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Geochemical evidence for enhanced productivity during S1 sapropel deposition in the eastern Mediterranean

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Abstract. The geochemistry of the youngest Mediterranean sapropel layer suggests changes in productivity and water column oxygen conditions during sapropel deposition. The Ba-enriched interval is broader than the organic-carbon-rich interval of this sapropel. We suggest that the Ba-enriched horizon records the original thickness of the sapropel prior to subsequent partial oxidation. The main carrier of Ba is barite, as microcrystals (0.5-5 μm) having a morphology characteristic of marine barite, particularly abundant beneath high productivity regions. Ba concentrations do not change at the sapropel layer oxidation front and diagenetic barite crystals are absent, thus the Ba-enriched layer reflects original oceanic conditions of increased biological productivity during sapropel deposition and not diagenetic Ba remobilization. Paleoredox indicators point to restricted oxygenated bottom water but not to fully anoxic conditions. Detrital elements within this layer indicate a lower eolian terrigenous input, enhanced humidity, and increased precipitation/runoff, thus likely higher nutrient supply.

1. Introduction

Results of the Deep Sea Drilling Project (DSDP), Ocean Drilling Program (ODP), studies of piston and gravity cores, and field studies in uplifted marine sections have demonstrated the cyclic deposition of sapropels and organic-rich layers (ORLs) in the Mediterranean. Sapropels were first discovered in the eastern Mediterranean [*Kullenberg*, 1952] and defined as a dark-colored discrete bed, >1 cm thick, containing >2% weight total organic carbon (TOC) [*Kidd et al.*, 1978]. These organic-rich sediments intercalated with normal organic-poor sediments have been described in many different cores recovered in the eastern Mediterranean. They appear to be related to climate changes and occur since the middle Miocene. ODP Leg 107 [*Kastens et al.*, 1987; *Emeis et al.*, 1991] confirmed the occurrence of sapropels also in the Tyrrhenian Sea. Subsequently, ODP Leg 160 obtained an excellent record of eastern Mediterranean sapropels [*Emeis et al.*, 1996; *Emeis and Sakamoto*, 1998], and ODP Leg 161 demonstrated the deposition of ORLs in the western Mediterranean [*Comas et al.*, 1996; *Murat*, 1999].

Several hypotheses have been proposed for the causes leading to sapropel deposition. The two main ones have been (1) the anoxia or organic matter preservation hypothesis and (2) the productivity or enhanced organic matter supply hypothesis. The anoxia hypothesis states that sapropels result from stagnation and basin anoxia, thus enhancing organic matter preservation [e.g., *Olausson*, 1961; *Vergnaud-Grazzini et al.*, 1977; *Sarmiento et al.*, 1988; *Tang and Stott*, 1993; *Aksu et al.*, 1995]. In this hipothesis, water column stratification due to extensive fresh or less saline surface water input led to basin-wide bottom water stagnation. Planktonic foraminifer assemblages and oxygen isotope studies are the strongest evidence in support of decreased surface salinity during sapropel deposition [e.g., *Rossignol-Strick*, 1983; *Vergnaud-Grazzini et al.*, 1986; *Kallel et al.*, 1997; *Emeis et al.*, 1998; *Emeis et al.*, in press, 2000]. The productivity hypothesis invokes increased primary productivity and organic matter supply resulting in high organic carbon deposition presumably in well-oxygenated bottom waters [*Calvert*, 1983; *Calvert and Pedersen*, 1992; *Castradori*, 1993]. Some authors have also considered a combination of bottom water anoxia and increased productivity [e.g. *Rohling and Hilgen*, 1991; *Emeis and Sakamoto*, 1998]. Several lines of evidence based on mineralogical, geochemical, and micropaleontological studies have been used to support these different hypotheses.

The primary objectives of this geochemical study of the most recent, thus probably the best preserved and least modified, sapropel layer (S1) in the eastern Mediterranean are to distinguish between geochemical proxies that indicate enhanced productivity versus organic matter preservation in suboxic conditions and to identify postdepositional processes that have altered the original geochemical record by diagenetic mobilization and/or alteration. Possible changes in productivity, in bottom water oxygenation, and in the sedimentary regime during sapropel deposition are thus emphasized.

In the sedimentary record some of the classical indicators of productivity, such as organic carbon, opal, or calcium carbonate contents, are often not well preserved because they are easily recycled, thereby biasing productivity signals, making it difficult to distinguish between preservation and productivity signatures. Advances in this field and the search for more refractory chemical indicators have demonstrated that Ba has a strong biogenic association, as its content increases with higher biological productivity [*Goldberg and Arrhenius*, 1958; *Schmitz*, 1987; *Dymond et al.*, 1992]. In the last two decades, Ba has therefore been suggested as a potential reliable indicator for productivity

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[e.g., *Dymond et al.*, 1992; *Francois et al.*, 1995; *Paytan,* 1995; *Paytan et al.*, 1996]. Water column studies show that most of the Ba in suspended particles is barite, which forms in the water column in microenvironments where organic matter decomposes, and Ba and S are released, thus promoting the formation of barite [*Dehairs et al.*, 1987; *Bishop,* 1988]. *Paytan* [1997], *Paytan and Kastner* [1996], and *Paytan et al.* [1996] also demonstrated that barite accumulation in oxic sediments is a potential more reliable proxy for productivity than Ba content. The use of Ba concentration for recording productivity depends on the Ba content of different carriers of Ba in the sediments and their potential diagenetic remobilization. Ba content may increase or decrease because of an increase in its detrital supply or mineral dissolution, or Ba may be remobilized because of sulfate reduction, therefore being unsuitable for paleoceanographic reconstruction [e.g., *Paytan et al.*, 1996; *McManus et al.*, 1998]. Because of the stability of barite, Ba content based on barite crystals is a favored productivity proxy in oxic oceanic environments. If sulfate reduction was negligible during and after this sapropel layer deposition, Ba-barite content in this layer could be an important indicator of the productivity; we therefore utilized barite and not Ba as a productivity proxy.

2. Material and Methods

Sapropel S1 was analyzed for mineralogy and geochemistry in two eastern Mediterranean deep-sea cores (Figure 1): one is a Pilot Core M25, 80 cm long, recovered in 1993 during a *Meteor* cruise on the Calabrian Rise in 3376 m water depth, (36°44'75"N, 17° 43'05"E), and the second one is core GL94 obtained during the cruise of the *Gelendzhik* (TTR-Programme) in 1994 at 36°04'75"N, 21°58'03"E and a water depth of 2687 m. In both cores a dark S1 sapropel layer is intercalated with light-colored sediments. Samples were dried after description of the cores, homogenized and split into representative portions. One portion of each sample was used for bulk and clay mineralogy studies and another one for chemical analyses.

2.1. X-ray Diffraction (XRD)

The bulk and clay mineralogy was determined by X-ray Diffraction (XRD) using a Philips PW 1710 diffractometer with Cu-Kα radiation. Semiquantitaive estimates were performed using the integrated peak as described by *Nieto et al.*, [1989].

2.2. Electron Microscopy

Morphological studies of clays, barite, and pyrite were performed using scanning electron microscopy (SEM) (Zeiss DSM 950). Microanalyses of clay minerals were obtained by transmission electron microscopy (TEM) (Philips CM-20 equipped with an EDAX microanalyses system).

2.3. Chemical Analyses

2.3.1. Organic carbon and carbonate measurements. The carbonate content was measured using a carbon dioxide coulometer (5010 CO_2 Coulometer). The error in the standard calcite determination was ± 0.1%. The total carbon (TC) and N contents were measured in a Perkin-Elmer 2400 CHN Elemental Analyzer. Standards and duplicate analyses controlled the measurement error, which was ± 0.05%. The percentage of TOC in the sediments was calculated by subtracting the inorganic carbon measured with the CO_2 coulometer from the TC values.

2.3.2. Major and trace element analyses. Inductively coupled plasma mass spectrometry (ICP-MS) (VG Plasma Quad and Perkin Elmer Sciex Elan-5000 spectrometer) was used for trace element analyses (Ba, Sb, As, Ni, Cu, Zn, U, Th, Zr, La, and Lu) following sample digestion with a mixture of hydrofluoric, nitric, and perchloric acids. The quality of the ICP-MS analyses was monitored with laboratory and international standards. Precision was better than ±2 and ±5% relative for analyte concentration of 50 and 5 ppm, respectively. X-ray fluorescence (XRF) was used for I and Br analyses at Berkeley Lawrence Livermore Laboratory. Major and trace elements were also analyzed by this technique after conventional preparation

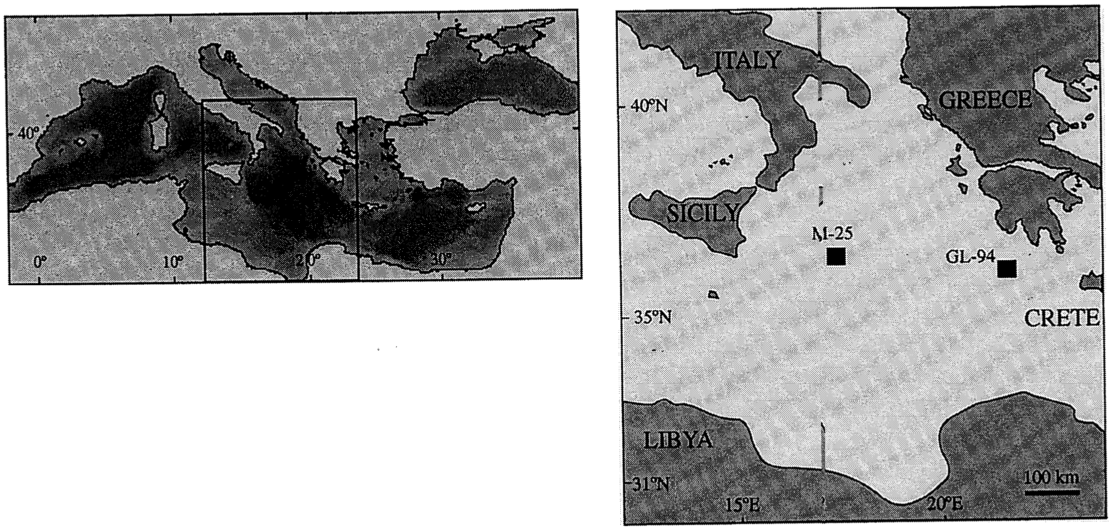

Figure 1. Maps showing the location of the two studied cores containing S1 sapropel.

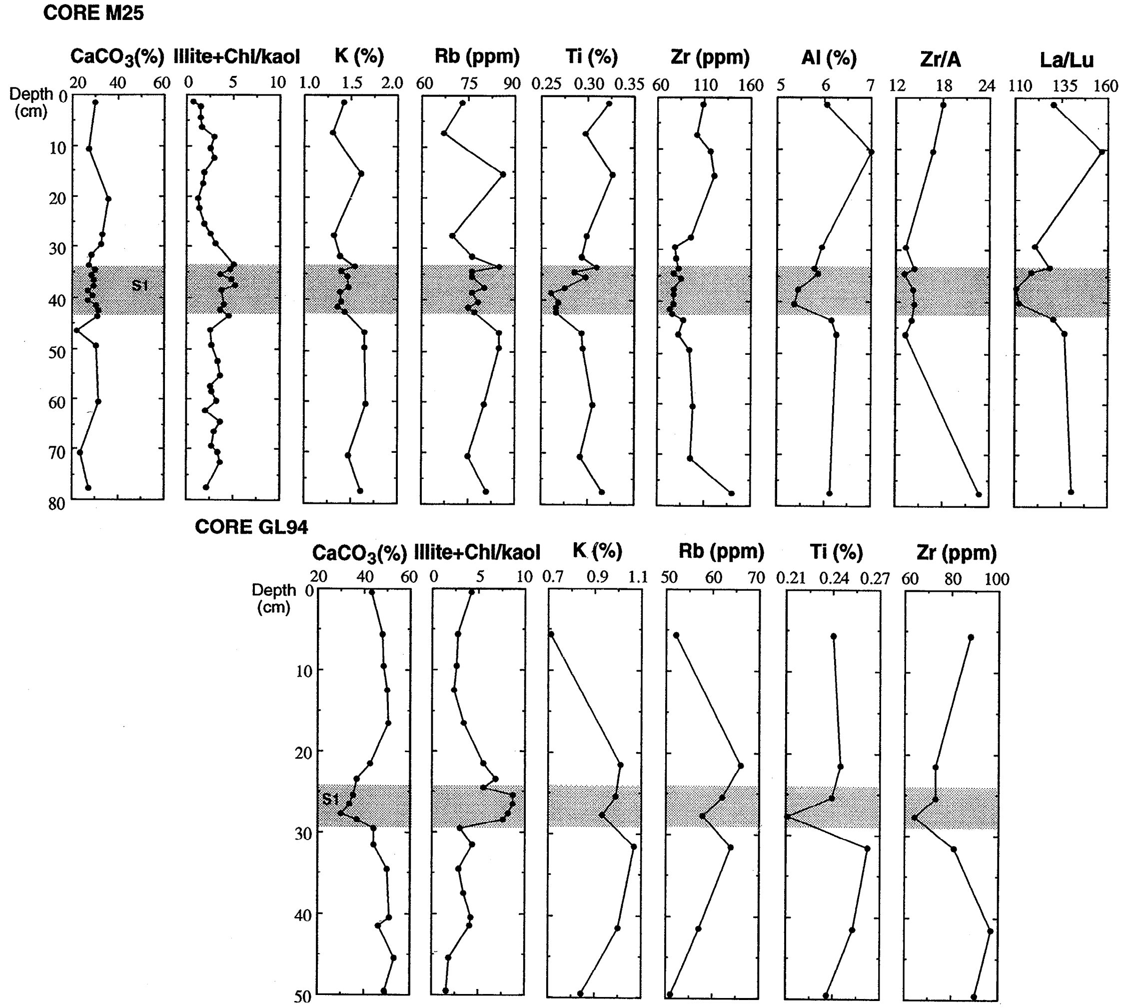

Figure 2. Concentration versus depth profiles of $CaCO_3$, illite+chlorite/kaolinite ratio and detrital elements (K, Rb, Ti, and Zr) in cores M25 and GL94. Al and Zr/Al and La/Lu ratios are also shown in core M25. The shaded area represents the interval enriched in organic carbon and defined as sapropel S1.

[*Giauque*, 1994]. Precision of these analyses was 2%, and accuracy was 5%. Al, Fe, and Mn were measured by atomic absorption spectrometry (AAS); analytical error was <2%.

2.3.3. Barite separation. For barite separation, samples were sequentially leached according to the procedure of *Paytan* [1997].

3. Results

The two cores (M25 and GL94) have similar lithology. It consists of an upper section of brownish calcareous ooze (33 and 25 cm in each core, respectively) that overlies a black sapropel (10 and 5 cm, respectively) capping a light gray calcareous ooze. Major phases are calcite, clay minerals, and quartz (Table 1)[1], together with traces of feldspar and dolomite. In the sapropel layer, traces of pyrite are also present. The clay-mineral assemblage throughout consists of smectites, illite, chlorite, and kaolinite. Trace amounts of palygorskite, as broken fibers, are present in samples below and above the sapropel layer but not within it. Smectite content does not change significantly in the sapropel interval while illite and chlorite contents increase and kaolinite decreases (Figure 2). Detrital element concentration and mineral data versus depth profiles are presented in Figure 2. Other solid phase data are given in Figure 3. In each case sapropel S1 is indicated by the shaded area. The element concentration in the sapropels and in sediments above and below has also been normalized using Al and Ti as an index of the relative abundance of detrital phases. However, as the normalized profiles are about the same as the unnormalized ones, the bulk concentrations are represented in Figures 2-4. Only certain elements are plotted normalized to Al to better illustrate their fluctuations in relation to this element.

Sedimentation rates do not vary significantly and cannot explain the observed geochemical changes due to dilution effects.

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[1] Supporting table is available on diskette or via Anonymous FTP from kosmos.agu.org, directory APEND (Username = anonymous, Password=Guest). Diskette may be ordered by mail from AGU, 2000 Florida Ave., N. W., Washington, DC 20009 or by phone at 800-966-2481; $15.00. Payment must accompany order.

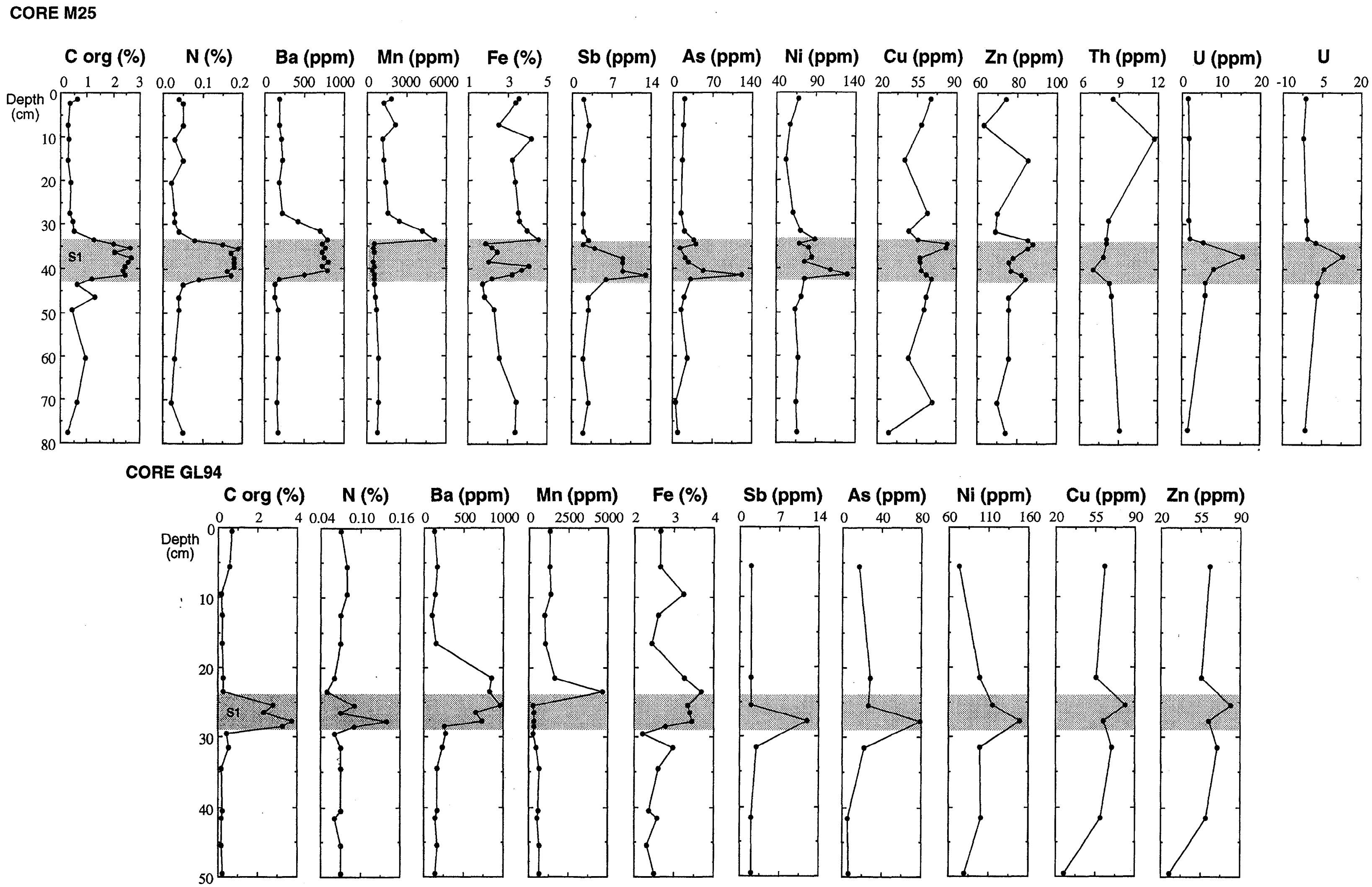

Figure 3. Concentration versus depth profiles of total organic carbon (TOC) and N, Fe, Mn, and trace elements in cores M25 and GL94. Th, U, and authigenic uranium are also shown in core M25. The shaded area represents the interval enriched in organic carbon and defined as sapropel S1. Note the difference of thickness between the TOC-enriched interval and the Ba-enriched interval which indicates the oxidation of the original sapropel. Mn peak marks the penetration of the oxidation front.

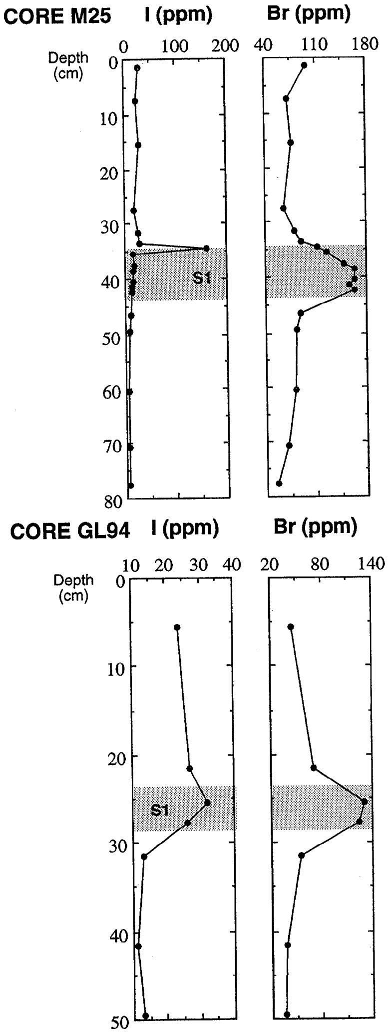

Figure 4. I and Br concentrations versus depth profiles in cores M25 and GL94. Iodine profile in core M25 indicates I diffused and reprecipitated upon encountering the oxidation front.

This is supported by radiocarbon ages for core M25 published by *Emeis et al.* [in press, 2000], four samples were dated using mixed planktonic foraminifera tests (>63 μm at 12-13 cm depth ^{14}C age is 2235); these ages show no significant fluctuations in sedimentation rates during S1 sapropel and the sediments above, and the sediments below the sapropel have just slightly higher rates. Therefore the mineralogical and chemical compositions of sapropel S1 and sediments above and below it are used as indicators for environmental depositional and postdepositional conditions. Major and trace elements concentrations show significant variations in response to either paleoceanographic changes at the time of sapropel deposition or to postdepositional alteration.

4. Paleoproductivity Proxies

In both cores, Ba content is enriched in the S1 sapropel layer, as well as immediately above it. Thus the thickness of the Ba-enriched layer is somewhat larger than of the organic-carbon-rich interval (Figure 3); the difference signifies the burndown zone of the upper part of the sapropel [*Pruysers et al.*, 1993; *Thomson et al.*, 1993, 1995; *Higgs et al.*, 1994; *Van Santvoort et al.*, 1996, 1997]. The mean Ba concentration background is 150-200 ppm, and in the Ba-enriched layer, concentrations increase up to 5 times over the background value. However, to consider this enrichment as a productivity signal, it must be demonstrated that this Ba is in the form of biogenically mediated marine barite. Samples from above and below the sapropel with a background Ba value and sapropel S1 samples enriched in Ba were analyzed for barite content by the modified sequential leaching method of *Paytan et al.* [1993]. These analyses showed that carbonate and aluminosilicate sediment fractions carry most of the Ba in the nonsapropel layer and that marine barite is responsible for the excess Ba throughout the broader, original sapropel layer; the barite crystals range in size from 0.5 to 5 μm, as shown in Figures 5a-5c. Several observations indicate that barite is a primary phase.

1. Crystal size and morphology correspond to biologically mediated marine barite crystals and not to barite precipitated as a consequence of diagenetic remobilization of Ba. These crystals are identical in morphology and size to barite crystals observed in the water column [*Dehairs et al.*, 1980; *Bishop*, 1988] and reported in sediments beneath areas of high biologic productivity, such as the equatorial Pacific [*Paytan et al.*, 1993; *Paytan*, 1997] and south Atlantic sediments [*Gingele and Dahmke*, 1994]; they are distinctly different in morphology and size from detrital, hydrothermal, or diagenetically precipitated barite crystals formed at geochemical fronts [e.g., *Torres et al.*, 1996].
2. Ba is enriched within a thicker interval than that of the visible sapropel layer, suggesting oxidation of the organic carbon in the uppermost section of this interval. Also, Ba concentration does not change at the oxidation front marked by the Mn peak (Figure 3); unlike Mn, Ba is not affected by this oxidation front.
3. Ba shows a broad profile (Figure 3) rather than a defined reprecipitation peak which would suggest a diagenetic origin.

The barite reported here in S1 sapropel therefore has a marine origin that formed in microenvironments of decaying organic matter in high-productivity zones, and the barite profile has not been altered diagenetically after deposition. The absence of diagenetic alteration is also supported by sulfur isotope data of associated pyrite. *Passier et al.* [1997] reported $\delta^{34}S$ pyrite values of -37.3‰ to -38.2‰ in S1 sapropel, indicating that SO_4^{2-} reduction took place in an open system with seawater exchange. Thus the pore water sulfate reduction did not lower sulfate concentrations to the extent necessary for barite dissolution and remobilization of Ba. In anoxic sediments where sulfate often approaches zero concentrations, interstitial waters become undersaturated with respect to barite. As a consequence, barite dissolves, and Ba diffuses to where barite may precipitate diagenetically, occasionally concentrated in layers [e.g., *Brumsack*, 1989; *Van Os et al.*, 1991; *Van Os*, 1993; *Gingele and Dahmke*, 1994; *Torres et al.*, 1996; *McManus et al.*, 1998]. Although barite formation occurs in euxinic basins, in depleted oxygen environments [*Falkner et al.*, 1993; *Francois et al.*, 1995] it is poorly preserved. If Ba remobilization has occurred, the Ba profile should have shown concentration maxima above and below the sapropel layer [e.g., *Van Os et al.*, 1991; *Van Os*, 1993; *Passier et al.*, 1998], which is not the case. Its distribution, shown in Figure 3, thus indicates that (1) barite is a paleoproductivity proxy in S1 sapropel, (2) the barite profiles indicate an increase in productivity during its deposition, and (3) its preservation is also a

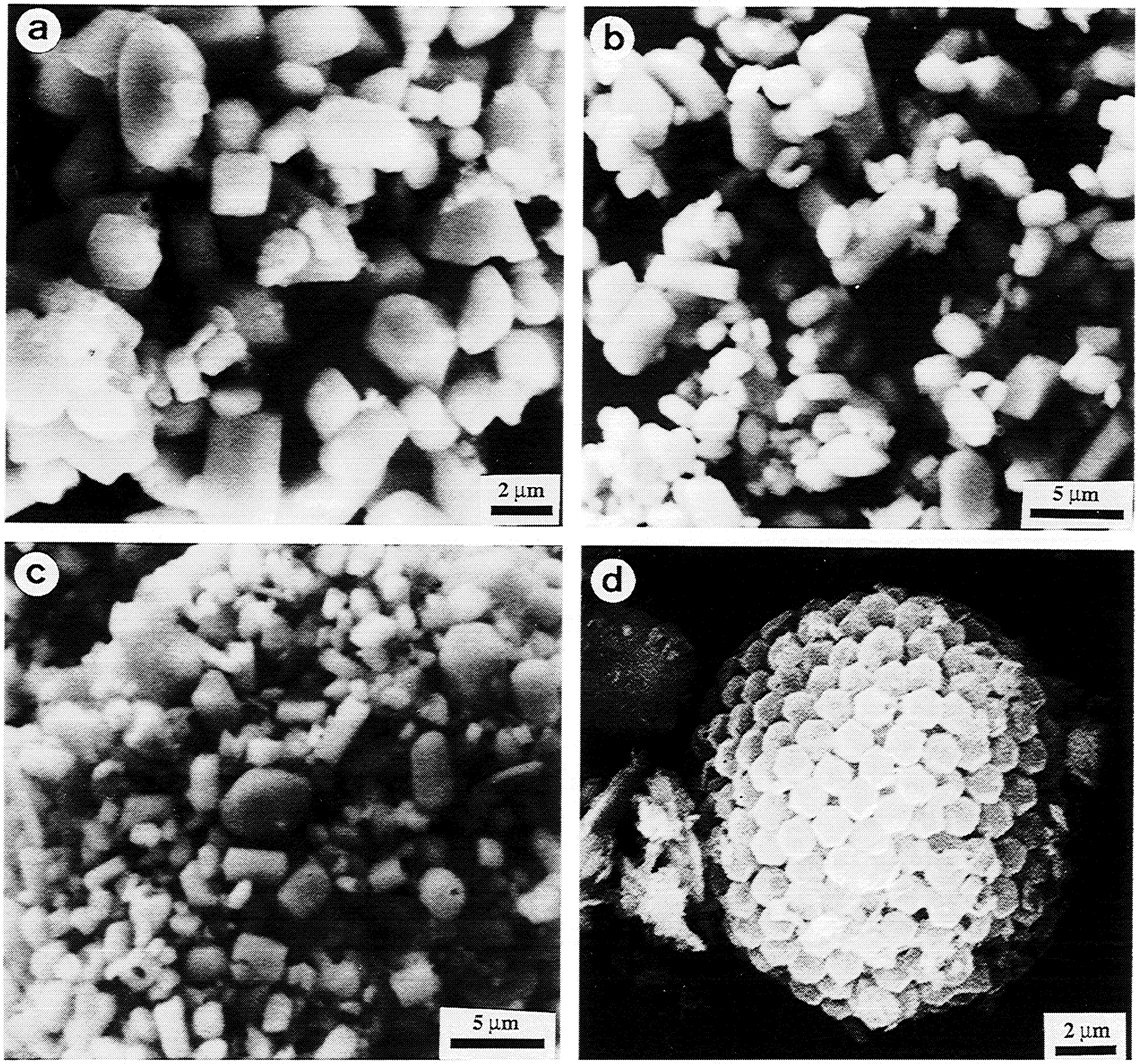

Figure 5. Scanning electron microscopy (SEM) micrographs of barite crystals from cores M25 and GL94 obtained by sequential leaching of samples enriched in Ba and pyrite framboids from sapropel S1. (a) Barite from sediments located at 31.5 cm depth in core M25 which are enriched in Ba but not in organic carbon, (b) Barite separated from sediments enriched in organic carbon at 39.5 cm depth in core M25, (c) Barite separated from sediments enriched in Ba in core GL94 at 26.5 cm depth, and (d) Pyrite framboid from S1 in core M25.

proxy of water column conditions at the time of this sapropel deposition. Calcareous nannofossils and planktonic foraminerfera studies in later Quaternary sapropels from the Ionian Sea also support the suggestion of increased productivity leading to sapropel deposition [e.g., *Negri et al*., 1999].

5. Postdepositional Alteration and Element Redistribution

C and N enrichments are observed in the two studied cores only in the visible sapropel layer but are not enriched in the interval above the dark layer where Ba concentration and barite are enriched (Figure 3). It is suggested that the interval of the visible sapropel (including that above it where Ba is enriched), represents the original thickness of the organic-rich sapropel layer (Figure 3). The discrepancy between the C, N, and Ba concentration profiles is a strong indicator of postdepositional oxidation of the organic matter at the top of the sapropel layer. Oxidation of organic matter of sapropel layers has also been reported in several cores from the eastern Mediterranean [*Van Santvoort et al*., 1997] and ascribed to a progressive downward moving oxidation front [*Pruysers et al*., 1993; *De Lange et al*., 1994; *Thomson et al*., 1993, 1995; *Higgs et al*., 1994; *Van Santvoort et al*., 1996, 1997].

The oxidation of the sapropel layer is also demonstrated by concentration-depth profiles of redox sensitive elements, such as Fe and Mn; unlike Ba, both show peak concentrations at the top of the visible sapropel (Figure 3). During and after sapropel deposition, oxygen was consumed in situ by oxidation of organic matter. The oxygen-depleted conditions led to remobilization and upward diffusion of Mn. When the organic carbon was consumed, oxygen diffused into the sediments from above and oxidized these reduced species, Mn and Fe oxyhydroxides thus precipitated at the oxidation front, enriching it in these elements. In some Eastern Mediterranean cores a double Mn peak has been reported [*Van Santvoort et al.*, 1996], but in the two cores studied here double Mn peaks have not been observed. Oxyhydroxides commonly contain considerable amounts of other transition metals [*Hem et al.*, 1989]. In these cores, Zn and Cu (Figure 3) are also enriched in the oxidation front, and they most likely coprecipitated with or were scavenged by the Fe-Mn oxyhydroxides. As, Sb, and Ni are also enriched within the sapropel layer (Figure 3). Origin of the minor amounts of pyrite in S1 sapropel was attributed to organic matter decomposition via partial microbial sulfate reduction and ferrous Fe mobilization, resulting in Fe sulfide formation during sapropel deposition or shortly after its burial [*Pruysers et al.*, 1993; *Passier et al.*, 1996, 1999a, b].

6. Indicators for Bottom Water Oxygenation

The well-preserved barite in S1 sapropel in the studied cores indicates that bottom water oxygen concentration was high enough to prevent extensive sulfate reduction and barite dissolution. To investigate bottom water oxygenation during sapropel deposition, the additional redox indicators that have been analyzed are pyrite framboid size [*Wilkin et al.*, 1996, 1997], authigenic uranium content, Ni/Co ratios [*Jones and Manning*, 1994], and iodine and bromine concentrations [*Calvert*, 1990].

Wilkin et al. [1996, 1997] proposed that pyrite framboid size is an indicator of water column oxygenation. Framboids <7 μm diameter are consistent with nucleation and growth within the Black Sea anoxic water column, followed by transport to the sediments, while larger framboids (mean diameter ~10 μm) form in sediments underlying the oxic and dysoxic water columns; in sapropel S1, pyrite framboids are large, 10-15 μm in diameter (Figure 5d). This size range indicates that it formed diagenetically in situ in the sediment and not in the water column [*Wilkin et al.*, 1996, 1997] and that the water column was not anoxic during S1 sapropel formation. This agrees with observations on pyrite microtextures by *Passier et al.* [1999a] suggesting that oxic to suboxic rather than euxinic conditions existed in the water column during formation of S1 sapropel.

Because Th is relatively immobile in the sedimentary environment and is concentrated in the detrital fraction and U in its 6^+ valence is soluble but in its 4^+ valence it precipitates and concentrates in reducing environments, thus raising the U/Th ratio, the U/Th ratio is also a redox indicator. *Wignall and Myers* [1988] proposed authigenic U content (Ua) as an index of bottom water oxygenation and defined Ua as U authigenic = total U - Th/3 [*Jones and Manning*, 1994]. According to *Jones and Manning* [1994], Ua values >12 are typical of anoxic environments. As shown in Table 1, except for one sample in S1, all the Ua values obtained in the sapropel and the sediments above and below it have Ua values of <12. Furthermore, no significant change in Ua is observed at the onset of sapropel deposition, suggesting that deposition of sapropel S1 was not caused by a change to anoxic conditions. The highest Ua value within the visible sapropel is thought to reflect the threshold of maximum oxygen consumption due to organic matter accumulation; however, the entire sapropel interval was not fully anoxic.

The Ni/Co ratio has been used as another indicator of redox conditions [e.g., *Dill*, 1986; *Jones and Manning*, 1994]. All the Ni/Co ratios in S1 sapropel (Table 1), the value for dysoxic conditions according to *Jones and Manning* [1994], suggest that sapropel deposition occurred in oxic to dysoxic rather than fully anoxic bottom waters.

To further verify whether changes in water column oxygenation occurred, the sediments were also analyzed for iodine and bromine concentrations (Figure 4). I and Br concentrations in marine sediments appear to be mostly controlled by their main carrier phase, the organic matter fraction, and the diagenetic oxidation of this organic matter. Iodate is the stable iodine species in oxic seawater [*Sillén*, 1961], and iodide is the dominant iodine stable species in anoxic seawater [*Wong and Brewer*, 1977] and interstitial water of anoxic sediments [*Ulman and Aller*, 1980; *Kennedy and Elderfield*, 1987b]. In anoxic environments, organic-rich sediments at the sediment/water interface have I/C_{org} ratios similar to those of marine plankton, whereas in oxic environments an enrichment in iodine is observed at the sediment-water interface from adsorption of iodate, thus having higher concentrations than the buried sediments or marine plankton [*Price and Calvert*, 1973, 1977]. Organic matter decomposition leads to the release of iodide during diagenetic alteration. Iodate is utilized as an oxidant for organic matter oxidation once both O_2 and NO_3^- have been consumed [*Kennedy and Elderfield*, 1987a]. The iodide released to the pore water diffuses upward to the sediment-water interface. Subsequently, in oxic bottom water environments, iodide is oxidized to iodate, IO_3^- ion, which is adsorbed onto the organic matter, thus promoting iodine enrichment by a cycle of reduction and oxidation [*Ullman and Aller*, 1985; *Kennedy and Elderfield*, 1987a, b]. However, in reducing bottom waters, iodide is not oxidized, and therefore is not effectively absorbed on organic compounds and lost to bottom water; in anoxic environments the reduction-oxidation cycle does not occur. In contrast to iodine, the speciation of bromine is not affected by redox conditions, and therefore the I/Br and I/C_{org} ratios have been used as a bottom water oxygenation indicators [*Price and Calvert*, 1977; *Calvert*, 1990; *Calvert and Pedersen*, 1993]. However, I/C_{org} can be significantly altered during early diagenetic processes. When sediments with high content in adsorbed iodine are buried and become anoxic, iodine is released from the organic matter [*Kennedy and Elderfield*, 1987b], whereas Br changes to a lesser degree.

Bromine is enriched in the sapropel layer in both cores and is clearly correlated with the organic matter. Iodine however, does not show a clear enrichment in the sapropel, indicating that iodine and organic carbon became decoupled during early diagenesis. This circumstance suggests an upward moving flux of iodine from the sapropel layer that eventually precipitates and becomes immobilized by oxidation. The iodine concentration profile is similar to that of Mn, suggesting a postburial oxidation front penetration into the sediments. Iodine concentrations in this oxidation front are up to 10 times the concentration in the S1 sapropel, suggesting an initial high I/C_{org} ratio. The high iodine concentration in the oxidation front marking the top of the visible sapropel has also been observed in other eastern Mediterranean cores [*Van Santvoort et al.*, 1996, *Thomson et al.*, 1999]. If organic matter had reached anoxic bottom waters, iodine would have been lost to the seawater, and no concentration could have occurred in the sediments. Iodine concentrations therefore indicate that bottom waters were not anoxic; therefore iodine was not lost to seawater.

7. Sedimentary Regime and Detrital Input

Environmental indicators that suggest changes in the nature of the detrital input and sedimentary regime during sapropel S1 deposition are the following. (1) The concentrations of typical detrital elements, such as Al, Ti, Rb, Zr, and K (Figure 2), decrease. (2) The ratio of illite+chlorite/kaolinite (Figure 2) increases, suggesting a higher input of illite+chlorite, probably a fluvial input derived from the European margin, and/or a lower eolian input of kaolinite from the African margin. This also correlates with the absence of palygorskite within the sapropel layer. (3) Zr/Al ratios in sapropel S1 (Figure 2) are low, which also support a lower eolian supply during sapropel deposition; eolian deposits are typically enriched in Zr [e.g., *Gallet al al.*, 1998]. Low Zr/Al ratios have also been reported in Pliocene sapropels [*Wehausen and Brumsack*, 1998]. (4) La/Lu ratios (Figure 2) are lower, which also indicates a change in the nature of the detrital input, most likely related to lower eolian input from the African margin. La/Lu ratios of bulk sediments from the Nile delta have been suggested by *Hamroush and Stanley* [1990] to indicate climate change, influencing the relative contribution of sediments from Central Africa and Ethiopian plateau sources. Higher La/Lu ratios correlate with higher sediment input from Central African plateau.

These geochemical proxies thus indicate that sapropel S1 originated during a period of increased humidity and precipitation/runoff in the circum-Mediterranean. The $^{87}Sr/^{86}Sr$ ratios and detrital element concentrations in sediments from eastern Mediterranean cores containing the S1 interval reported by *Krom et al.* [1999] indicate that there was a major change in the nature of the detrital input during S1 sapropel deposition caused by a simultaneous increase in riverine input and a decrease in Saharan dust input, which agrees with the data reported here. In addition, alkenone unsaturation ratios and planktonic $\delta^{18}O$ records from sediments of the Alboran, Ionian, and Levantine basins have shown that salinity of surface waters during sapropel deposition has changed and is consistent with multiple sources of freshwater [*Emeis et al.*, in press, 2000]. All these data support higher precipitation over Mediterranean borderlands and lower eolian dust input during S1 deposition. Enhanced precipitation and runoff would lead to higher nutrient input and therefore enhanced productivity leading to sapropel deposition.

8. Conclusions

In the two eastern Mediterranean cores studied, sapropel S1 has been partially oxidized, and the upper part of the sapropel layer has lost its original high organic C content. Mn and I concentration profiles clearly delineate the postdepositional oxidation front. These elements became mobilized post-burial in an oxygen-depleted environment, diffused upward, and precipitated upon encountering the oxidation front that is marking the top of the remaining visible sapropel. However, the Ba profiles, which show enrichment over a wider interval than the TOC, record the original sapropel thickness. Excess Ba is present in small, well-preserved barite crystals, with morphologies and dimensions characteristic of marine barite that forms in high-productivity zones. The increase in Ba concentration derived from marine barite in both the visible sapropel and oxidized horizon of the original sapropel suggests enhanced productivity during sapropel formation, thus indicating that the origin of at least the S1 sapropel is related to an increase in biological production. Enhanced preservation of organic carbon may have occurred as well from the increased organic carbon supplied to the seafloor as a consequence of enhanced productivity. The loss of some of the organic C by oxygen consumption preserved the rest of it. Several paleo-redox indicators point to decreased oxygenation of bottom waters but not anoxic conditions. Detrital elements and detrital clay-mineral supply during S1 deposition indicate a lower eolian terrigenous input during sapropel deposition, suggesting enhanced humidity, involved increasing precipitation, and runoff.

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