

## LETTERS

# Synchronous basin-wide formation and redox-controlled preservation of a Mediterranean sapropel

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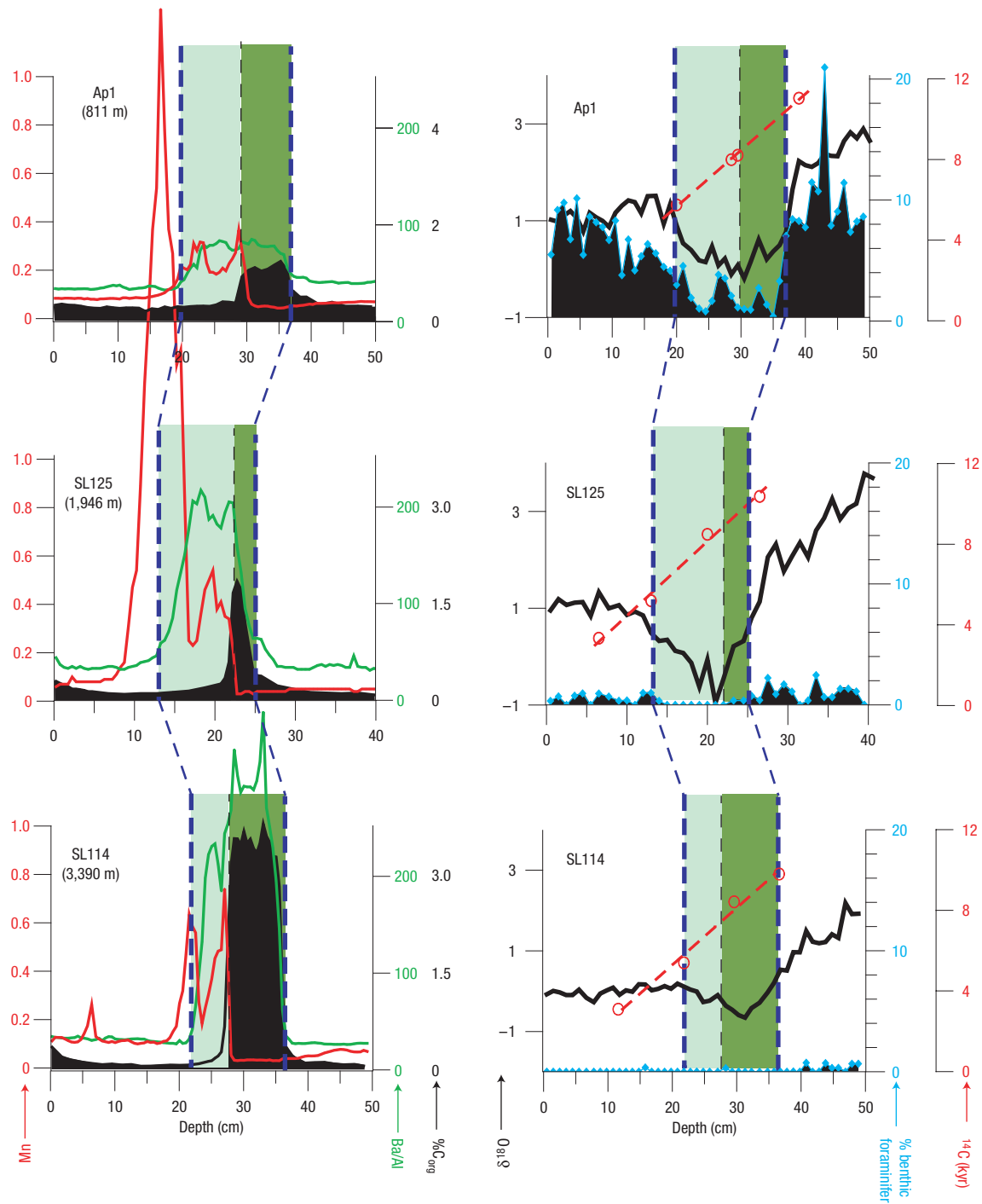
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Organic-rich sedimentary units called sapropels have formed repeatedly in the eastern Mediterranean Sea, in response to variations of solar radiation. Sapropel formation is due to a change either in the flux of organic matter to the sea floor from productivity changes or in preservation by bottom-water oxygen levels. However, the relative importance of surface-ocean productivity versus deep-water preservation for the formation of these organic-rich shale beds is still being debated, and conflicting interpretations are often invoked<sup>1–7</sup>. Here we analyse at high resolution the differences in the composition of the most recent sapropel, S1, in a suite of cores covering the entire eastern Mediterranean basin. We demonstrate that during the 4,000 years of sapropel formation, surface-water salinity was reduced and the deep eastern Mediterranean Sea, below 1,800 m depth, was devoid of oxygen. This resulted in the preferential basin-wide preservation of sapropel S1 with different characteristics above and below 1,800 m depth as a result of different redox conditions. We conclude that climate-induced stratification of the ocean may therefore contribute to enhanced preservation of organic matter in sapropels and potentially also in black shales.

Sapropels have formed repetitively in the eastern Mediterranean in response to solar insolation variations (see the Supplementary Information). Generally, the balance between the flux of organic matter to the sea floor and its oxidation by water column O<sub>2</sub> results in organic carbon (C<sub>org</sub>) contents of 0.2–2% in oceanic sediments. The Holocene eastern Mediterranean sediment is characterized by C<sub>org</sub>-poor sediments (0.1–0.2% (refs 3–9)) that are interrupted by a distinct interval of C<sub>org</sub>-rich sapropel S1 sediments (~2%). The sapropel unit is thought to be associated with enhanced productivity or with preservation due to sedimentary or even bottom-water anoxia<sup>3–9</sup>. The transition from anoxic to oxic sedimentary conditions is most prominently signalled by the distinct Mn peak at the S1 upper boundary<sup>6–9</sup>. The upper part of sapropel S1 has suffered post-depositional oxidation, which removed most of the C<sub>org</sub> content but not the biogenic Ba (barite). The latter can thus be taken as a primary signal reflecting initial

C<sub>org</sub> accumulation rates<sup>6–9</sup> (see the Supplementary Information). The close relationship of sapropel formation with orbital precession implies that an enhanced flux of fresh water to the surface eastern Mediterranean Sea must be involved in their formation<sup>10–12</sup>. The freshwater input that drove S1 formation is revealed in the more negative surface-ocean δ<sup>18</sup>O values measured basin-wide in the shallow-dwelling planktonic foraminifer *Globigerinoides ruber*. This reduced surface-water salinity began ~10,500 <sup>14</sup>C yr BP, systematically before sapropel formation started, and continued until 5,000 <sup>14</sup>C yr BP, after sapropel formation ended (Figs 1,2). S1 formation as defined on the Ba/Al and %C<sub>org</sub> criteria began at ~9,770 ± 350 <sup>14</sup>C yr and on the Ba/Al and Mn/Al criteria finished at ~5,710 ± 440 <sup>14</sup>C yr BP, indicating nearly synchronous sapropel formation at all water depths (Fig. 2).

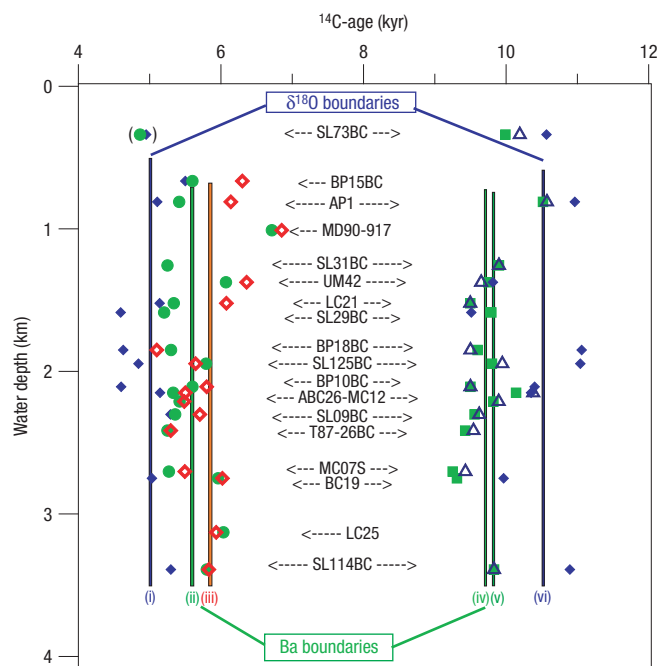
A synchronous basin-wide time slice can be illustrated only for the unoxidized lower fraction of sapropel units, and we use the 8–8.5 <sup>14</sup>C kyr which is still preserved in most S1 examples (Fig. 2; Supplementary Information, Fig. S3). For these unaltered samples, the C<sub>org</sub> content, Ba/Al ratio and S content all increase with water depth, as noted previously<sup>13</sup> (not shown in figure). An objective comparison between sediments from different cores and water depths requires conversion from concentrations into fluxes (see the Supplementary Information). This requires accurate dating, and thus for sapropels is limited to the most recent S1. The non-sapropel C<sub>org</sub> fluxes from 5.0–5.5 kyr are low and even decrease slightly as a function of water depth (Fig. 3b), consistent with the commonly reported decrease with water depth caused by continuing C<sub>org</sub> remineralization during settling through an oxygenated water column. In contrast, the preserved C<sub>org</sub> and biogenic-Ba fluxes for 8–8.5 kyr in sapropel times increase down to ~1.8 km water depth and remain approximately constant at all greater depths (Fig. 3b,c). This is incompatible with a fully oxygenated water column. Furthermore, the biogenic-calcite fluxes versus water depth for the 8–8.5 kyr time slice remain constant (Fig. 3a). Thus, the major differences that occur in the preserved biogenic-C<sub>org</sub> and -Ba fluxes are not reflected in other sedimentary components.



**Figure 1** Detailed sedimentary profiles for shallow–intermediate–deep-water cores Ap1–SL125–SL114 (811–1,946–3,390 m water depth). Mn (red),  $C_{org}$  (black), Ba/Al (green) (left panel) and  $\delta^{18}O_{ruber}$  (black), % benthic foraminifers (blue) and  $^{14}C$  age (red) (right panel) versus depth in sediment in Ap1 (811 m water depth), SL125 (1,946 m water depth) and SL114 (3,390 m water depth). From left to right, vertical dashed line boundaries represent: top of initial S1 unit ( $5.71 \pm 0.44$   $^{14}C$  kyr), top of residual S1 unit and bottom of S1 unit ( $9.77 \pm 0.35$   $^{14}C$  kyr). Post-depositional oxidation has degraded the upper part (light-green shading) of the initial sapropel unit.

In sapropel times, the  $\%C_{org}$  and Ba/Al values for our basin-wide cores are consistently related to water depth but are unrelated to spatial differences or distance to land. This clear relationship is supported by a similar depth-related trend observed in a suite of seven cores from 818–1,809 m water depth from one location, Erathostenes Seamount ( $\sim 34^{\circ} 30' N$ ,  $33^{\circ} 30' E$ ). The

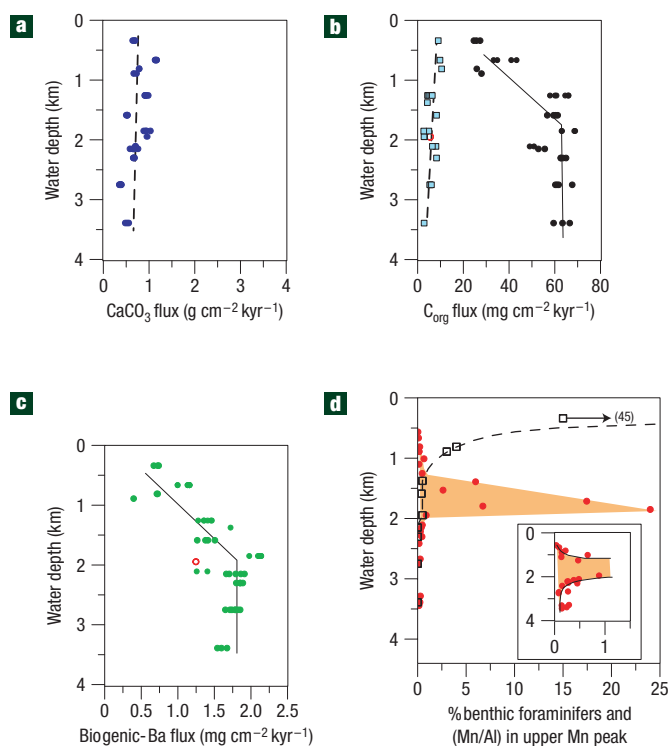
alternative three possibilities that could produce differences in the  $C_{org}$  contents of a single bed as a function of water depth are: a consistent change in grain size, dilution by other sedimentary components and improved preservation. In the absence of any systematic change of grain size or sedimentation rate versus water depth or  $C_{org}$  content, the first two arguments are rejected, leaving



**Figure 2** Age (in uncorrected  $^{14}\text{C}$  kyr) versus water depth for various distinct boundaries associated with sapropel S1 formation. Vertical lines indicate: (i), (blue:  $5.01 \pm 0.30$ ) and (vi), (blue:  $10.53 \pm 0.55$ ) top and bottom of interval with low  $\delta^{18}\text{O}_{\text{ruber}}$  values (blue diamonds); (ii), (green:  $5.57 \pm 0.43$ ) and (iv), (green:  $9.72 \pm 0.33$ ) top and bottom of interval with enhanced Ba/Al values (green circles and squares); (iii), (red:  $5.85 \pm 0.44$ ) upper manganese peak (red circles) coincident with the end of S1; (v), (dark green:  $9.81 \pm 0.37$ ) bottom of interval with enhanced  $C_{\text{org}}$  (black triangles) values. The combined evidence results in S1 upper and lower boundaries with mean ages of  $\sim 5,710 \pm 440$   $^{14}\text{C}$  yr BP (defined by Ba/Al and Mn/Al) and  $\sim 9,770 \pm 350$   $^{14}\text{C}$  yr (defined by Ba/Al and  $\%C_{\text{org}}$ ) (calibrated ages are:  $6.1 \pm 0.5$  and  $10.8 \pm 0.4$  kyr cal. BP). Not all cores had a distinct upper Mn peak or full penetration; the top of the S1 unit in SL73BC was bioturbated so that there was no clear upper Mn-peak maximum and the upper Ba/Al and  $\delta^{18}\text{O}$  limits were uncertain.

improved preservation as the main cause for the observed  $C_{\text{org}}$  trend versus water depth.

In the present eastern Mediterranean, the extensive remineralization of  $C_{\text{org}}$  is caused by the well-mixed water column that has high dissolved  $\text{O}_2$  contents at all depths due to the regular formation of new deep and bottom waters in the Adriatic and Aegean seas<sup>14–16</sup>. The low and slightly decreasing  $C_{\text{org}}$  flux with water depth for the 5–5.5  $^{14}\text{C}$  kyr time slice is consistent with such a fully oxic water column. In contrast, low  $\text{O}_2$  contents in bottom waters are indicated during sapropel formation by (1) low or absent concentrations of benthic foraminifera in sapropel sediments<sup>16</sup> (Fig. 1); (2) formation of pyrite with a relatively light  $\delta^{34}\text{S}$  ( $-40\%$ ) that indicates that anoxic sulphidic conditions must have developed within the upper few centimetres of the sediments, thus at most leading to a slight decrease in the sulphate concentration in surficial pore water and near-bottom water<sup>17</sup>; (3) the rapid degradation of S1 organic matter if exposed to  $\text{O}_2$  (ref. 18); and (4) an excellent preservation of delicate organic dinoflagellate cysts and tree pollens in visual residual sapropels<sup>19,20</sup> that retain high  $\%C_{\text{org}}$  and Ba/Al. In contrast, organic dinoflagellate cysts and pollen are rare if present in the overlying oxidized sapropel, in accordance with extensive ( $>90\%$ ) degradation of bulk organic matter even though Ba/Al remains elevated because of the initial enhanced  $C_{\text{org}}$  fluxes. In



**Figure 3** Preserved fluxes of calcite,  $C_{\text{org}}$  and biogenic Ba, and of the maximum Mn/Al ratio, versus water depth for  $^{14}\text{C}$ -dated basin-wide cores. **a**, Calcite ( $\text{CaCO}_3$ ) for time interval 8.0–8.5  $^{14}\text{C}$  kyr. **b**,  $C_{\text{org}}$  for the time intervals 5–5.5  $^{14}\text{C}$  kyr (blue squares) and 8.0–8.5  $^{14}\text{C}$  kyr (black circles). **c**, Biogenic Ba for the time interval 8.0–8.5  $^{14}\text{C}$  kyr. Biogenic Ba = total Ba –  $0.033 \times \text{Al}$  (ref. 28). The open red circle in **b, c** represents data from the oxidized part of the upper S1 unit in core SL125. **d**, % benthic foraminifers (open squares) and the maximum Mn/Al value (red circles) for the upper Mn peak in each core at  $\sim 5.7$   $^{14}\text{C}$  kyr. Inset: The enlarged lower portion of the Mn peak. Water content data were not available for all  $^{14}\text{C}$ -dated cores; Marion Dufresne cores have been excluded as the upper sections of this type of core are often reported to have been ‘stretched’<sup>29</sup>.

summary, bottom waters were certainly low in oxygen and possibly oxygen-free during sapropel deposition, in contrast to the oxic bottom-water conditions before and after sapropel times that resulted in extensive  $C_{\text{org}}$  degradation. Enhanced  $C_{\text{org}}$  preservation in low-oxygen environments must be critical in the formation of sapropel and other organic-rich units.

Sedimentary organic matter preservation seems to be controlled by the average time that accumulating  $C_{\text{org}}$  resides in oxic conditions at or near the water–sediment interface<sup>21–23</sup>, concurring with our observations that the highest  $C_{\text{org}}$  contents and an absence of benthic foraminifera occur in S1 units from water depths  $> 1.8$  km. Oxygen supplied with newly formed deep water must have rarely reached the deepest basin during full sapropel S1 times to allow development of more intense suboxic conditions and an improved organic matter preservation. In contrast, the lower values of the  $C_{\text{org}}$  in S1 units from shallower water depths imply that the frequency of ventilation events that reached these shallower depths was higher than that reaching water depths  $> 1.8$  km during sapropel times. This is in accordance with an enhanced freshwater supply during S1 times, indicated by a more negative  $\delta^{18}\text{O}$ , and a consequent lower density of the new deep water that can be formed from less-saline surface waters. This interpretation is also consistent with modelling exercises undertaken on eastern Mediterranean

circulation that indicate new deep water sinking to shallower depths during sapropel times than at present<sup>24,25</sup>. The gradually changing sea surface salinities would then result in a shoaling in the average depth achieved by newly formed deep water at the onset of sapropel formation and a return to greater depths when sapropel formation ceased. The former, and by inference the latter, has been estimated to take a few hundred years. This would explain the fact that  $\delta^{18}\text{O}_{\text{ruber}}$  and by implication sea surface salinities were lower for a slightly longer period (10.4–5.0  $^{14}\text{C kyr BP}$ ) than the actual formation period of S1 (9.8–5.7  $^{14}\text{C kyr BP}$ ). Thus, the longer period of reduced sea surface salinities is consistent with a more limited period of deep-water suboxic conditions.

Basin-wide parallel increases in  $C_{\text{org}}$  and biogenic Ba fluxes with water depth as illustrated for the time interval 8–8.5  $^{14}\text{C kyr}$  are evidence of their concomitant preservation (Fig. 3b,c). Ventilation events would not only introduce oxygen to the deep water thus resulting in enhanced degradation of  $C_{\text{org}}$  until the introduced oxygen was consumed, but they would also bring in surface waters with a lower barite saturation (lower dissolved Ba content) thus promoting enhanced barite dissolution at depth<sup>26</sup>.

Resumption of regular ventilation of the entire water column at the end of the sapropel period also explains the basin-wide occurrence of the (upper) Mn-rich layer that is observed at the top of each S1 sapropel unit<sup>6–9</sup> (Figs 1–3). The lower Mn peak also seen in most cores is a diagenetic product of later oxidation<sup>7</sup>. The upper Mn peak is not accompanied by any Fe enrichment, which indicates that the deep-water suboxic conditions on average did not surpass the  $\text{Mn}^{2+}/\text{MnO}_2$  redox couple. In other words, it is unlikely that substantial reduction of deep-water sulphate content or related barite mobilization has occurred during S1 formation. At greater water depths where oxygen is continuously low or absent, sedimentary Mn would dissolve and diffuse out of the sediments into the water column, but this dissolved Mn would re-precipitate whenever well-oxygenated water was encountered higher in the water column. The very large upper Mn peak ('bathtub ring') found in all cores taken around 1.5–2 km water depth (for example, core SL125 in Figs 1 and 3d) with maximum contents of 17–26% Mn for 5-mm-thick sediment intervals in cores from ~1.8 km depth (cores BP018 and PS19BC) clearly indicate that the boundary between near-permanently suboxic waters and waters that more frequently contained some  $\text{O}_2$  was around 1.8 km. In addition, the basin-wide occurrence of cores with elevated Mn contents (marked with '+' in Supplementary Information, Fig. S1) and of the discrete sedimentary Mn increase at 1.5 and 2.0 km (Fig. 3d, inset) all indicate that this has been a basin-wide phenomenon. The observed constant high  $C_{\text{org}}$  and bio-Ba fluxes below 1.8 km are further evidence for their enhanced preservation below this depth level. In contrast, the decrease in these fluxes with decreasing water depth above this level is consistent with the near-continuous presence of benthic foraminifera<sup>16</sup>, and the intermittent presence of oxygen replenished at increasing frequency. The age of the upper Mn peak for all cores above 1.8 km being older than for those below this boundary concurs with such earlier oxygenation. All indications are thus consistent with reduced surface-water densities resulting in intermediate rather than deep-water formation during sapropel formation.

To our knowledge this is the first comprehensive evidence that the whole eastern Mediterranean basin has been predominantly oxygen-free below ~1.8 km during 4 kyr of basin-wide synchronous sapropel S1 formation, 9.8–5.7  $^{14}\text{C kyr}$  (or 10.8–6.1 kyr cal. BP). In addition, our results indicate that preservation of sedimentary organic matter is directly related to the frequency and duration of bottom-water redox conditions, which thus is a dominant prerequisite for the occurrence and extent of sapropel S1 and by inference of other organic-rich units.

## METHODS

Major and minor elements were analysed by inductively coupled plasma atomic emission spectrometry, after a routine digestion; total-C and organic-C content were determined respectively before and after being decarbonated, using a Fisons Instruments NCS NA 1500 analyser<sup>7,23</sup>. Similar %  $\text{CaCO}_3$  values were calculated from the % total-C and from %Ca. In one area, a substantial amount of aragonite with inferred near-coastal origin occurred in three cores<sup>27</sup> (BP10, BP15, BP18); this contribution was small in other cores. The fluxes in Fig. 3 are reported as calcite.

The  $\delta^{18}\text{O}$  analyses were made on *G. ruber* planktonic foraminifer in the 300–400  $\mu\text{m}$  size range using a VG SIRA-24 mass spectrometer equipped with an Isocarb phosphoric acid bath. Accelerator mass spectrometry radiocarbon analysis was carried out on cleaned and handpicked planktonic foraminifera (*G. ruber*) 150–400  $\mu\text{m}$  in size at the Utrecht University accelerator mass spectrometry facility (G. J. van de Graaff Laboratorium) or in mixed planktonic foraminifera of the same size at the NERC Radiocarbon Laboratory. As residence times may have been different for different areas and for sapropel versus non-sapropel periods, we have chosen to report our data throughout the text as uncalibrated  $^{14}\text{C}$  ages. However, for the convenience of a direct comparison of the final upper and lower boundary ages with other calibrated ages, we also give calibrated ages in the caption of Fig. 3 and in the last paragraph (using Calib 5.0.2).

Calculation of sediment component fluxes requires that the sediments have been accurately dated, when:

$$\text{Flux} = \text{concentration in } \mu\text{g g}^{-1} \times \text{dry sediment density in } \text{g cm}^{-3} \times \text{accumulation rate in cm kyr}^{-1}.$$

This conversion takes variations in sediment accumulation rate and in water content into account. For the sediments in this study, variations in sediment accumulation rate were small, but water content increased with organic matter content.

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### Author contributions

G.J.D.L. and J.T. were responsible for geochemical results and interpretation; A.R. and C.P.S. contributed to geochemical results; M.S.P., E.E. and C.C. were responsible for micropalaeontological results. All authors agree to all of the content in the manuscript including the data as presented.

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