Duration of S1, the most recent sapropel in the eastern Mediterranean Sea, as indicated by accelerator mass spectrometry radiocarbon and geochemical evidence

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Abstract. Slowly accumulated (<5 cm kyr⁻¹) and rapidly accumulated (5-20 cm kyr⁻¹) sediments have been compared to define the initiation and termination times of the most recent sapropel (S1) in the eastern Mediterranean Sea. The Ba/AI ratio has been employed as a more persistent index of productivity than Corg. Accelerator mass spectrometry radiocarbon dating of pelagic foraminifera indicates a maximum duration for increased Ba/AI levels in S1 from ~9500-6000 (uncorrected radiocarbon convention years B.P.) in the rapidly accumulated sediments and ~9500-5300 years B.P. in the slowly accumulated sediments. This difference is ascribed to bioturbation affecting the slower accumulated S1 sediments. In the two most rapidly accumulated S1 units, from the Adriatic and Aegean Seas, there is a "saddle" of lower values centered on 7500 years B.P. in the Corg and Ba/AI profiles, so that the visual S1 unit appears as a doublet. Geochemical evidence indicates that this intervening period is best interpreted as an episode of increased ventilation and bottom water oxygenation during the period of sapropel accumulation.

1. Introduction

Dark-colored units, with sharply defined contacts, high organic carbon (Corg) contents and high S contents in the form of pyrite [Calvert, 1983; Passier et al., 1996] occur episodically in the otherwise Corg-poor sedimentary record of the eastern Mediterranean Sea. Such units are termed sapropels [Kidd et al., 1978], and their repeated occurrence demonstrates the sensitivity of sedimentation in this topographically isolated basin to climatic changes [e.g., Emeis et al., 1996]. There is no agreement on the precise mechanisms or sequence of events that lead to sapropel formation because of the uncertainty on the relative roles of productivity and preservation in the development of high sediment Corg contents [Thunell and Williams, 1989; Calvert, 1983; Calvert and Pedersen, 1992; Bethoux, 1993; Rohling, 1994]. Sapropel formation does appear to be closely related to times of planetary Northern Hemisphere summer insolation maxima and resultant monsoon intensification [Rossignol-Strick et al., 1982; Lourens et al., 1996]. These wet periods are believed to induce enhanced water column stability and perhaps increased surface ocean productivity. The resultant decreased ventilation of the deep water column may then allow development of anoxia (or at least low oxygen levels) which may in turn lead to improved preservation of Corg. Improved timing records of sapropel deposition may constrain cause and effect interpretations, and such records are most accessible for the most recent sapropel (S1 Hieke, [1976]) because it is within the radiocarbon dating range.

Geochemical studies of S1 have revealed that although this sapropel is <10 kyr old, it has already suffered extensive postdepositional alteration which has oxidized Corg from the upper reaches of the original S1 unit [De Lange et al., 1989; Higgs et al., 1994; Thomson et al., 1995, 1999; van Santvoort et al., 1996]. This carries implications for geochemical, micropaleontological, paleoenvironmental, and sedimentological studies because it means that the true duration of sapropel formation is not coincident with the visual evidence in the sediments but rather occurs over a longer sediment interval. Thomson et al., [1999] proposed that the Ba/AI ratio was a more persistent criterion than color or Corg content for the study of sapropel productivity pulses, and this contention has been borne out in older sapropels [van Santvoort et al., 1997]. This paper uses a combination of the Ba/AI ratio and accelerator mass spectrometry (AMS) radiocarbon data to study the development of S1 in cores with different sediment accumulation rates and from different water depths, from widely separated eastern Mediterranean basin locations.

2. Material and Methods

Samples from box and piston cores from various eastern Mediterranean localities were obtained from the core archives at Free University, Amsterdam, Laboratoire des Sciences du
Climat et de L’Environnement (LSCE), Gif-sur-Yvette, and British Ocean Sediment Core Repository (BOSCOR), Southampton (Table 1; and Figure 1). Cores were sub sampled at 1 cm intervals with sufficient sediment taken to give a dry weight of >3 g. Samples were freeze-dried or oven-dried at 105°C then ground and homogenized using a tungsten carbide swing mill. A Philips PW1400 automatic sequential wavelength dispersive X-ray spectrometer was used to determine Ba and S on pressed powder pellets and Al and Mn on lithium meta-tetraborate fusion discs. Accuracy and precision were ascertained by running the international standard reference material MAG-1 (marine mud); the precision for trace element determination was 5% relative standard deviation (RSD), while for major element analyses it was typically <1% RSD. Organic carbon and CaCO3 were determined coulometrically from released CO2. Inorganic C (biogenic calcium carbonate) was measured as the CO2 evolved by the addition of 10% (vol/vol) H3PO4 and total C was measured as the CO2 generated by total sample combustion at 900°C. Organic carbon (Corg) was then calculated as total C minus inorganic C, and CaCO3 was calculated as 100 (inorganic C)/12. Precision for both CaCO3 and Corg analyses was determined by replicate analysis of an in-house standard (a deep-sea carbonate sediment) at <1% RSD for CaCO3 and <3% RSD for Corg measurements, respectively.

Planktonic foraminifera >150 μm in size were handpicked for AMS radiocarbon analysis because they have an unequivocal surface ocean source and are the sediment size fraction least liable to post-depositional transport (Troelstra et al., 1991). Species differentiation was not attempted because the total sediment sample available (~5 g wet) was often sufficient only to provide the 10-12 mg of biogenic CaCO3 in the >150 μm size range necessary for a single AMS analysis. Samples were prepared as graphite targets at the NERC Radiocarbon Laboratory and analyzed at the Lawrence Livermore National Laboratory AMS Facility (CAMS analyses) or at the Scottish Universities Research and Reactor Center and analyzed at the Arizona Radiocarbon Facility (AA analyses). Further species specific (Globigerinoides bulloides or G. ruber) AMS radiocarbon analyses from LSCE were available for one core (Siani, 1999, GifA analyses, Table 2).

3. Results and Discussion

Primary production of Corg and its preservation in the sediments are separated by remineralization by oxic or anoxic mechanisms during sinking through the water column and after deposition at the seafloor. Although sapropel S1 is the sediment record of a sustained phase of either or both increased surface ocean productivity and improved Corg preservation, it is not yet clear whether either the start or finish of S1 can be regarded as exactly synchronous across the entire eastern Mediterranean basin (Troelstra et al., 1991; Fontugne et al., 1994; Strohle and Krom, 1997). Vergnaud-Grazzini et al. (1986) estimated the duration of S1 to be 9000-7000 years from a review of early radiocarbon analyses. The compilation by Fontugne et al. (1994), which included newer AMS radiocarbon data, also returned a modal value of 9000-7000 years, although outlier values in the range 15000-4000 years were encountered.
Sapropel S1 is evident in most cores as a single, dark, C_org- rich horizon up to ~10 cm thick. The visual S1 units in certain cores studied here are unusually thick at up to 50 cm, and in some the dark coloration is in two parts (Table 1). "Double" S1 units have been reported before from various eastern Mediterranean localities (see listing by Robling et al. [1997]), although these have often been ascribed implicitly or explicitly to sedimentological disturbances. High mean accumulation rates can be the result of high surface-ocean productivity or land-derived detrital fluxes, but they can also result from down-slope redeposition of sediment or from a current-driven augmentation of accumulation in the form of drift deposits or contourites. Redeposition from turbidites will produce a discontinuous sediment record, while contourite formation may produce continuous but irregular records reflecting the waxing and waning of current strength through time. Sediment redeposition is certainly a common process in the Mediterranean basin, and Stanley [1985] estimates that two thirds of the volume of recent basin sediments are affected by downslope mass flow. It is therefore necessary to establish whether or not redeposition has affected the studied cores and, in particular, to validate the accumulation records containing double sapropels. This involves assessment of whether either or both sections are of S1 age, whether both dark sections represent continuous accumulation, and the nature of the central lighter zone. This is achieved by defining S1 in terms of the Ba/Al productivity index rather than C_org content or color and by using multiple AMS radiocarbon ages to confirm that the units are consistently of S1 age.

3.1. Productivity Records From Ba/Al and C_org

The element Ba is central to the geochemical interpretation of the productivity fluctuations recorded by S1. From the work of J.Dymond and coworkers [Dymond et al., 1992; Dymond and Collier, 1996] it is established that settling material from surface ocean organic productivity develops a Ba enrichment during its descent through the water column before deposition. At times of high productivity this flux of biogenic Ba (Ba_{bio} = measured Ba - measured Al x [Ba/Al]_{initial}) becomes sufficiently large that it may be readily identified against detrital Ba in the sediments through increases in the sediment Ba/Al ratio. Normalization to Al is necessary because of the dilution effects of CaCO3 content on the assumption that detrital phases have fairly constant Al and Ba contents which dominate the trace Ba content of CaCO3. Barium has been used in this manner as a palaeoproductivity indicator for many years, but the mechanism and rate of progressive Ba_{bio} enrichment in settling C_{org} and therefore its quantification, remain elusive [Dymond and Collier, 1996]. In the case of eastern Mediterranean sapropels, there is the added uncertainty of the behavior of Ba in anoxic or poorly oxygenated as opposed to oxic water columns.

In S1 examples previously investigated [Thomson et al., 1995; van Santvoort et al., 1996, 1997], the presence of high-Ba but low-C_{org} levels immediately above visual S1 units has been taken as evidence that postdepositional oxidation of S1 has remineralized C_{org} but has not affected Ba_{bio}. This pattern is again observed in core T87-26B, where the Ba/Al ratio profile relative to the C_{org} and S profiles (both of which suffer oxidation loss) indicates that ~9 cm of oxidation has occurred (lighter shaded area of Figure 2). A corollary of this interpretation from slowly accumulated S1 Ba/Al and C_{org} profiles is that less oxidized and, consequently, less altered examples ought to exist in areas of rapid accumulation, but this has not been demonstrated until now. The sediments of cores MD81-LC21 and MD90-917 are the most rapidly accumulated among those studied (15 and 20 cm kyr^{-1}, respectively, see below), and these two cores are used to test the prediction of an initial correspondence between the Ba/Al ratio and C_{org} contents in the absence of post depositional oxidation.

The Ba/Al ratio and C_{org} contents of the dark intervals in MD81-LC21 and MD90-917 are the most rapidly accumulated among those studied (15 and 20 cm kyr^{-1}, respectively, see below), and these two cores are used to test the prediction of an initial correspondence between the Ba/Al ratio and C_{org} contents in the absence of post depositional oxidation.
Table 2. Radiocarbon Convention Ages Obtained by the Accelerator Mass Spectrometric Technique

<table>
<thead>
<tr>
<th>Core</th>
<th>Depth in Core, Analysis</th>
<th>^14C age, convention years</th>
<th>± 1σ, years</th>
<th>δ13C, (per mille)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDVAL90-9502</td>
<td>25-26* AA-28393</td>
<td>5,830</td>
<td>55</td>
<td>n.d.</td>
</tr>
<tr>
<td>MDVAL90-9502</td>
<td>30-31* AA-28394</td>
<td>6,980</td>
<td>60</td>
<td>n.d.</td>
</tr>
<tr>
<td>MDVAL90-9502</td>
<td>41-42 AA-28395</td>
<td>7,940</td>
<td>60</td>
<td>n.d.</td>
</tr>
<tr>
<td>MDVAL90-9502</td>
<td>53-54* AA-28396</td>
<td>7,530</td>
<td>60</td>
<td>n.d.</td>
</tr>
<tr>
<td>MDVAL90-9502</td>
<td>57-58* AA-28397</td>
<td>8,150</td>
<td>65</td>
<td>n.d.</td>
</tr>
<tr>
<td>LC21</td>
<td>49.5-50.5 CAMS-41314</td>
<td>3,370</td>
<td>60</td>
<td>-1.0</td>
</tr>
<tr>
<td>LC21</td>
<td>95-96 CAMS-41313</td>
<td>4,290</td>
<td>60</td>
<td>1.2</td>
</tr>
<tr>
<td>LC21</td>
<td>137-138* CAMS-41311</td>
<td>5,590</td>
<td>60</td>
<td>0.4</td>
</tr>
<tr>
<td>LC21</td>
<td>161-162* CAMS-41315</td>
<td>7,480</td>
<td>60</td>
<td>0.9</td>
</tr>
<tr>
<td>LC21</td>
<td>174-174.5* CAMS-41312</td>
<td>8,120</td>
<td>60</td>
<td>-0.1</td>
</tr>
<tr>
<td>LC21</td>
<td>188-191* AA-30364</td>
<td>9,085</td>
<td>65</td>
<td>n.d.</td>
</tr>
<tr>
<td>LC21</td>
<td>218.5-219.5 AA-30365</td>
<td>11,765</td>
<td>80</td>
<td>n.d.</td>
</tr>
<tr>
<td>LC21</td>
<td>252-253 CAMS-41316</td>
<td>14,450</td>
<td>60</td>
<td>0.3</td>
</tr>
<tr>
<td>LC25</td>
<td>50-51* AA-30366</td>
<td>4,805</td>
<td>50</td>
<td>n.d.</td>
</tr>
<tr>
<td>LC25</td>
<td>60-61* CAMS-43635</td>
<td>6,320</td>
<td>60</td>
<td>1.0</td>
</tr>
<tr>
<td>LC25</td>
<td>70.5-71.5* CAMS-43636</td>
<td>7,270</td>
<td>50</td>
<td>-0.2</td>
</tr>
<tr>
<td>LC25</td>
<td>84.5-85.5* CAMS-43637</td>
<td>8,770</td>
<td>50</td>
<td>-1.0</td>
</tr>
<tr>
<td>LC25</td>
<td>92-93 CAMS-43638</td>
<td>8,980</td>
<td>60</td>
<td>0.5</td>
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<tr>
<td>LC25</td>
<td>225-226 CAMS-43639</td>
<td>11,110</td>
<td>50</td>
<td>1.0</td>
</tr>
<tr>
<td>MD90-917</td>
<td>164-167* GifA-96201</td>
<td>4,750</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>MD90-917</td>
<td>175-178* GifA-96202</td>
<td>5,000</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>MD90-917</td>
<td>190-192* GifA-96729</td>
<td>5,680</td>
<td>70</td>
<td></td>
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<tr>
<td>MD90-917</td>
<td>221-222* CAMS-45865</td>
<td>6,500</td>
<td>60</td>
<td>n.d.</td>
</tr>
<tr>
<td>MD90-917</td>
<td>229-230* CAMS-45866</td>
<td>6,990</td>
<td>40</td>
<td>n.d.</td>
</tr>
<tr>
<td>MD90-917</td>
<td>230-232* GifA-96730</td>
<td>6,920</td>
<td>90</td>
<td></td>
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<tr>
<td>MD90-917</td>
<td>239-242* GifA-96203</td>
<td>7,930</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>MD90-917</td>
<td>242-243* CAMS-45867</td>
<td>7,750</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>MD90-917</td>
<td>250-253.5* GifA-96204</td>
<td>8,020</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>MD90-917</td>
<td>250-253.5* GifA-96205</td>
<td>8,170</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>MD90-917</td>
<td>251-252* CAMS-45868</td>
<td>7,910</td>
<td>140</td>
<td>n.d.</td>
</tr>
<tr>
<td>MD90-917</td>
<td>252-253* GifA-96731</td>
<td>8,040</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>MD90-917</td>
<td>258-259 CAMS-45869</td>
<td>9,750</td>
<td>80</td>
<td>n.d.</td>
</tr>
<tr>
<td>MD90-917</td>
<td>275-278 GifA-96207</td>
<td>10,390</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>MD90-917</td>
<td>295-297* GifA-96732</td>
<td>10,800</td>
<td>90</td>
<td></td>
</tr>
</tbody>
</table>

Here n.d. means not determined.
*Depths were used in calculation of regression lines in text.
*These are monospecific samples (G. bulloides or G. ruber).

Ba/AI and Corg (Figure 4). The maximum Corg and Ba/AI levels in the core LC21 S1 both consistently exceed those of core 90-917, although the slope of the Ba/AI:Corg relationship is similar in the two cores (Figure 4). Most of the Corg values in both cores fail to achieve the >2% Corg criterion proposed by Kidd et al. [1978] to define a sapropel, but this criterion appears to be only an approximate guide to the Corg content necessary to develop the dark color of sapropels [Calvert, 1983]. In low accumulation rate S1 examples, Thomson et al. [1995] and van Santvoort et al. [1996] noted that the S1 Ba/AI ratio depth profile is quasi-Gaussian in shape. The improved resolution provided by the rapid accumulation rates of MD81-LC21 and MD90-917 shows central "saddle" sections in the Ba/AI and Corg profiles of both cores that are responsible for the double sapropel feature. Although values in these central sections are lower than those in the over-lying and underlying dark units, they are also markedly higher than the "background" levels which predate and postdate the S1 productivity pulse where
Ba/Al is <0.004 and Corg is <0.5 wt %. The significance of this central section in these two cores will be discussed further below.

3.2. Rates of Accumulation From Radiocarbon Data

As in most previous AMS radiocarbon dating of sapropel S1, radiocarbon data (Table 2) are quoted throughout this paper as unmodified radiocarbon convention ages in years before present (B.P., i.e., before 1950 A.D.). The quoted ages are neither corrected for the surface ocean reservoir effect which is ~ 400 years in the present-day ocean [Bard, 1988; Siani et al., 1999] nor corrected for the time-varying difference between calibrated (dendrochronological) time and radiocarbon convention time. This difference is +730 to +990 years in the radiocarbon convention time range 5000-9000 years B.P. [Stuiver and Becker, 1993; Kromer and Becker, 1993]. As a combined result of these two effects, the marine radiocarbon convention ages used here are expected to underestimate calibrated time by 300-600 years in the marine radiocarbon time range 5000-9000 years B.P. [Stuiver and Braziunas, 1993].
To achieve a common basis on which to compare the different S1 units, a chronology for the sapropel region in each core is derived by fitting a linear regression of marine radiocarbon convention age on depth. In some cores the radiocarbon data show that whole core rates of accumulation have been irregular through time, and in such cases, age values immediately above, within, and immediately below the S1 unit are preferred for construction of local floating regressions in the vicinity of the units. The explicit assumption in selective omission of data points is that any redeposition process must introduce sediment with a radiocarbon age older than newly deposited sediment, and such ages are therefore expected to exceed the regression lines through selected data.

3.2.1. Low (< 5 cm kyr⁻¹) accumulation rate sediments: Cores T87-26B, MC7S, and MC12. AMS radiocarbon analyses have been reported for box core T87-26B [Troelstra et al., 1991] and multicore MC12 and MC07S [Thomson et al., 1995]. All the AMS radiocarbon data for T26B were regressed on depth to give a whole core accumulation rate (Figure 5a). The accumulation rates for these three cores (2.2-4.3 cm kyr⁻¹) are typical of those measured in the central Mediterranean basin but are slower than those for the cores discussed below.

3.2.2. Low (< 5 cm kyr⁻¹) accumulation rate sediments: Core MDVAL 90-9502. This core from the far east of the Mediterranean basin (Figure 5b) contains a dark visual unit from 28 to 65 cm, and it was sampled with the expectation that it was a rapidly accumulated S1 unit. Although the radiocarbon data confirm that the dark unit is entirely of S1 age, the progression of radiocarbon age on depth is irregular, and this core is now interpreted as a slowly accumulated unit with redeposition of sapropel material with higher Ba/Al values in the center of the dark unit. Unlike the other cores where redeposition is inferred, compositional data do not indicate unequivocally the precise depths of the re-deposited section in this core because the redeposited material is also sapropelic. The depositional record is estimated from the extrapolations of the lines between the upper and lower data point pairs as shown (Figure 5b). The section from 32 to 52 cm is then inferred to be redeposited and disregarded in subsequent discussion. Note that the line between the upper two points intercepts the origin on extrapolation. This is the least secure interpretation of all the cores studied.

3.2.3. Intermediate (5-10 cm kyr⁻¹) accumulation rate sediments: Core MD81-LC25. On the basis of the Ba/Al criterion, S1 is present in this Herodotus Abyssal Plain piston
core from 61 to 87 cm and 94 to 100 cm. The intervening section at 87-94 cm is clearly a turbidite on visual and compositional evidence (Figure 5b). Several other turbidites deposited before and after S1 are also present in this core, one of which is 1.2 m thick and has its top at 100 cm in core. From their dark color and mineralogy both turbidites emplaced during S1 time have been interpreted to originate from slope failures on the Nile fan [Cita et al., 1984; Reeder et al., 1998]. The regression line (8.9 cm kyr⁻¹) to establish accumulation rate was determined from the upper four radiocarbon analyses in the section with high Ba/Al values and extrapolated into the section at depths 94 to 100 cm by subtraction of 7 cm to account for the presence of the smaller turbidite at 87 to 94 cm. It was not possible to locate the base of S1 in this core because the pelagic sample at 225 cm underlying the larger turbidite at 100 to 224 cm had background Ba/Al levels, and its radiocarbon age clearly predated S1 (Table 2).

3.2.4. Rapid (>10 cm kyr⁻¹) accumulation rate sediments: Core MD81-LC21. The radiocarbon data from this piston core from the southeast Aegean Sea do not all conform to a straight line, indicating that its accumulation rate has been variable in time (Figure 5b). Besides containing a double S1 unit, this core contains a thick-gray ash layer from 82 to 92 cm that was suspected to have been deposited from the explosive eruption of the Santorini/Thera volcano [Guichard et al., 1993; Hardy and Renfrew, 1990]. Recent estimates place the Santorini event at 1627/1628 B.P. [Kuniholm et al., 1996], which corresponds to a radiocarbon convention age of ~3300-3400 years [Stuiver and Becker, 1993; Bruins and van der Plicht, 1996], so that the best estimate for the corresponding marine radiocarbon convention age is ~3700-3800 yr. The actual radiocarbon determinations 32 cm above and 3 cm below the ash layer in MD81-LC21 are 3370 and 4290 radiocarbon years, respectively, which by interpolation, indicates an age of 4210 years for the ash level. This straddling of the probable Santorini age estimate by the data is taken as confirmation that the ash layer in core MD81-LC21 is, in fact, from Santorini, even though the interpolated layer age is ~450
years older than expected. The effects of bioturbation in the surface sediment mixed layer are expected to have increased the radiocarbon age of surficial sediment blanketed by the ash fall [Trauth et al., 1997].

From the eight AMS radiocarbon analyses available for this core the four analyses spanning the depth range 137-191 cm were selected to estimate a mean accumulation rate of 14.9 cm kyr\(^{-1}\) by linear regression (Figure 5b). The duration of the light-colored central section (162-173 cm) is estimated by this regression at 7320-8060 years.

### 3.2.5. Rapid (>10 cm kyr\(^{-1}\)) accumulation rate sediments:

**Core MD90-917**

Additional monospecific foraminiferal AMS ages for core MD90-917 from the southern Adriatic Sea [Siani, 1999] reveal that the sapropelic sediments accumulated more rapidly than the sediments which preceded and postdated them. (Only values immediately above, in, and below the S1 unit of the available GifA ages are included in Table 2 and Figure 5b.) The regression of the nine AMS radiocarbon analyses in the depth range 221-253.5 cm yields a sediment accumulation rate of 19.5 cm kyr\(^{-1}\). The duration of the light-colored central section at 240-245 cm is estimated at 7520-7780 years by this regression.

### 3.3. S1 Development in Slowly Accumulated Sediments

The fits to the radiocarbon data derived above allow the Ba/Al records of all cores to be compared directly as a function of time by conversion of sample depth to radiocarbon convention years with the individual regression equations. When the Ba/Al profiles of cores T87-26B, MC07S, and MC12 (Figure 5a) are compared as a function of radiocarbon time over 4000-10,000 years, a striking agreement is found between the three slowly accumulated core records (Figure 6a). In all cases the increase in productivity indicated by the increase in the Ba/Al ratio begins after 10,000 years and ends at ~5300 years, a considerably longer span of time than the 9000-7000 years interval usually quoted for the duration of S1 [Vergnaud-Grazzini et al., 1986; Fontugne et al., 1994].

### 3.4. S1 Development in Rapidly Accumulated Sediments

When the Ba/Al indexes of the sediments that accumulated at 10-20 cm kyr\(^{-1}\) and the MDVAL 90-9502 data are plotted as a function of radiocarbon time, a less coherent picture of the S1 Ba/Al episode emerges than was seen for the slowly accumulated sediments (Figure 6b). The initiation of high Ba/Al ratio values and hence S1 formation is clearly underway in all cores by 9000 years except for Adriatic core 90-917. High Ba/Al values in this latter core start later and end earlier (8200-6300 years) so that they are present over a much more restricted time interval than in any other core.

The high Ba/Al values of the S1 pulse end by 6000 years in all of the rapidly accumulated sediments except those in core LC21, several hundred years earlier than the end of high Ba/Al indicated in the slowly accumulated sediments. Few radiocarbon ages <6000 years have been reported for C\(_{org}\)-rich S1 material [Perissoratis and Piper, 1992], but the value of 5590±60 years in the 137-138 cm interval in core MD81-LC21 is immediately above the upper face of the S1 unit and is in trend with the remainder of data in this core (Figure 5b).

At face value, the differences in time between the slowly and rapidly accumulated sediments might represent a slightly earlier start and later end to sapropel formation in the slowly accumulated sediments. As these three box cores are generally from greater water depths than the rapidly accumulated sediments (Table 1), it is conceivable that water column anoxia might have developed earlier and been maintained longer in the deeper parts of the basin. This is contrary to the arguments of Strohle and Krom [1997] who envisaged that S1 formation occurred first in a midwater oxygen minimum zone that subsequently expanded downward. The Herodotus Abyssal Plain core MD81-LC25 is critical to the water depth argument because it is from the deepest water depth of the available cores. High productivity in that core begins before 9000 years B.P. and is completed by 6100 years B.P. (Figure 6b), so that it does not appear as if the offsets in S1 time can be related simply to water depth.

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**Figure 6a.** Ba/Al ratio as a function of radiocarbon time (uncorrected convention years) in cores MC12, MC07S and T87-26B with slowly accumulated sediments.

**Figure 6b.** Ba/Al ratio as a function of radiocarbon time (uncorrected convention years) in core MDVAL 90-9502 with slowly accumulated sediments and cores LC21, LC25, and 90-917 with rapidly accumulated sediments.
A different possibility is that the difference between the slowly and rapidly accumulated cores is a function of bioturbative mixing affecting both the AMS radiocarbon ages and the Ba/Al ratio values before and after sapropel formation in the slowly accumulated cores. Thomson et al. [1995] have demonstrated by means of $^{210}$Pb excess distributions that the present-day sediment surface mixed layer (SML) in deep basin cores is <3 cm deep on the 100 year timescale, which corresponds to a mixing of up to 1000 years of deposition in these slowly accumulated sediments. Most open ocean deep-sea cores have SMLs 9.8±4.5 cm thick [Boudreau, 1994], and thin SMLs are most likely a consequence of a low flux of $C_{org}$ reaching the present-day sea floor in the eastern Mediterranean, as observed in oligotrophic regions elsewhere [Legeleux et al., 1994]. Bioturbation may have been more intense immediately before and after S1 formation when bottom water oxygen content was still finite but the surficial sediments had high $C_{org}$ contents. In this view the chronologies from the rapidly accumulated S1 units must be preferred over those from the slowly accumulated units because the former are less sensitive to bioturbation artifacts. Our best estimate for the duration of S1 based on the Ba/Al ratio is therefore 9500-6000 radiocarbon years (Figure 7).

The magnitudes of the S1 Ba/Al values in the slowly accumulated S1 sediments are consistently higher than those in the rapidly accumulated S1 sediments (Figures 5 and 6). Given that Ba/Al has been shown above to be related to initial $C_{org}$ and that the slower accumulated cores are from deeper water depths, this observation is consistent with the report by Murat et al. [1990] that maximum $C_{org}$ contents in S1 increase nearly linearly with water depth, from 1% $C_{org}$ at 1000 m to 3% $C_{org}$ at 3000 m. A similar increase of maximum Ba/Al ratio in S1 units occurs with water depth (Figure 8). Recent sediment trap investigations have shown that $Ba_{bio}$/$C_{org}$ ratios increase systematically with water depth, but the ratio is largely (75%) set at depths <1200 m with the additional 25% added between 1200 and 3800 m [Dymond and Collier, 1996]. Recognizing this fact, the Ba/Al data for all cores may be modeled to a first approximation as a constant $Ba_{bio}$ flux of 1000-1500 µg cm$^{-2}$ kyrs$^{-1}$ superimposed on a variable background flux with a constant AI content of 49,900 ppm (average Al content of all data in all cores), a (Ba/Al)$_{detritus}$ ratio of 0.0035 (the background value suggested by Figure 5), and an assumed dry bulk density of 0.5 g cm$^{-3}$ (Figure 9). It may be significant that the deepest and shallowest cores studied fall farthest above and below the model lines of Figure 9, respectively, compared with the remainder of the cores, which is what would be anticipated from the constant $Ba_{bio}$ flux approximation. Any effect of water depth on Ba/Al or $C_{org}$ content therefore appears secondary to flux dilution; that is, high Ba/Al or $C_{org}$ values in S1 are primarily a result of slower sediment accumulation rates with less dilution in deeper, more remote parts of the basin.

### 3.5. Ventilation of the Eastern Mediterranean Sea During S1 Times?

The differences in the timing of the S1 records above may result from different oxygenation histories of the water column in different parts of the basin. The salient features of the Ba/Al profiles as a function of time are first that the saddle in the Ba/Al ratio corresponding to the double sapropel phenomenon is observed only in the shallow depth cores (Figure 10), and MD90-917 (1010 m) and to a lesser extent in MC12 (2211 m). The minimum Ba/Al values are centered at 7500 years B.P. in all three cores. There is no such feature at this time in any other core, which are either from greater water depths (87-26B, MC07S, and MC12) or from the northern half of the eastern Mediterranean basin (LC25) or from shallower water depth in the far east of the basin (MD9502). Second, the duration of the S1 unit in core MD90-917 is markedly shorter than in any of the other cores.

Double S1 sapropel units have been reported frequently from the southern Adriatic Sea [van Straaten, 1972; Fontugne et al., 1989] and from the northern Aegean Sea.
Oligotrophic as those which preceded and followed sapropel Ba/AI values does not record a return to conditions as of the eastern Mediterranean is complex but is driven by the deposition (Figure 3). Rohling et al. [1997, p. 97] interpreted these basin from sources in the Adriatic and Aegean Seas [Wust, central sections in Adriatic and Aegean cores as a "200 year downwelling of denser, oxygenated water in the north of the deep water (>1000 m) is maintained by a seasonal (winter) cooling. At present, the ventilation of eastern Mediterranean formation of new deep water by increases in salinity and/or by geochemical evidence is that the central section with lower interruption of Holocene sapropel formation." Despite the Northern Hemisphere insolation which produces monsoon conditions and high runoff into the eastern Mediterranean Sea. The resultant wetter and warmer conditions are believed to cause enhanced water column stabilization and hence limited winter ventilation during times of sapropel formation [Rossignol-Strick et al., 1982; Mangini and Schl Amer, 1986; Bethoux, 1993; Rohling, 1994]. From a reinterpretation of several marine and land pollen records, Rossignol-Strick [1995] has proposed a duration of 9000-6000 years for the most recent period of high summer moisture and mild winters around the eastern Mediterranean.

If the S1 sapropel has an unusually short duration in the Adriatic Sea area compared with the remainder of the basin, it appears likely that ventilation may not have been shut down completely during S1 sapropel formation but rather may have been intermittent or present at a reduced level which was insufficient to oxygenate the deep water column of the entire basin. This is opposite to the contention of Fontagne et al. [1989] who interpret a very late resumption of ventilation from what may be a later diagenetic feature. It is implicit in this explanation that oxic deep waters will cause more remineralization of the C_organ flux through the water column and on the seafloor, contrary to the interpretation of S.E. Calvert and coworkers [Calvert, 1983; Calvert and Pedersen, 1992].

Thomson et al. [1995] have argued that a prominent Mn peak coincident with the top of many S1 Ba/AI profiles is evidence of bottom water reoxygenation at the end of S1 formation. In slowly accumulated S1 examples a second underlying Mn peak occurs within the high Ba/AI region which marks the extent of postdepositional oxidation of S1 [van Santvoort et al., 1996]. A different (small) secondary Mn peak is present at the base of the Ba/AI and C_organ saddle in the two cores with well-developed double sapropels (Figure 10), but there is no corresponding feature in any other core. In a similar manner to the argument that the larger upper Mn peaks mark a return to higher bottom water oxygen levels, these smaller Mn peaks in cores MD81-LC21 and MD90-917 are consistent with the argument that the saddle feature represents a short period of improved deep water oxygenation within S1 times. The Mn oxyhydroxide forming these small Mn peaks must now be metastable in anoxic conditions, so that the peaks probably had higher Mn contents on formation. This contention of a temporarily increased bottom water oxygen content during the S1 episode is substantiated compellingly by benthic foraminiferal evidence. In another Adriatic core with a double S1 sapropel, Rohling et al. [1997] found that while the two lobes of S1 with high C_organ contents were barren or had very low benthic foraminiferal contents, the intervening saddle section contained a reestablishment of benthic foraminifera which necessitates some level of bottom water oxygen. By extension of this explanation, the double sapropel observed in both the Adriatic and Aegean Seas may represent an episode of improved ventilation in these basins during S1 times. This period is centered at 7500 years marine radiocarbon years B.P., which corresponds to a calibrated time of ~7900 cal B.P. (Figure 6). A Holocene excursion in climate close to 8200 B.P. is seen in many paleoclimatic records from diverse marine and terrestrial localities [Alley et al., 1997]. The cause of this short interval remains unknown, but it shares cold, dry, and windy characteristics with the last glacial and Younger Dryas periods. It appears likely that this cooler and less humid interval enabled intensified ventilation during the S1 period which otherwise exhibits a much reduced ventilation caused by monsoonal conditions. From pollen records, Rossignol-Strick [1995] has also interpreted a brief excursion to dry/cold conditions at ~8000 years during the generally moist/warm 9000-6000 year period. During this excursion the semidesert Artemisia species increases in abundance while the Pistacia species indicative of mild winters decreases.

4. Conclusions

A reevaluation of the duration of the most recent sapropel in the eastern basin of the Mediterranean Sea has been undertaken using the Ba/AI productivity index and AMS radiocarbon dating to define the timings of S1 formation. The most rapidly accumulated S1 sediments (>10 cm kyr^-1) are
unaffected by substantial post depositional oxidation because the Ba/Al index correlates with Corg throughout the visual S1 units. Low accumulation rate S1 sediments (< 5 cm kyr⁻¹) consistently indicate a duration between <10,000 and 5300 marine radiocarbon convention years B.P., but more rapidly accumulated S1 sediments generally indicate a somewhat shorter duration between ~9500 and 6000 years B.P. This difference is interpreted as an artifact of bioturbation on either or both the Ba/Al index and the dated foraminifera in slowly accumulated sediments rather than a water depth effect.

The S1 unit in the Adriatic Sea core studied has a shorter duration than in any other core, which is interpreted to mean that while ventilation may have been generally restricted during the S1 episode, it may not have been shut down fully or continuously. In this and two other cores from the north of the eastern Mediterranean basin, all from 1000-2200 m water depth, a simultaneous decrease in Corg and Ba/Al levels during S1 occurs around 7500 radiocarbon years B.P. It is suggested that this “double sapropel” phenomenon is caused by a temporary resumption of ventilation in the source areas of new deep water (the Adriatic and Aegean Seas to the north of the basin) during the brief interval of global cooling at 8 kyr in S1 time. This same cooling has already been reported in and around the eastern Mediterranean basin from pollen records, and an apparently simultaneous increase in deep water oxygenation has been reported in benthic foraminiferal records.

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