoort et al., 1996). This peak has been broadened by bioturbation, and is typically 2-4 cm thick (e.g. Thomson et al., 1995). The lower peak results from the oxidation of upward diffusing Mn<sup>2+</sup> and the subsequent precipitation of Mn-oxides. It is accompanied by a large Fe-oxide peak, which results from the oxidation of upward-diffusing Fe<sup>2+</sup> and the subsequent precipitation of Fe-oxides. With time and depth the progress of the oxidation front will slow down, thereby precipitating increasing amounts of Mn- and Fe-oxides at each subsequent level. Other redox-sensitive elements, such as I, Se and V, are also mobilised in a predictable sequence with regard to the oxidation front, forming distinct peaks near the redox-front, above as well as within the remaining sapropel sediment (Thomson et al., 1995).

#### 6.2. Mn and Fe in Poseidon Basin sediments

In Poseidon Basin sediments, a single, sharp, 1.2 cm thick Mn-oxide peak exists, well above the organic-rich sediment (Fig. 5). The pore water Mn<sup>2+</sup> profile indicates this peak to be the active boundary between oxic and suboxic sediments at present. The area around the Mn-peak does not contain enhanced iron oxide levels. Only a small Fe-oxide peak is found 2.1 cm below the Mn-peak (Fig. 6A), whereas in normal eastern Mediterranean sediments the lower Mn-peak and the Fe-oxide peak do not show a separation of more than 1 cm (Thomson et al., 1995; Van Santvoort et al., 1996; unpublished results). This separation is thought to be due to a preferential mobilisation of Mn relative to Fe due to thermodynamics and kinetics (Lynn and Bonatti, 1965; Froelich et al., 1979; Burdige and Gieskes, 1983; De Lange, 1986; Pruysers et al., 1993; Thomson et al., 1995; Stumm and Morgan, 1996). The absence of a clear link between the solid Mn- and Fe-oxide profiles in BC15 confirms, therefore, our earlier statement that no downward oxidation is taking place in this boxcore. This is further substantiated by pyrite, which shows, like organic carbon, no sharp boundary between the organic-rich and organic-poor sediments



Fig. 7. Fe-pyrite vs. Mn-pyrite in BC15 (dots) and 'normal' eastern Mediterranean sediments containing sapropel S1 (circles). The solid line indicates a linear best fit forced through zero for BC15 ( $Mn_{pyr}$  (ppm) =  $10.3 \times 10^{-3}$  Fe<sub>pyr</sub> (ppm)), the hatched line a linear best fit for the 'normal' sapropel S1 ( $Mn_{pyr}$  (ppm) =  $3.4 \times 10^{-3}$  Fe<sub>pyr</sub> (ppm) + 0.23). The results for the 'normal' eastern Mediterranean sediments were obtained applying the sequential extraction to sediments from boxcore ABC 26 (site BC12/UM26 of Van Santvoort et al., 1996).

(Fig. 6B), in contrast with 'normal' eastern Mediterranean sediments, where pyrite sharply increases just below the oxidation front. Moreover, a good correlation exists between pyrite and organic carbon in BC15 (compare Fig. 2B and Fig. 6B). The Mn/Fe ratio of the pyrite found in the Poseidon Basin is about twice as high as that in the 'normal' sapropel S1 pyrite (Fig. 7). The  $Mn^{2+}$  concentration is also twice as high in the pore water of the brine sediment of BC15 than it is in the pore water of 'normal' sapropel S1 sediment (5-6 μM versus 2-3  $\mu$ M; e.g. Van Santvoort et al., 1996). The Mn<sup>2+</sup> concentration in BC15 is comparable to that found in the Tyro Basin brine (De Lange et al., 1990). The correspondence between the Mn/Fe ratio in pyrite and the Mn<sup>2+</sup> in pore water indicates that formation of pyrite in BC15 took place in a brine environment. The  $Mn^{2+}$  concentration in the brine might have originally been controlled by either the input of Mn oxides, which are subsequently reduced, or by a combined equilibrium of Mn with sulphide and carbonate phases. The good pyrite– $C_{org}$  relationship suggests that pyrite formation in the brine environment of BC15 has been organic-carbon-limited (Berner, 1984). However, Henneke et al. (1997) found no good correlation of pyrite with the organic carbon content in the brine-filled Tyro and Bannock Basins. They proposed a mainly syngenetic and Fe-limited formation of pyrite. At this moment, we cannot give a satisfactory explanation for this difference.

# 6.3. Se in 'normal' pelagic sediments and Poseidon Basin sediments

The absence of a downward-moving oxidation front is clearly indicated by the Se-profile (Fig. 4). In oxidised sediments Se will be in the form of selenate (SeO $_4^{2-}$ ), which is a soluble species. Reduction of this species forms elemental Se and further reduction may even result in the formation of the selenide anion (Se<sup>2-</sup>) (Howard, 1977; Brookins, 1988; Masscheleyn et al., 1990). The latter species are highly insoluble, giving rise to the preferential accumulation of Se in organic-rich sediments. In 'normal' eastern Mediterranean sapropels, a large Se-enrichment is encountered just below the redox front (Thomson et al., 1995; Van Santvoort et al., 1996). It forms upon the downward oxidation of the sapropel, where Se is mobilised when encountering oxygen. Subsequently, selenate continuously diffuses downwards, is reduced and concentrated just below the redox front. The Se-profile resulting from such downward oxidation does not correlate with the organic carbon content (Fig. 8B). In sediments of the Poseidon Basin, however, Se correlates well with the organic carbon content (Fig. 8B), and no enrichments are found near the oxic/suboxic boundary (Fig. 4B). Another redox-sensitive element, vanadium, is also enriched in the sapropel, correlating with the organic carbon content (not shown; V<sub>non-clav</sub>  $(\text{ppm})/\text{C}_{\text{org}}$  (wt%) = 29.3 with  $r^2 = 0.94$ ). Like Se, no diagenetic peak is found for V. Consequently, the sapropel sediments in BC15 have not been diagenetically altered by oxygen penetration. In addition, it appears that the distribution of Se, V and probably other trace elements still reflect their initial correlation with the organic carbon flux to sapropel S1 sediments in the eastern Mediterranean.

# 7. Preservation of organic-rich S1 sediments in the anoxic Poseidon brine compared to that in oxic pelagic sediments

## 7.1. Opal

High opal contents have been found in the organic-rich sediment of the Poseidon Basin (Table 2). whereas in 'normal' eastern Mediterranean sediments, including sapropels, insignificant amounts, if any, occur. The preservation of biogenic silica is thought to occur due to the high dissolved silica concentration in the brine (Björklund and De Ruiter, 1987). De Lange et al. (1990) measured a dissolved silica concentration of 266 µM in the Tyro brine, as opposed to concentrations of  $\sim 10 \ \mu M$  in eastern Mediterranean bottom water (Kremling and Petersen, 1981; Hydes et al., 1988). The high silica concentrations in the brine will result in a much lower opal dissolution rate, as this concentration lies much more near the saturation concentration of opal than that of 'normal' eastern Mediterranean sediments. Consequently, opal is much better preserved in anoxic brine sediments than in oxic 'normal' eastern Mediterranean sediments.

#### 7.2. Carbonate

The average carbonate content is slightly higher in the sapropelic sediments (12.3-31.2 cm) than it is in the top sediments (0-6.6 cm) of BC15 (Fig. 2C). Nearby core T 83-48 (Ten Haven et al., 1987) shows no changes in the carbonate sedimentation in the Holocene. The change of the average carbonate content in BC15, therefore, indicates that carbonates are preserved better in brine sediments. This agrees with the chemical reactions taking place in oxic compared to anoxic conditions. Namely, oxic breakdown of organic material produces acid, which dissolves some carbonates, whereas anoxic conditions produce bicarbonate, resulting in enhanced preservation of carbonates (De Lange et al., 1989). Sr/Ca ratios may give further information about the preservation of carbonates in marine sediments. The Sr/Ca ratio is thought to be indicative of the aragonite content in eastern Mediterranean sediments (Pruysers et al., 1991; Thomson et al., 1995), because aragonite contains more Sr than calcite due to the



Fig. 8. (A) Organic carbon vs. Ba in BC15 (dots) and its best polynomial fit (hatched line;  $C_{org}$  (wt%) =  $-1.88 \times 10^{-6}$  (Ba)<sup>2</sup> +4.48 × 10<sup>-3</sup> Ba - 0.373; Ba in ppm) have been indicated. In addition, the best polynomial fit in 'normal' eastern Mediterranean S1-sapropels (thick solid line) and the position of oxidised S1-samples have been given (Van Santvoort et al., 1996). (B) Organic carbon vs. Se in BC15 (dots) and 'normal' eastern Mediterranean top sediments (open symbols; unpublished results from boxcore UM 35). Diamonds indicate values from 'diagenetic' Se-peaks in 'normal' sediments. The hatched line indicates the best linear fit for BC15 samples (Se (ppm) = 2.7 C<sub>org</sub> (wt%) - 0.5).

relative ease with which Sr can substitute Ca in the aragonite structure (e.g. Winland, 1969). Sr/Ca ratios of eastern Mediterranean sapropels are clearly higher than those found in recent oxic top sediments (Thomson et al., 1995), suggesting enhanced preservation of aragonite during periods of sapropel deposition. The average Sr/Ca ratio in the sapropel of BC15 is higher than that found in normal eastern Mediterranean sapropels of similar depths, 5.56 mg/g (Fig. 2D) versus 4.99 mg/g at  $\sim$ 3300 m water depth (unpublished results UM15, Van Santvoort et al., 1996). Brine conditions, therefore, seem to enhance aragonite preservation relative to 'normal' sapropels. The Sr/Ca ratio of the foraminiferal ooze has the lowest value recorded in BC15, confirming that this ooze originates from outside the brine basin.

#### 7.3. Organic matter

Van Santvoort et al. (1996) have shown that Ba is a reliable indicator of organic carbon accumulation for unoxidised S1 sediments. In addition, Dymond et al. (1992) showed a clear relationship between

organic carbon and barite fluxes in sediment traps. Therefore, Ba can be considered as a palaeoproxy for past organic carbon fluxes, even when diagenesis has removed most of the organic carbon signal. Indeed, Ba shows a good correlation with organic carbon in Poseidon Basin sediments (Fig. 4A). However, when Ba is plotted versus the organic carbon content (Fig. 8A), the resulting slope, i.e. the  $C_{org}/Ba$  ratio, is lower than for average eastern Mediterranean sapropels (Van Santvoort et al., 1996). At first glance this suggests lower preservation of organic matter in the brine, in contrast with other biogenic-related components (opal, carbonates). However, the lower  $C_{org}$ /Ba ratio in BC15 is thought partly to be due to the greater depth of BC15 compared to other cores, and the commonly recorded decrease of Corg/Ba ratios with depth in the water column (Von Breymann et al., 1990; Dymond et al., 1992; Van Santvoort et al., 1996). It may also in part be related to the unknown preserved Ba fraction in brine sediments compared to the 'normal' average 30% preservation of Ba (Dymond et al., 1992). In view of the sulphate concentration of the Tyro brine being twice as high as that of normal sea water (De Lange et al., 1990),

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a better preservation of barite in brine compared to 'normal' sediments is thought to result. This is likely to be the case, at least in the top 50 cm of brine sediment, where sulphate reduction does not appear to take place at a significant rate (Henneke et al., 1997). Consequently, the lower  $C_{org}/Ba$  ratio in BC15 implies a better preservation of barite relative to organic carbon in brine sediments, but is as yet inconclusive for the organic carbon preservation potential of brine relative to 'normal' sediments.

# 8. Conclusions

Several differences could be established in diagenesis and preservation of biogenic components, between anoxic brine sediments and oxic 'normal' eastern Mediterranean sediments:

(1) There has been no oxidise-down front in sapropel sediments deposited in the Poseidon brine, whereas there is one in those deposited in the 'normal' eastern Mediterranean basin.

(2) Consequently, there has been no mobilisation of Se (and other trace elements) and the trace element/ $C_{org}$  ratio has been preserved in the brine but not in the 'normal' sapropel sediments.

(3) Biogenic opal, aragonite and calcite have been better preserved in the brine than in the 'normal' sapropel sediments.

(4) The preservation of barite relative to that of organic carbon seems to be higher in shallow brine sediments than it is in unoxidised 'normal' Mediterranean sediments. However, our data are inconclusive for the preservation potential of organic carbon in brine relative to 'normal' sediments, hence the difference of organic carbon preservation of brine compared to 'normal' sediments.

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#### References

- Aghib, F.S., 1996. Anoxic versus oxic sedimentation in the Bannock Basin area, 35,000 yrs B.P. to present. Riv. Ital. Paleontol. Stratigr. 102, 293–302.
- Bard, E., 1988. Correction of accelerator mass spectrometry <sup>14</sup>C ages measured in planktonic foraminifera: paleoceanographic implications. Paleoceanography 3, 635–645.
- Berner, 1984. Sedimentary pyrite formation: an update. Geochim. Cosmochim. Acta 48, 605–615.
- Björklund, K.R., De Ruiter, R., 1987. Radiolarian preservation in eastern Mediterranean anoxic sediments. Mar. Geol. 75, 271– 281.
- Brookins, D.G., 1988. Eh-pH Diagrams for Geochemistry. Springer-Verlag, Berlin, 176 pp.
- Bruins, H.J., Van der Plicht, J., 1996. The exodus enigma. Nature 382, 213–214.
- Burdige, D.J., Gieskes, J.M., 1983. A pore water/solid phase diagenetic model for manganese in marine sediments. Am. J. Sci. 283, 29–47.
- Calvert, S.E., Pedersen, T.F., 1992. Organic carbon accumulation and preservation in marine sediments: How important is anoxia? In: Whelan, J., Farrington, J.W. (Eds.), Organic Matter: Productivity, Accumulation, and Preservation in Recent and Ancient Sediments. Columbia University Press, New York, pp. 231–263.
- Cita, M.B., Vergnaud-Grazzini, C., Robert, C., Chamley, H., Ciaranfi, N., d'Onofrio, S., 1977. Paleoclimatic record of a long deep sea core from the eastern Mediterranean. Quat. Res. 8, 205–235.
- De Lange, G.J., 1986. Early diagenetic reactions in interbedded pelagic and turbiditic sediments in the Nares Abyssal Plain (western North Atlantic): consequences for the composition of sediment and interstitial water. Geochim. Cosmochim. Acta 50, 2543–2561.
- De Lange, G.J., 1992a. Shipboard routine and pressure–filtration system for pore-water extraction from suboxic sediments. Mar. Geol. 109, 77–81.
- De Lange, G.J., 1992b. Distribution of various extracted phosphorus compounds in the interbedded turbiditic/pelagic sediments of the Madeira Abyssal Plain, eastern North Atlantic. Mar. Geol. 109, 115–139.
- De Lange, G.J., Ten Haven, H.L., 1983. Recent sapropel formation in the eastern Mediterranean. Nature 305, 797–798.
- De Lange, G.J., Middelburg, J.J., Pruysers, P.A., 1989. Discussion: Middle and Late Quaternary depositional sequences and cycles in the eastern Mediterranean. Sedimentology 36, 151–158.
- De Lange, G.J., Middelburg, J.J., Van der Weijden, C.H., Catalano, G., Luther III, G.W., Hydes, D.J., Woittiez, J.R.W., Klinkhammer, G.P., 1990. Composition of anoxic hypersaline brines in the Tyro and Bannock Basins, eastern Mediterranean. Mar. Chem. 31, 63–88.
- De Lange, G.J., Van Os, B., Pruysers, P.A., Middelburg, J.J., Castradori, D., Van Santvoort, P., Müller, P.J., Eggenkamp, H., Prahl, F.G., 1994. Possible early diagenetic alteration of palaeo proxies. NATO ASI Ser. I 17, 225–258.

- De Rijk, S., Hayes, A., Rohling, E.J., 1998. Eastern Mediterranean sapropel S1 interruption; an expression of the onset of climatic deterioration around 7 ka BP. Mar. Geol. 153 (this volume).
- Dymond, J., Suess, E., Lyle, M., 1992. Barium in deep-sea sediment: a geochemical proxy for paleoproductivity. Paleoceanography 7, 163–181.
- Erba, E., Parisi, E., Cita, M.B., 1987. Stratigraphy and sedimentation in the western Strabo Trench, Eastern Mediterranean. Mar. Geol. 75, 57–75.
- Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim. Cosmochim. Acta 43, 1075–1090.
- Hayes, A., Rohling, E.J., De Rijk, S., Kroon, D., Zachariasse, W.J., 1998. Mediterranean planktonic foraminiferal faunas during the last glacial cycle. Mar. Geol. 153 (this volume).
- Henneke, E., Luther III, G.W., De Lange, G.J., Hoefs, J., 1997. Sulphur speciation in anoxic hypersaline sediments from the eastern Mediterranean Sea. Geochim. Cosmochim. Acta 61, 307–321.
- Higgs, N.C., Thomson, J., Wilson, T.R.S., Croudace, I.W., 1994. Modification and complete removal of eastern Mediterranean sapropels by postdepositional oxidation. Geology 22, 423– 426.
- Howard, J.H., 1977. Geochemistry of selenium: formation of ferroselite and selenium behaviour in the vicinity of oxidising sulfide and uranium deposits. Geochim. Cosmochim. Acta 41, 1665–1678.
- Hydes, D.J., De Lange, G.J., De Baar, H.J.W., 1988. Dissolved aluminium in the Mediterranean. Geochim. Cosmochim. Acta 52, 2107–2114.
- Jongsma, D., Fortuin, A.R., Huson, W., Troelstra, S.R., Klaver, G.T., Peters, J.M., Van Harten, D., De Lange, G.J., Ten Haven, L., 1983. Discovery of an anoxic basin within the Strabo Trench, eastern Mediterranean. Nature 305, 795–797.
- Jorissen, F.J., Asioli, A., Borsetti, A.M., Capotondi, L., De Visser, J.P., Hilgen, F.J., Rohling, E.J., Van der Borg, K., Vergnaud-Grazzini, C., Zachariasse, W.J., 1993. Late Quaternary central Mediterranean biochronology. Mar. Micropaleontol. 21, 169–189.
- Kidd, R.B., Cita, M.B., Ryan, W.B.F., 1978. Stratigraphy of Eastern Mediterranean sapropel sequences recovered during DSDP Leg 42A and their paleoenvironmental significance. Init. Rep. DSDP 42, 421–443.
- Kremling, K., Petersen, H., 1981. The distribution of zinc, cadmium, copper, manganese and iron in waters of the open Mediterranean Sea . 'Meteor' Forschungsergeb. Reihe A/B 23, 5–14.
- Kostka, J.E., Luther III, G.W., 1994. Partitioning and speciation of solid phase iron in saltmarsh sediments. Geochim. Cosmochim. Acta 58, 1701–1710.
- Lord III, C.J., 1982. A selective and precise method for pyrite determination in sedimentary materials. J. Sediment. Petrol. 52, 664–666.
- Luther III, G.W., Catalano, G., De Lange, G.J., Woittiez, J.R.W.,

1990. Reduced sulphur in the hypersaline anoxic basins of the Mediterranean Sea. Mar. Chem. 31, 137–152.

- Lynn, D.C., Bonatti, E., 1965. Mobility of manganese in diagenesis of deep-sea sediments. Mar. Geol. 3, 457–474.
- Masscheleyn, P.H., Delaune, R.D., Patrick, W.H., 1990. Transformations of selenium as affected by sediment oxidation-reduction potential and pH. Environ. Sci. Technol. 24, 91–96.
- MEDRIFF Consortium, 1995. Three brine lakes discovered in the seafloor of the Eastern Mediterranean. Eos 76, 313 + 318.
- Middelburg, J.J., De Lange, G.J., Van der Weijden, C.H., 1987. Manganese solubility control in marine pore waters. Geochim. Cosmochim. Acta 51, 759–763.
- Müller, P.J., Schneider, R., 1993. An automated leaching method for the determination of opal in sediments and particulate matter. Deep Sea Res. I 40, 425–444.
- Parisi, E., Erba, E., Cita, M.B., 1987. Stratigraphy and sedimentation in the anoxic Bannock Basin (Eastern Mediterranean). Mar. Geol. 75, 93–117.
- Pruysers, P.A., De Lange, G.J., Middelburg, J.J., 1991. Geochemistry of eastern Mediterranean sediments: primary sediment composition and diagenetic alterations. Mar. Geol. 100, 137–154.
- Pruysers, P.A., De Lange, G.J., Middelburg, J.J., Hydes, D.J., 1993. The diagenetic formation of metal-rich layers in sapropel-containing sediments in the eastern Mediterranean. Geochim. Cosmochim. Acta 57, 527–536.
- Rasmussen, T.L., 1991. Benthonic and planktonic foraminifera in relation to the Early Holocene stagnation in the Ionian Basin, Central Mediterranean. Boreas 20, 357–376.
- Rimoldi, B., Alexander, J., Morris, S., 1996. Experimental turbidity currents entering density-stratified water: analogues for turbidites in Mediterranean hypersaline basins. Sedimentology 43, 527–540.
- Rohling, E.J., Jorissen, F.J., De Stigter, H.C., 1997. 200 years interruption of Holocene sapropel formation in the Adriatic Sea. J. Micropaleontol. 16, 97–108.
- Ruttenberg, K.C., 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. Limnol. Oceanogr. 37, 1460–1482.
- Schmitz, B., 1987. The TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio in the Cenozoic Bengal abyssal fan sediments and its use as a paleostream energy indicator. Mar. Geol. 76, 195–206.
- Scientific staff of Cruise Bannock 1984-12, 1985. Gypsum precipitation from cold brines in an anoxic basin in the eastern Mediterranean. Nature 314, 152–154.
- Shimmield, G.B., 1992. Can sediment geochemistry record changes in coastal upwelling palaeoproductivity? Evidence from northwest Africa and the Arabian Sea. In: Prell, C.P., Emeis K.C. (Eds.), Upwelling Systems: Evolution Since the Early Miocene. Geol. Soc. Spec. Publ. 64, 29–46.
- Stuiver, M., Pearson, G.W., Braziunas, T., 1986. Radiocarbon age calibration of marine samples back to 9000 cal yr BP. Radiocarbon 28, 980–1021.
- Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry. Wiley, New York, 1022 pp.
- Ten Haven, H.L., De Lange, G.J., McDuff, R.E., 1987. Interstitial water studies of Late Quaternary Eastern Mediterranean

sediments with emphasis on early diagenetic reactions and evaporitic salt influences. Mar. Geol. 75, 119–136.

- Thomson, J., Higgs, N.C., Wilson, T.R.S., Croudace, I.W., De Lange, G.J., Van Santvoort, P.J.M., 1995. Redistribution and geochemical behaviour of redox-sensitive elements around S1, the most recent eastern Mediterranean sapropel. Geochim. Cosmochim. Acta 59, 3487–3501.
- Troelstra, S.R., 1987. Late Quaternary sedimentation in Tyro and Kretheus Basins, southeast of Crete. Mar. Geol. 75, 77–91.
- Troelstra, S.R., Ganssen, G.M., Van der Borg, K., De Jong, A.F.M., 1991. A Late Quaternary stratigraphic framework for eastern Mediterranean sapropel S1 based on AMS <sup>14</sup>C dates and stable oxygen isotopes. Radiocarbon 33, 15–21.
- Van der Borg, K., Alderliesten, C., De Jong, A.F.M., Van den Brink, A., De Haas, A.P., Kersemaekers, H.J.H., Raaymakers, J.E.M.J., 1997. Precision and mass fractionation in <sup>14</sup>C analysis with AMS. Nucl. Instr. Meth. Phys. Res. B 123, 97–

101.

- Van Santvoort, P.J.M., De Lange, G.J., 1996. Messinian salt fluxes into the present-day Eastern Mediterranean: implications for budget calculations and stagnations. Mar. Geol. 132, 241–251.
- Van Santvoort, P.J.M., De Lange, G.J., Thomson, J., Cussen, H., Wilson, T.R.S., Krom, M.D., Ströhle, K., 1996. Active post-depositional oxidation of the most recent sapropel (S1) in sediments of the eastern Mediterranean Sea. Geochim. Cosmochim. Acta 60, 4007–4024.
- Von Breymann, M.T., Suess, E., Lyle, M.W., 1990. Depth dependent enrichment of barium and copper in the Peru margin and Nazca Plate sediments; utility as productivity proxies. Eos 71, 116–117.
- Winland, H.D., 1969. Stability of calcium carbonate polymorphs in warm, shallow seawater. J. Sediment. Petrol. 39, 1579– 1587.