

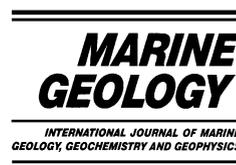


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Controls on phosphorus regeneration and burial during formation of eastern Mediterranean sapropels

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Abstract

The carbon (C) and phosphorus (P) geochemistry of sapropels from four sites in the eastern Mediterranean Sea was determined to obtain more insight into the role of differences in sediment accumulation rates and bottom water anoxia on P regeneration and burial in sediments. Sediment C_{org}/P_{org} (with org = organic) ratios above Redfield indicate enhanced regeneration of P relative to C from organic matter during formation of the most recent sapropel S1 and a Pliocene sapropel (ODP-site 969E; i-282c). Release of P from Fe-oxides was relatively unimportant. Increased burial of Ca-P (authigenic carbonate fluorapatite and/or biogenic hydroxyapatite) occurred but was of minor importance compared to the enhanced P release from organic matter. For sapropel S1, C_{org}/P_{org} and C_{org}/P_{reac} , (with reac = reactive, defined as the sum of organic, Fe-bound, authigenic and biogenic Ca-P) ratios decreased with increasing sedimentation rate and oxygen exposure and decreasing water depth. Whether the water column in the deep basin was dysoxic/semi-euxinic (S1) or euxinic (Pliocene) does not appear to affect the estimated burial efficiencies of P_{org} and P_{reac} . Enhanced C_{org} burial under the euxinic water column explains the much higher C_{org}/P_{org} and C_{org}/P_{reac} ratios in the Pliocene sapropel (on average ~ 2860 and ~ 760 , respectively) compared to sapropel S1 (on average ~ 530 and ~ 160 , respectively).

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1. Introduction

Phosphorus (P) is an essential nutrient for the growth of marine phytoplankton. On geological time scales, it is the limiting nutrient for global marine productivity (Holland, 1978; Broecker, 1982; Tyrell, 1999). P has also been found to limit productivity on shorter time scales in various ma-

rine environments (Benitez-Nelson, 2000), including open ocean, oligotrophic areas in the North Atlantic and North Pacific (Cotner et al., 1997; Karl et al., 1997), the Baltic Sea (Granéli et al., 1990) and the eastern Mediterranean Sea (Krom et al., 1991).

Since burial in sediments is the only sink for P in the marine environment, changes in the burial rate of P can modify the P inventory in the bottom water. Provided there is sufficient vertical mixing to transport dissolved P from the bottom water to the surface water, this can affect primary

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productivity and carbon (C) cycling on both a regional (Slomp et al., 2002; Filippelli et al., 2003) and a global scale (Holland, 1978; Broecker, 1982; Van Cappellen and Ingall, 1994, 1996). The elemental cycles of C and P are coupled via the C/P ratio of the marine phytoplankton and the C/P ratio of the organic matter preserved in marine sediments. The C/P ratio of marine phytoplankton is generally close to the Redfield ratios of 106 (Redfield et al., 1963) or 117 (Anderson and Sarmiento, 1994). The C/P ratio of organic matter buried in marine sediments ($C_{\text{org}}/P_{\text{org}}$), in contrast, varies over a wide range (50–4500; Ingall and Van Cappellen, 1990; Ingall et al., 1993; Anderson et al., 2001). Values of $C_{\text{org}}/P_{\text{org}}$ below the Redfield ratio are mostly found in oxic, low sedimentation rate environments with low C_{org} concentrations. This has been attributed to errors in the C_{org} (e.g. Anderson et al., 2001) and P_{org} analyses (e.g. Mach et al., 1987) and to concentration of refractory detrital organic compounds enriched in P or of in situ synthesized bacterial remains (Ingall and Van Cappellen, 1990). Values of $C_{\text{org}}/P_{\text{org}}$ above the Redfield ratio indicate either a terrestrial source of organic matter (Ruttenberg and Goni, 1997) or preferential regeneration of P relative to C during organic matter decomposition. This preferential regeneration is most pronounced in sediments overlain by anoxic bottom waters (Ingall et al., 1993; Ingall and Jahnke, 1997; Van Cappellen and Ingall, 1994, 1997; Eijssink et al., 1997; Schenau and De Lange, 2001; Slomp et al., 2002) when it may be further augmented by phosphate release from Fe-oxides upon their reductive dissolution (e.g. Einsele, 1936; Mortimer, 1941; McManus et al., 1997; Colman and Holland, 2000). There are two feedback mechanisms, however. First, the P released from the organic matter can precipitate in the sediment as authigenic carbonate fluorapatite (CFA or P_{auth} ; e.g. Ruttenberg and Berner, 1993; Slomp et al., 1996a; Schenau et al., 2000; Filippelli, 2001). Second, enhanced burial of biogenic Ca-P (P_{bio} ; fish debris, hydroxyapatite) can occur in sediments overlain by anoxic bottom waters (Schenau and De Lange, 2000; Slomp et al., 2002). Both Ca-P forms can act as a sink of reactive P (P_{reac}), which is defined as the sum of

organic, Fe-bound, authigenic and biogenic P (Ruttenberg, 1993). This makes it important to evaluate not only sediment $C_{\text{org}}/P_{\text{org}}$ ratios but also $C_{\text{org}}/(P_{\text{org+auth+bio}})$ (Slomp et al., 2002) and $C_{\text{org}}/P_{\text{reac}}$ ratios (e.g. Anderson et al., 2001; Filippelli, 2001) to assess the potential effects of preferential regeneration of P relative to C_{org} on water column chemistry and marine productivity.

The type of sedimentary environment plays an important role in determining the regeneration and burial of P in marine sediments (e.g. Föllmi, 1996; Filippelli, 1997; Delaney, 1998). Key factors on short times scales include the redox conditions in the sediment and water column (Ingall et al., 1993; Ingall and Jahnke, 1994; Sundby et al., 1992; McManus et al., 1997; Slomp et al., 1998; Colman and Holland, 2000; Filippelli, 2001), the supply of P to the sediment and its reactivity or solubility (e.g. Van Cappellen and Berner, 1988; Schenau and De Lange, 2001), the sediment accumulation rate (Ingall and Van Cappellen, 1990; Filippelli, 1997) and the rate of sediment mixing (e.g. Slomp et al., 1996a; Schenau et al., 2000). The relative importance of each of these factors in determining the P burial efficiency (BE, defined as the fraction of the deposited P that is buried in the sediment) in different types of marine sediments is still incompletely understood.

We expect that P burial efficiencies are lowest and enhanced regeneration of P relative to C is most pronounced in sedimentary environments where net sediment accumulation rates are low, sediment mixing is absent and both a major part of the water column and the sediment are dysoxic or anoxic. In such environments, P is preferentially released from organic matter in the water column and/or close to the sediment–water interface in the sediment. Release of P from reductively dissolving Fe-oxides may be an additional source of P. CFA formation is expected to be limited due to low porewater phosphate concentrations but biogenic Ca-P burial may be enhanced. This was shown to be the case for the most recent sapropel S1 in the deep-basin of the eastern Mediterranean Sea (Slomp et al., 2002).

In this paper, we use the C and P geochemistry for sapropels from four sites in the eastern Med-

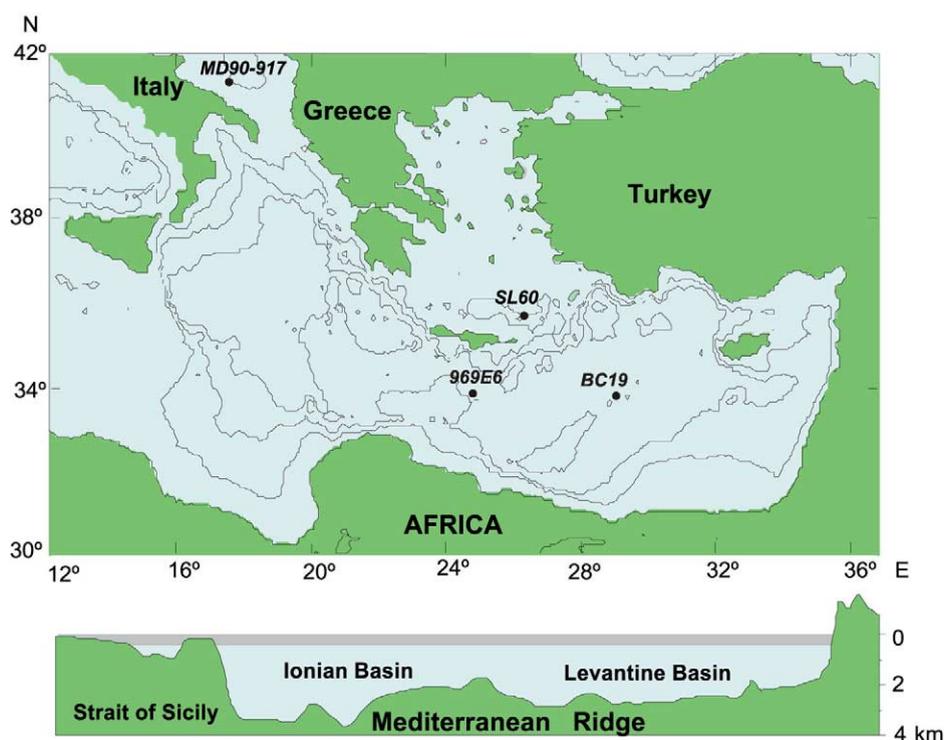


Fig. 1. Sample locations of the four cores studied.

Table 1
Site and sapropel characteristics

	Box core BC19	Piston core SL60	Piston core MD90-917	ODP-core 969E ^a
Location	Levantine Basin	SE Aegean Sea	Adriatic Sea	Levantine Basin
Latitude	33°47.85'N	35°39.69'N	41°18'N	33°50.5'N
Longitude	28°36.50'E	26°34.99'E	17°37'E	24°53.0'E
Cruise	<i>Marflux-I MD69</i>	<i>Medineth</i>	— ^b	ODP Leg 160
Research Vessel	<i>Marion Dufresne</i>	<i>Logachev</i>	— ^b	Joides resolution
Water depth (m)	2750	1522	1010	2201
Sedimentation rate (cm/kyr) ^c	2.9	8.4	~ 10	3
Sapropel	S1	S1	S1	i-282c
Epoch	Holocene	Holocene	Holocene	Pliocene

^a Section 160-969E06H-6 from 50.7 mbsf, insolation cycle i-282c.

^b Sampled at the core archive at the Laboratoire des Sciences du Climat et de L'Environnement, Gif-sur-Yvette.

^c Sources of sedimentation rates: BC19: Slomp et al. (2002); SL60: estimated from thickness of sapropel in core SL60 and radiocarbon dates for the S1 boundaries in core LC21 from the same site (Mercone et al., 2000, 2001); MD90-917: based on radiocarbon dates of Mercone et al. (2000), taking into account that the Calypso corer extends upper core sections by an average factor of 2 without affecting the stratigraphy (Thouveny et al., 2000); 969E: Emeis et al. (1996).

iterranean Sea to obtain more insight into the factors controlling P regeneration and burial in slowly accumulating sediments overlain by dysoxic or anoxic bottom waters. We look at the combined effect of differences in sediment accumulation rates and oxygen exposure by comparing $C_{\text{org}}/P_{\text{org}}$ and $C_{\text{org}}/P_{\text{reac}}$ ratios for 3 sites containing sapropel S1 (dysoxic/semi-euxinic bottom water; with oxygen exposure increasing with decreasing water depth; see Section 2). We study the effect of different water column redox conditions by comparing $C_{\text{org}}/P_{\text{org}}$ and $C_{\text{org}}/P_{\text{reac}}$ ratios and C and P burial efficiencies for the most recent sapropel S1 to that of a Pliocene sapropel (euxinic bottom water) at two sites with comparable sedimentation rates. We conclude with a brief discussion of the general implications of our findings.

2. Materials and methods

Samples for box and piston cores from four locations in the eastern Mediterranean Sea were selected for this study (Fig. 1; Table 1). Sedimentation rates range from 2.9 to ~ 10 cm/kyr. The general geochemistry of the sediment at all of these sites has been described extensively in the past (e.g. BC19: Slomp et al., 2002; SL60 (LC21-site) and MD90-917: Mercone et al., 2000, 2001; 969E: Bosch et al., 1998; Passier and De Lange, 1998; Passier et al., 1999a,c; Nijenhuis and De Lange, 2000).

Sapropels in the eastern Mediterranean Sea (including the SW-Aegean and Adriatic) are the result of climatic changes which led to periods of decreased circulation, increased surface water productivity, dysoxic or anoxic bottom waters and increased preservation of organic matter (Calvert et al., 1992; Rohling, 1994; Thomson et al., 1999). Sapropel S1 was deposited between 6.0 and 9.5 kyr BP (Mercone et al., 2000) and is relatively organic-poor (up to 4 wt% C_{org}). That the bottom water was dysoxic or semi-euxinic during S1 formation has been deduced from, e.g. the trace metal, Fe and S geochemistry, abundances of benthic foraminifera, evidence for occasional bioturbation and preservation efficiencies of C_{org} in this sapropel (Passier et al., 1999c; Mercone et al., 2001;

Slomp et al., 2002). There is a close linear relation between C_{org} and water depth during sapropel S1, which has been explained as the result of a decrease in availability of oxygen in the water column with water depth (Murat and Got, 2000). Observed abundances of oxiphilic benthic foraminifera support such a trend of bottom water oxygen with water depth and indicate that bottom water anoxia during S1 times may have been spatially restricted and/or of an intermittent nature, particularly at shallower sites (Casford et al., 2003). The Pliocene sapropel has an age of 2.943 Ma (Lourens et al., 1996; Passier et al., 1999a) and is laminated and extremely organic-rich (up to 27 wt% C_{org}). The presence of specific molecular fossils and the trace metal, Fe and S geochemistry of this sapropel (Bosch et al., 1998; Passier et al., 1999a) provide evidence for its deposition under a euxinic (i.e. sulfide-rich) water column that reached into the photic zone. The organic matter in these sapropels is predominantly of marine origin (Emeis et al., 1996; Bosch et al., 1998; Bouloubassi et al., 1999).

Sediment samples (0.5 and 1 cm depth resolution) were freeze-dried and ground in an agate mortar (BC19, SL60, 969E) or in a tungsten carbide swing mill (MD90-917). For cores BC19, SL60 and 969E, total concentrations of Al, S, Ba, Ca and P were determined after digestion in a mixture of HF, HNO₃ and HClO₄ and final solution in 1 M HCl using ICP-OES (Perkin Elmer Optima 3000). For core 969E, Ba in sapropel samples was determined separately in solutions prepared by the same procedure but using only 40 mg of sample to prevent BaSO₄ precipitation. CaCO₃ concentrations were calculated from total Ca contents. Ca in clays has been shown to account for less than 1% of total Ca and thus is negligible (Rutten, 2002). The reproducibility of the measurements was monitored by including laboratory standards. The relative error in the analysis was <5% for all elements. C_{org} was determined on a Fisons Instruments CNS NA 1500 analyzer. Inorganic C was removed prior to the analysis by shaking the sample with 1 M HCl twice (12 h and 4 h). The sample was then rinsed twice with demineralized water, freeze-dried and ground in an agate mortar. C_{org} contents were

corrected for carbonate weight loss during the HCl dissolution step. The relative error in the analysis was less than 1%.

For core MD90-917, total concentrations of Al, S, Ba and Mn were determined using a Philips PW1400 automatic sequential wavelength dispersive X-ray fluorescence spectrometer on samples prepared either as pressed powder pellets or as lithium meta-tetraborate fusion discs. C_{org} and CaCO_3 were determined coulometrically via the release of CO_2 . Further analytical details are given by [Mercone et al. \(2001\)](#). Total concentrations of P of a selected number of samples (19) were determined after digestion in a mixture of HF, HNO_3 and HClO_4 and final solution in 1 M HCl using ICP-OES (Perkin Elmer Optima 3000).

Sediment P forms in selected samples from cores BC19, SL60, MD90-917 and 969E were determined using a sequential extraction procedure modified from that of [Ruttenberg \(1992\)](#) by [Slomp et al. \(1996a\)](#). Briefly, inorganic sediment P was fractionated into Fe-bound P, authigenic+biogenic Ca-P and detrital Ca-P. Fe-bound P was determined as the sum of the P extracted with citrate–dithionite–bicarbonate (CDB: 0.30 M Na-citrate, 1.0 M NaHCO_3 and 0.5 g of Na-dithionite in 22.5 ml of citrate bicarbonate solution, pH=7.3, 8 h, 20°C) and a subsequent wash step with 1 M MgCl_2 . The sediment residue was then rinsed with 1 M Na-acetate buffer (pH=4, 6 h, 20°C) and a 1 M MgCl_2 wash solution. Authigenic+biogenic Ca-P was calculated as the sum of the P extracted in these last two steps. The sediment residue was then treated with 1 M HCl (24 h, 20°C) and the amount of extracted P was used as a measure of detrital Ca-P. With the exception of core MD90-917, all extractions were carried out in duplicate. P_{org} was determined non-sequentially as the difference between total P and 1 M HCl extractable P (24 h). Inorganic P concentrations determined as the sum of Fe-bound P, authigenic P and detrital Ca-P were approximately equal to P concentrations obtained with 1 M HCl in the one-step procedure (linear regression, slope=0.997; $r^2=0.79$).

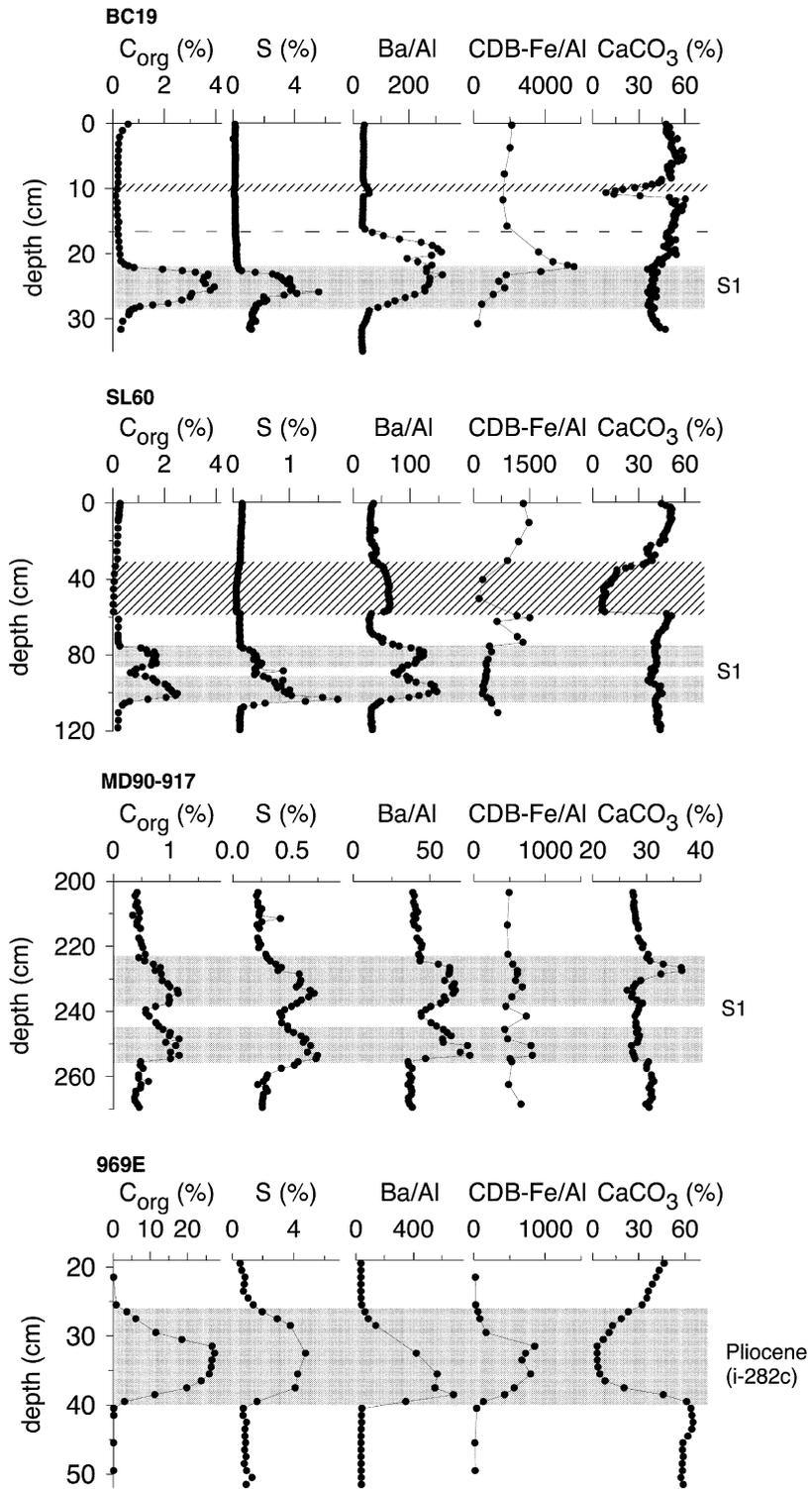
The P, Fe and Mn concentrations in the CDB solutions were measured using ICP-OES (Spectro Analytical Instruments; detection limits for P, Fe

and Mn were 0.05, 0.03 and 0.03 mg/l, respectively). All other P analyses were carried out using a Perkin Elmer spectrophotometer with the method of [Strickland and Parsons \(1972\)](#). The matrix of the blanks and standards matched the matrix of each sample solution analyzed. A reference sample was included in each extraction procedure and the relative error in the analysis ranged from ~5 to 30%, with the highest values for the P forms with the lowest concentration. The relative error of the individual P extractions was generally ~5%, with the exception of the CDB-step (~10%). CDB-extractable Fe was used as a measure of the Fe bound in Fe oxides and FeS ([Slomp et al., 1996b](#)).

3. Results

3.1. General sediment geochemistry

Cores BC19 and SL60 contain an ash layer which is identified as being from the Minoan eruption of Santorini at 3.6 kyr BP ([Fig. 2](#); [Bruins and Van der Plicht, 1996](#)). In all cores, the dark-colored visual sapropel is characterized by C_{org} (0.6–27%) and S (ca. 0.5–5%) concentrations that are higher than in the surrounding sediment. In cores SL60 and MD90-917, sapropel S1 consists of two dark-colored lobes, separated by a light-colored section. Maximum C_{org} contents in the Pliocene sapropel in core 969E are up to a factor 24 higher than values observed for the S1 sapropel. The depth profile of Ba/Al in core BC19 shows a Gaussian-shape starting at the base of the visual sapropel and returning to baseline values at ca. 5.5 cm above the top of the visual sapropel. Ba/Al ratios in cores SL60 and MD90-917 are elevated in the two dark-colored lobes of the sapropel. High CDB-Fe/total Al ratios are found above the visual sapropel in cores BC19 and SL60 and in the visual sapropel of cores MD90-917 and 969E. Apart from the diagenetic CaCO_3 peak in the sapropel of core MD90-917 (consisting of mixed [Ca, Mn(II), Mg] carbonate; [Mercone et al., 2001](#)), CaCO_3 concentrations in the ash layer and in the sapropels are generally lower than in the surrounding sediment. The sapropel in



core 969E is particularly poor in CaCO_3 due to the absence of both benthic and planktonic foraminifera (Nijenhuis and De Lange, 2000).

3.2. Solid phase P forms

Total P concentrations in all non-sapropel intervals are generally relatively constant at 10–16 $\mu\text{mol g}^{-1}$ (Fig. 3; Table 2). All sapropels are enriched in P relative to surrounding layers. In cores BC19 and SL60, additional enrichments, which consist of Fe-bound P, occur at the top of the visual sapropel S1. P_{org} concentrations in the sapropels are equal to or up to a factor ~ 5 higher than in the surrounding sediment. The sapropels are all locally enriched in authigenic+biogenic Ca-P. In core BC19, the enrichment can be totally attributed to biogenic P, as was shown by Slomp et al. (2002) using an extraction procedure specific for biogenic P (Schenau and De Lange, 2000). The enrichment in Fe-bound P in 4 samples of the Pliocene sapropel is most likely an artefact of the CDB-extraction. When CaCO_3 concentrations are low, as is the case for these samples (Fig. 2), some fish debris may dissolve in CDB-solutions (Williams et al., 1980; Schenau and De Lange, 2000; Slomp, unpubl. results). Calculated Fe-bound P and authigenic+biogenic P concentrations assuming the Fe-bound P enrichment is actually biogenic P are shown in Fig. 3 and Table 2. Detrital P concentrations in all cores are low and show little variation with depth.

3.3. C and P ratios and burial fluxes

$\text{C}_{\text{org}}/\text{P}_{\text{org}}$ ratios in non-sapropel layers, i.e. in the sediment that was deposited under oxic conditions, range from 6 to 183 (Fig. 4; Table 2). The average ratio calculated from burial fluxes after S1 times for core BC19 is 86 (Table 3). In the S1 and Pliocene sapropels, $\text{C}_{\text{org}}/\text{P}_{\text{org}}$ ratios are generally significantly higher and range from 75

to 1114 and from 870 to 4432, respectively. $\text{C}_{\text{org}}/\text{P}_{\text{reac}}$ ratios in the S1 and Pliocene sapropel (Fig. 4; Table 2) range from 20 to 255 and 248 to 1273, respectively, and thus are lower than $\text{C}_{\text{org}}/\text{P}_{\text{org}}$ ratios. Samples from the light colored section of the S1 sapropel in cores SL60 and MD90-917 have lower $\text{C}_{\text{org}}/\text{P}_{\text{org}}$ and $\text{C}_{\text{org}}/\text{P}_{\text{reac}}$ ratios than the dark colored parts of the sapropel (Fig. 4; Table 2).

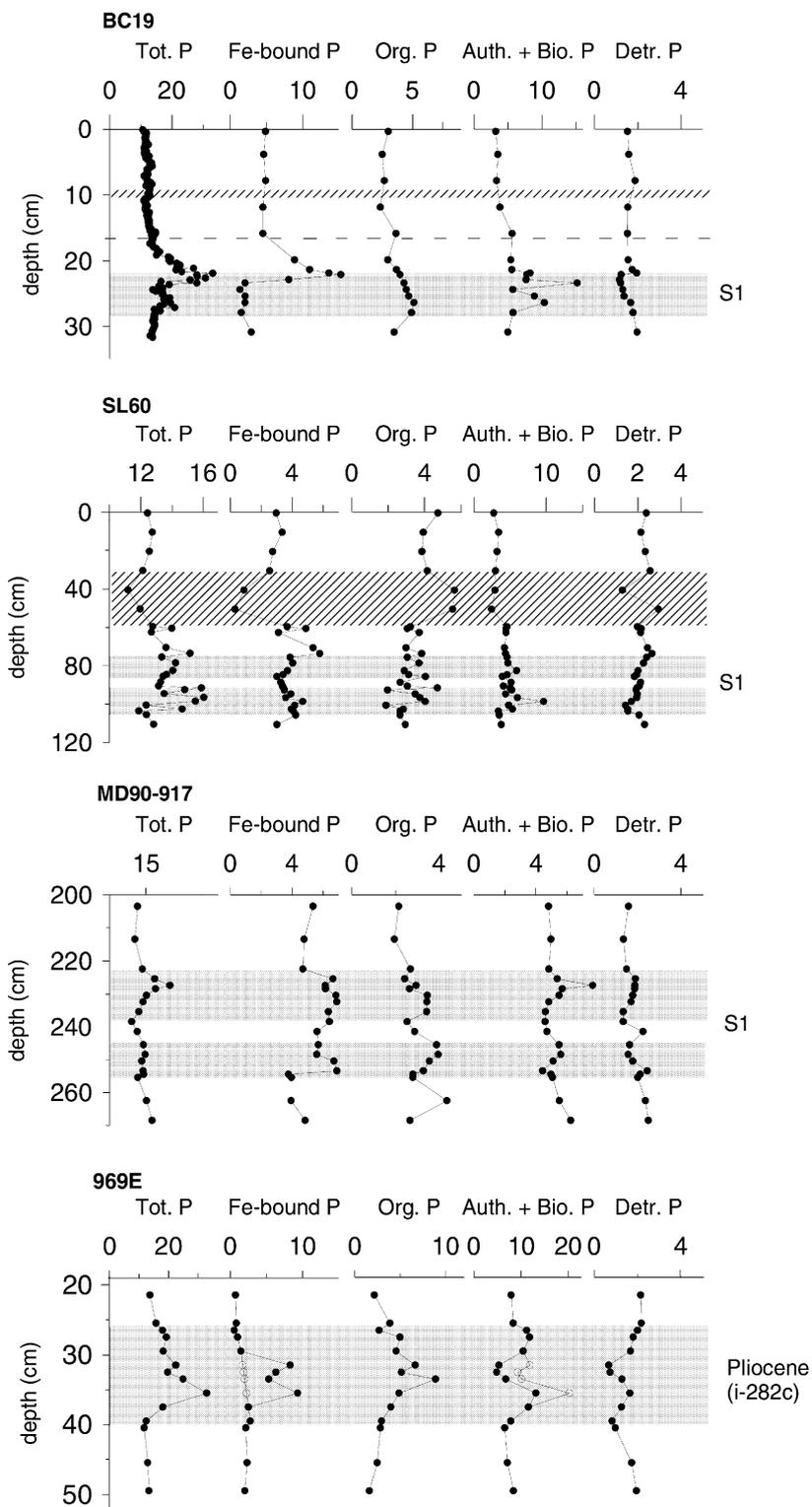
4. Discussion

4.1. The position of the S1 and Pliocene sapropels and the redox front

The zone of elevated Ba concentrations (Fig. 2) indicates the original thickness of the S1-sapropel. The Ba is in the form of biogenic barite and has been shown to be a reliable guide to the position of sapropels in which the initial high C_{org} contents have been partly or completely removed by oxidation (Van Santvoort et al., 1996, 1997; Lange-reis et al., 1997; Thomson et al., 1999). In core BC19, part of S1 is removed due to post-depositional downward oxidation (Van Santvoort et al., 1996; Slomp et al., 2002). The present-day redox front is located at the top of the visual sapropel and the Fe-oxide and Fe-bound P peaks are currently forming through precipitation of upward diffusing Fe^{2+} and HPO_4^{2-} (porewater profiles in Slomp et al., 2002).

The similar trends in the C_{org} and Ba profiles in cores SL60, MD90-917 and 969E indicate that in these cores the sapropel is unaffected by post-depositional oxidation. The interruption of sapropel S1 in core SL60 and MD90-917 centered on 7500 radiocarbon convention years (Mercone et al., 2000, 2001) is believed to be due to a short-term cooling event in which the bottom water ventilation and oxygenation in the Adriatic and Aegean Seas increased temporarily (De Rijk et al., 1999;

Fig. 2. Depth profiles of C_{org} (%), S (%), Ba/Al (ppm⁰%), CDB-Fe/total Al (ppm⁰%) and CaCO_3 (%) for cores BC19, SL60, MD90-917 and 969E. The visual sapropel is indicated by the shaded area. The Santorini ash layer in cores BC19 and SL60 is indicated by the hatched area. The dashed line in the BC19 plots indicates the top of the original sapropel. Ba and Fe profiles are normalized to Al to correct for fluctuations in carbonate content. For core 969E only the depth in the section is indicated.



Mercone et al., 2000, 2001; Casford et al., 2003). No porewater data are available for these cores, therefore it is not possible to determine the exact position of the present-day redox front in the sediment above the sapropel. Since the redox front is expected to move upwards upon sediment accumulation, we expect that in core SL60 the lower Fe-oxide and Fe-bound P enrichments are relicts of a former redox front and are slowly dissolving. The enrichments directly below the ash layer are then most likely actively forming. In cores MD90-917 and 969E, no Fe enrichment is present above the sapropel. Either an oxidation front was never present above these sapropels or the oxidized Fe was reduced and diffused upwards away from the sapropel. The enrichment of CDB-Fe in the sapropel of both cores can be attributed to dissolution of Fe-sulfides, as was shown for core 969E by Passier and De Lange (1998) previously. The amount of CDB-Fe in these enrichments is only $\sim 5\%$ of the total Fe in these sapropels.

Detailed study of both the S1 and Pliocene sapropel has shown that most of the diagenetic alteration of the visual, unoxidized sapropel has taken place during and shortly after its formation. Mn and Fe oxide reduction and methanogenesis in the sapropel are severely restricted due to the absence of significant amounts of reactive oxides (Passier and De Lange, 1998; Slomp et al., 2002) and due to the abundant presence of sulfate in the porewater (Emeis et al., 1996), respectively. The S and Fe geochemistry indicates that post-burial sulfate reduction and pyrite formation have been absent (S1) or limited (Pliocene) (Passier and De Lange, 1998; Passier et al., 1999a,b,c). Apparently, the reactivity of the organic matter is too low to sustain substantial rates of sulfate reduction (De Lange et al., 1994; Passier and De Lange, 1998). In the absence of significant active organic matter decomposition, the chemical signals in the visual sapropel can be used to reconstruct the diagenesis of P during sapropel formation.

4.2. Reconstruction of the sedimentary P cycle during sapropel formation

To obtain insight into the factors controlling P regeneration and burial during formation of the S1 and Pliocene sapropels, the sedimentary P cycle for cores BC19, and 969E was reconstructed using the approach outlined by Slomp et al. (2002) and briefly described here. Cores MD90-917 and SL60 were omitted because of the possible importance of oxic decomposition at these sites (Casford et al., 2003). Deposition rates of the three potential sources of P_{reac} to the sediment, (1) P_{org} , (2) Fe-bound P and (3) biogenic P, were estimated by using burial fluxes of C or P as proxies. Sediment–water exchange rates of HPO_4^{2-} were then calculated as the difference between the depositional and burial flux (Table 4) of P_{reac} . The depositional flux of P_{org} was estimated from the average burial flux of C_{org} (Tables 3 and 4), the BE of C in the sapropel, and the C/P ratio of the deposited organic matter:

$$P_{\text{org}} \text{ deposition flux} = \frac{C_{\text{org}} \text{ burial flux}}{\text{BE}_{C_{\text{org}}}} \times \frac{P_{\text{org}}}{C_{\text{org}}} \quad (1)$$

The Redfield ratio (106) was used as an approximation of the original C/P ratio of the deposited organic matter. Assuming all organic matter remineralization took place by sulfate reduction, the burial efficiencies of C_{org} in the sapropels can be calculated from the integrated amounts of C_{org} and S in the sediments, using appropriate values for sulfide reoxidation (Passier et al., 1999c):

$$\text{BE}_{C_{\text{org}}} = \frac{C_{\text{int}}}{2 \times \left(\frac{100}{100-b} \right) \times S_{\text{int}} + C_{\text{int}}} \times 100\% \quad (2)$$

where b is the percentage of total produced sulfide that was reoxidized, the factor 2 accounts for the fact that 2 mol of C are oxidized per mole of S produced, and C_{int} and S_{int} (both in mol m^{-2}) are the depth integrated amounts of C_{org} and reduced S in and below the sapropel, respectively. Here,

Fig. 3. Solid phase profiles of total P, Fe-bound P, P_{org} , authigenic+biogenic P, and detrital P (closed symbols; all in $\mu\text{mol/g}$) for cores BC19, SL60, MD90-917 and 969E. Open symbols in the plots for core 969E are corrected Fe-bound P and authigenic+biogenic P contents (see text).

Table 2
Sediment P forms in selected samples from cores BC19, SL60, MD90-917 and 969E

Site	Depth (cm)	Total P $\mu\text{mol/g}$	Fe-P $\mu\text{mol/g}$	Org. P $\mu\text{mol/g}$	Auth.+Bio. P $\mu\text{mol/g}$	Detr. P $\mu\text{mol/g}$	$C_{\text{org}}/P_{\text{org}}$ mol/mol	$C_{\text{org}}/P_{\text{reac}}$ mol/mol
BC19	0.4	10.9	4.88	3.01	3.23	1.54	135	36
	3.9	11.3	4.63	2.50	3.53	1.60	76	18
	7.9	12.0	4.89	2.68	3.34	1.89	64	16
	11.9	11.4	4.52	2.35	3.84	1.55	57	12
	15.9	14.8	4.52	3.65	5.62	1.53	47	13
	19.9	19.0	8.89	2.98	5.47	1.57	77	13
	21.4	21.3	10.99	3.69	5.61	1.75	86	16
	21.9	33.1	13.64	nd	8.30	1.96	nd	nd
	22.1	28.0	15.27	3.98	7.80	1.25	173	25
	22.9	25.8	8.08	nd	7.70	1.17	nd	nd
	23.4	28.1	2.06	4.32	15.23	1.21	711	142
	24.4	13.8	1.34	4.51	5.74	1.32	656	255
	25.4	17.4	2.05	4.68	8.91	1.38	687	206
	26.4	19.5	2.05	5.13	10.40	1.68	494	144
	27.9	14.7	1.53	4.94	5.81	1.79	262	106
	30.9	13.5	2.92	3.49	5.02	1.98	86	26
	SL60	0.5	12.4	2.97	4.74	2.75	2.40	50
10.5		12.7	3.36	3.93	3.42	2.15	44	16
20.5		12.6	2.74	3.85	3.19	2.36	40	16
30.5		12.1	2.54	4.16	3.00	2.58	33	14
40.5		11.2	0.89	5.67	2.90	1.30	9	5
50.5		11.9	0.30	5.56	2.44	2.97	6	4
59.5		12.8	3.68	3.23	4.58	1.99	32	9
60.5		14.0	4.89	3.05	4.44	2.16	48	12
62.5		12.7	3.11	3.71	4.44	2.14	50	16
70.5		13.6	5.34	2.99	4.22	2.46	57	14
73.5		15.2	5.77	3.85	4.37	2.67	45	12
75.5		13.3	3.85	3.06	4.60	2.42	75	20
78.5		14.2	4.04	3.70	4.69	2.27	364	108
82.5		14.1	3.69	2.89	5.90	2.03	470	109
84.5		13.6	3.41	3.13	4.59	1.96	450	127
85.5		13.4	3.00	4.05	3.92	1.86	236	87
88.5		13.3	3.27	2.67	5.17	2.14	262	63
90.5		13.1	3.36	3.06	4.08	2.09	239	69
91.5		15.9	3.43	4.70	5.04	1.97	225	80
92.5		14.8	3.49	1.97	5.23	1.93	658	121
94.5		13.5	3.91	3.49	4.39	1.98	408	121
96.5	16.0	3.58	3.75	6.01	1.96	475	134	
98.5	15.5	4.67	4.03	9.64	1.72	465	102	
100.5	12.3	4.16	1.87	4.81	1.44	1114	193	
102.5	14.7	3.95	2.83	5.34	1.55	610	142	
103.5	11.9	4.07	2.66	3.39	1.55	427	112	
105.5	12.4	4.23	2.65	3.50	2.07	146	37	
110.5	12.8	3.01	2.94	3.80	2.32	61	18	
MD90-917	203.5	13.8	5.34	2.15	4.82	1.59	164	29
	213.5	13.4	4.76	1.95	4.96	1.35	179	29
	222.5	14.5	4.69	2.69	4.83	1.49	175	36
	225.5	16.2	6.63	2.42	5.38	1.90	244	41
	227.5	18.3	6.14	2.95	7.67	1.88	210	38
	228.5	16.3	6.15	2.65	5.70	1.87	268	49
	230.5	15.0	6.82	3.45	5.49	1.78	208	54
232.5	14.6	6.87	3.43	4.83	1.70	244	65	

Table 2 (Continued).

Site	Depth (cm)	Total P $\mu\text{mol/g}$	Fe-P $\mu\text{mol/g}$	Org. P $\mu\text{mol/g}$	Auth.+Bio. P $\mu\text{mol/g}$	Detr. P $\mu\text{mol/g}$	$C_{\text{org}}/P_{\text{org}}$ mol/mol	$C_{\text{org}}/P_{\text{reac}}$ mol/mol
	235.5	14.0	6.32	3.43	4.61	1.33	239	65
	238.5	13.0	6.40	2.54	4.59	1.34	245	53
	241.5	13.8	5.60	2.89	4.71	2.25	183	46
	245.5	14.6	5.68	3.89	5.50	1.63	188	56
	248.5	14.9	5.59	3.96	5.61	1.57	244	73
	250.5	14.4	6.69	3.55	5.11	1.78	260	73
	253.5	14.6	6.88	3.28	4.43	2.44	296	80
	254.5	14.7	3.75	2.81	4.97	2.11	301	67
	255.5	13.9	3.94	2.81	5.07	2.00	144	34
	262.5	15.1	3.92	4.36	5.51	2.36	94	32
	268.5	15.8	4.83	2.67	6.25	2.49	133	27
ODP 969E	21.5	13.6	0.73	2.14	7.92	2.14	38	7
	25.5	15.7	0.82	3.86	8.33	2.17	173	50
	26.5	18.0	0.57	2.67	11.17	2.00	1142	248
	27.5	19.2	1.00	4.98	11.80	1.79	1019	339
	29.5	18.2	1.46	4.55	10.45	1.67	2106	634
	31.5	22.5	8.28 (1.72)	6.66	5.29 (11.85)	0.67	3332	931
	32.5	19.7	6.30 (1.85)	5.14	4.83 (9.28)	0.73	4432	1103
	33.5	24.9	5.33 (1.98)	8.88	6.76 (10.10)	1.28	2493	962
	35.5	33.0	9.32 (2.24)	4.87	13.13 (20.21)	1.65	4435	913
	37.5	18.0	2.50	3.97	11.55	1.26	4171	1273
	39.5	12.4	2.76	2.95	7.81	0.83	870	284
	40.5	11.6	2.16	2.81	6.55	0.97	38	11
	45.5	12.9	2.34	2.45	7.11	1.72	30	8
	49.5	13.3	2.02	1.59	8.37	1.94	44	9

nd=no data. Numbers between brackets for core 969E are corrected Fe-P and auth+bio P values (see text). Data in bold are for intact sapropels. The interruption in sapropel S1 in cores SL60 and MD90-917 is indicated with italics.

Table 3

Average burial fluxes of sediment, C_{org} , P_{org} , Fe-bound P, authigenic+biogenic P and total P and the ratios of the burial fluxes of C_{org} and several P forms for cores BC19, SL60, MD90-917 and 969E during sapropel formation and for core BC19 after sapropel formation

Burial flux	BC19 (2750 m)		SL60 (1522 m)	MD90-917 (1010 m)	969E (2201 m)
	after S1	during S1	during S1	during S1	during Pliocene (i-282c)
Bulk sediment (cm kyr^{-1})	2.9	2.9	8.4	~ 10	3.0
Dry sediment ($\text{g cm}^{-2} \text{yr}^{-1}$)	2.7×10^{-3}	1.3×10^{-3}	6.7×10^{-3}	8.0×10^{-3}	3.9×10^{-3}
– C_{org} ($\text{mmol m}^{-2} \text{yr}^{-1}$)	6	33	82	56	556
– P_{org} ($\mu\text{mol m}^{-2} \text{yr}^{-1}$)	70 (23%)	62 (24%)	209 (23%)	248 (22%)	195 (24%)
– P_{Fe} ($\mu\text{mol m}^{-2} \text{yr}^{-1}$)	126 (41%)	24 (9%)	244 (27%)	386 (34%)	73 (9%)
– $P_{\text{auth.+bio.}}$ ($\mu\text{mol m}^{-2} \text{yr}^{-1}$)	94 (31%)	119 (46%)	339 (37%)	404 (35%)	467 (57%)
– P_{total} ($\mu\text{mol m}^{-2} \text{yr}^{-1}$)	307	257	915	1150	822
$C_{\text{org}}/P_{\text{org}}$	86	528	393	228	2858
$C_{\text{org}}/P_{\text{reac}}$	21	161	104	54	758

Values between brackets are percentages of the total P flux. The fluxes were calculated from the integrated amounts of each component in the intact sapropel (flux during sapropel formation) and from concentrations in the upper ~ 12 cm of the sediment (flux after S1, only for core BC19) using the dry bulk density and the sedimentation rate for each location. P_{Fe} = Fe-bound P, $P_{\text{auth.+bio.}}$ = authigenic and biogenic P, P_{total} = total P. The corrected P_{Fe} and $P_{\text{auth.+bio.}}$ data (see text) for core 969E were used. $P_{\text{reac}} = P_{\text{org}} + P_{\text{Fe}} + P_{\text{auth.+bio.}}$. Note that the C_{org} flux for BC19 (and consequently other related parameters in Tables 3 and 4) is slightly lower than the $40 \text{ mmol m}^{-2} \text{yr}^{-1}$ reported by Slomp et al. (2002). The value given here is a more accurate estimate.

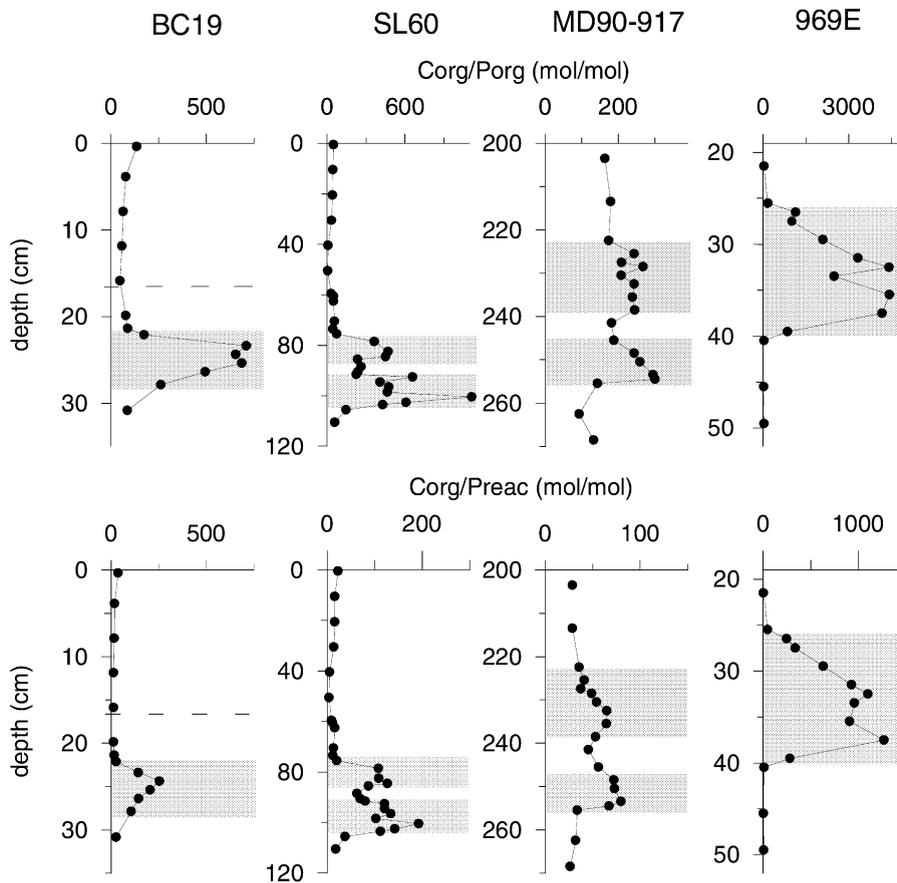


Fig. 4. C_{org}/P_{org} and C_{org}/P_{react} (mol/mol) versus depth in the sediment of cores BC19, SL60, MD90-917 and 969E.

we assumed either a sulfide reoxidation percentage of 80%, which is a maximum value for sapropel S1 (Passier et al., 1999c), or no sulfide reoxidation. Due to the more abundant presence of oxygen, sulfide reoxidation probably was more important (i.e. closer to 80%) during sapropel S1 formation than during formation of the Pliocene sapropel (Passier et al., 1999c). Calculated C_{org} burial efficiencies for BC19 and 969E are 21 to 44% (S-ox 80%) and 57 to 80% (S-ox 0%; Table 4), respectively. These values all fall within the range of burial efficiencies (~ 10 –80%) reported by Canfield (1989) for euxinic environments.

The depositional flux of Fe-bound P will have depended on the oxygen concentration in the water column. As a rough approximation, it is assumed here that this flux amounted to ~ 1

(969E) or ~ 3 (BC19) times the burial fluxes of Fe-bound P. These estimates are of the same order of magnitude as present-day fluxes of Fe-bound P in the surface sediment (Table 3). The depositional flux of biogenic P was calculated from the burial flux of authigenic and biogenic P, assuming a background flux of P_{auth} as calculated for core BC19 from the P_{auth} profile ($\sim 31 \mu\text{mol m}^{-2} \text{yr}^{-1}$; Slomp et al., 2002), and assuming a BE for biogenic P of 10% (Schenau and De Lange, 2000).

Burial fluxes of total P range from ~ 260 to $1150 \mu\text{mol m}^{-2} \text{yr}^{-1}$ (Table 3) and thus are equal to or slightly higher than typical values for open ocean regions (20 – $750 \mu\text{mol m}^{-2} \text{yr}^{-1}$; Filippelli, 1997). Calculated maximum rates of P release from the sediment to the water column during

Table 4

Burial efficiencies (BE) and burial and depositional fluxes of C_{org} , P_{org} , and P_{reac} (defined as the sum of organic, Fe-bound, authigenic and biogenic P), rates of C_{org} decomposition and sediment–water exchange rates of HPO_4^{2-} for cores BC19 and 969E during sapropel formation

	BC19 (S1) (2750 m)		969E (Pliocene) (2201 m)	
	Sox-0%	Sox-80%	Sox-0%	Sox-80%
BE for C_{org}	57%	19%	80%	44%
Burial flux C_{org} ($\text{g m}^{-2} \text{yr}^{-1}$)		0.4		6.7
Depositional flux C_{org} ($\text{g m}^{-2} \text{yr}^{-1}$)	0.7	2.6	8.4	15.2
BE for P_{org}	11%	4%	3%	2%
Depositional flux ($\mu\text{mol m}^{-2} \text{yr}^{-1}$) of				
– P_{org}	547	1490	6590	11957
– Fe-bound P		75		73
– Biogenic P		878		4061
Depositional flux P_{reac} ($\mu\text{mol m}^{-2} \text{yr}^{-1}$)	1500	2443	10724	16090
Burial flux P_{reac} ($\mu\text{mol m}^{-2} \text{yr}^{-1}$)		205		734
Sediment–water exchange flux of HPO_4^{2-} ($\mu\text{mol m}^{-2} \text{yr}^{-1}$)	1295	2238	9990	15356
BE for P_{reac}	14%	8%	7%	5%

Sox-0%: no sulfide reoxidation, Sox-80%: 80% of the sulfide formed is reoxidized.

sapropel formation range from ~ 1295 to $\sim 15360 \mu\text{mol m}^{-2} \text{yr}^{-1}$ (Table 4). These fluxes are significantly higher than present day fluxes in oxic environments with comparably low sedimentation rates (generally $< 1000 \mu\text{mol m}^{-2} \text{yr}^{-1}$; Colman and Holland, 2000; Slomp et al., 2002). When compared to values reported for continental margin environments overlain by anoxic bottom waters ($\sim 2900\text{--}59000 \mu\text{mol m}^{-2} \text{yr}^{-1}$; McManus et al., 1997; Slomp et al., 2002), the fluxes for core 969E fall within the typical range but those for BC19 are relatively low. Estimated burial efficiencies of organic and reactive P range from 2 to 11% and 5 to 14%, respectively (Table 4). The burial efficiencies of P_{reac} compare well to the values of 6 and 12% observed by Ingall and Jahnke (1994) for the anoxic Peru Margin and Santa Monica basin, respectively.

Since the major source of P to the sediment is P_{org} (Table 4; assuming S-ox closer to 80% than 0% for S1) and the depositional flux of P_{org} is based on the depositional flux of C_{org} , the reconstructed sediment–water exchange fluxes and burial efficiencies are particularly sensitive to the assumed organic C/P ratio. Use of the Redfield C/P ratio (106) makes the P_{org} deposition fluxes maximum values. Some loss of P relative to C will

probably have occurred during downward transport through the water column. When using a C/P ratio of 228, which is the average value for the sapropel in core MD90-917, sediment–water exchange rates are a factor ~ 0.6 lower and burial efficiencies of P_{reac} will increase by a factor of ~ 1.5 when S-ox is 80% at sites BC19 and 969E. These values are still reasonable compared to those determined for other systems. When we assume that the depositional flux of biogenic P is zero (with S-ox 80% for S1) burial efficiencies comparable to those in modern sediments overlain by anoxic bottom waters are only obtained if we assume Redfield C/P ratios for the organic matter. Calculated burial efficiencies are not sensitive to possible errors in sedimentation rates, since this equally affects both the estimated depositional and burial rates.

4.3. Regeneration and burial of C and P from organic matter

Burial efficiencies of C_{org} are expected to increase with sedimentation rate (e.g. Canfield, 1994), with enhanced sulfurization of organic matter (e.g. Van Kaam-Peters et al., 1998; Sinighe Damsté et al., 1998) and with decreased

exposure of the organic matter to oxygen (e.g. Hartnett et al., 1998). Assuming 80% reoxidation for S1 and less than 80% for the Pliocene sapropel, estimated burial efficiencies for C_{org} (Table 4), indicate that C_{org} preservation was higher during Pliocene sapropel formation than during S1 times. A similar conclusion was reached by Passier et al. (1999c) and was suggested to be the result of the much larger uptake of reduced sulfur by organic matter during formation of the Pliocene sapropel in core 969E (Passier et al., 1999b). The more limited exposure of organic matter to oxygen during Pliocene sapropel formation compared to S1 may also play a role.

Burial efficiencies for P_{org} are a factor ~ 5 to 27 lower than burial efficiencies for C_{org} (Table 4). This is in accordance with the elevated $C_{\text{org}}/P_{\text{org}}$ ratios in the sapropels (Tables 2 and 3; Fig. 4) and indicates enhanced release of P from organic matter relative to C under bottom water dysoxial/anoxia. When the bottom water was temporarily more oxygenated during the ‘interruption’ of S1 in cores SL60 and MD90-917, P_{org} burial relative to C_{org} increased (reflected in decreased $C_{\text{org}}/P_{\text{org}}$ ratios; Table 2; Fig. 4). Decreasing $C_{\text{org}}/P_{\text{org}}$ ratios with sedimentation rate and water depth (Table 3; Fig. 4) can be attributed to (1) higher oxygen exposure at the shallower sites; (2) faster burial and therefore better preservation of the deposited organic matter at the high sedimentation rate sites (Ingall and Van Cappellen, 1990); (3) a greater input of (residual) organic matter with low $C_{\text{org}}/P_{\text{org}}$ ratios at the shallower sites. Increased terrestrial input at the more near coastal sites SL60 and MD90-917 compared to site BC19 would lead to higher (Ruttenberg and Goni, 1997) instead of lower C/P ratios at the former sites and thus can be excluded.

Assuming S-ox is close to 80% for S1, burial efficiencies for P_{org} for core BC19 and 969E are surprisingly close at 2–4% (Table 4). This suggests that the ~ 5 -fold difference in average $C_{\text{org}}/P_{\text{org}}$ ratios for S1 and the Pliocene sapropel can largely be attributed to an enhanced BE of C_{org} . P_{org} burial efficiencies are apparently not affected when water column conditions change from dysoxic to euxinic.

The enhanced regeneration of P from organic

matter under anoxia in these sediments is quantitatively more important than the increased release from Fe-oxides. This particularly holds for the Pliocene sapropel when no Fe-oxides are expected to have survived transport through the euxinic water column (although we assume a small depositional flux in Table 4). For S1, we estimated the relative contribution for core BC19 as follows. Enhanced release of P from organic matter was calculated as the difference between the burial flux of P_{org} if there were no enhanced P regeneration (the C_{org} burial flux in the sapropel divided by the Redfield C/P ratio) and the actual P_{org} burial flux. The release of Fe-bound P was estimated from the difference in the depositional and burial fluxes of Fe-bound P (Tables 3 and 4). Enhanced P-release from organic matter during S1 was calculated to be ~ 5 times more important than release from Fe-oxides.

4.4. Burial of inorganic P_{reac}

The enhanced release of P from organic matter and Fe-oxides in sediments overlain by anoxic bottom waters may be partly counteracted by an increased burial of other P_{reac} phases, such as authigenic CFA and biogenic apatite. Slomp et al. (2002) showed that authigenic CFA formation did not occur at the BC19 site during S1 formation. Biogenic apatite burial was enhanced during this time, but showed a high spatial variability and only partly compensated the enhanced P release from organic matter.

Similar to P_{org} , P_{reac} retention can be expected to increase with increasing sedimentation rate and oxygen exposure. This will either be the result of decreased dissolution of Fe-bound and biogenic P due to the shorter residence time near the sediment–water interface or due to increased transformation of Fe-bound, organic and biogenic P to CFA. Sapropel $C_{\text{org}}/P_{\text{reac}}$ ratios indeed show a decrease (Tables 2 and 3, Fig. 4) with increasing sedimentation rate and oxygen exposure. At sites SL60 and MD90-917, $P_{\text{auth+bio}}$ accounts for a major proportion of the burial flux in the sapropel, but – apart from some spikes – there is only a minor increase relative to surrounding layers and the surface sediment. This suggests that a

major part of the $P_{\text{auth+bio}}$ flux (and thus the P_{reac} flux) may in fact be a ‘background’ flux of $P_{\text{auth+bio}}$ formed elsewhere. Whether the small enrichments are CFA or biogenic Ca-P can not be deduced from these data. Even if it is all CFA, the small enrichments suggest that only limited transformation has taken place. We conclude that (1) P forms other than P_{org} may be major sources of P_{reac} to the sediment at these sites; (2) the dissolution kinetics of these P forms may play an important role in determining P_{reac} burial in sediments.

The average $C_{\text{org}}/P_{\text{reac}}$ ratio for the Pliocene sapropel is a factor ~ 5 higher than that for the deep-basin S1 sapropel in core BC19 (Table 3). Estimated burial efficiencies for P_{reac} in these sapropels are rather similar (Table 4). This suggests that – as with the $C_{\text{org}}/P_{\text{org}}$ ratios – the ~ 5 -fold difference in $C_{\text{org}}/P_{\text{reac}}$ ratios between S1 and the Pliocene sapropel can be attributed to an enhanced burial efficiency of C_{org} . Apparently, the presence of a euxinic instead of a dysoxic or semi-euxinic water column does not significantly affect the burial efficiency of P_{reac} in sediments. Whether the $P_{\text{auth+bio}}$ enrichment in the Pliocene sapropel is largely authigenic or biogenic cannot be deduced from these data with certainty. That biogenic P may be important is suggested by the ‘corrected’ $P_{\text{auth+bio}}$ profile (Fig. 3; Table 2). Even if all of the $P_{\text{auth+bio}}$ were authigenic (i.e. including the background flux), transformation of P_{org} to CFA cannot have significantly counteracted the enhanced regeneration of P. Enhanced release of P at this site (calculated as described in Section 4.3) will have amounted to $\sim 5050 \mu\text{mol m}^{-2} \text{yr}^{-1}$. This is ~ 11 times higher than the total $P_{\text{auth+bio}}$ burial flux ($467 \mu\text{mol m}^{-2} \text{yr}^{-1}$; Table 4).

5. Conclusions and implications

The C and P geochemistry of sapropels from 4 sites in the eastern Mediterranean Sea indicate enhanced regeneration (i.e. decreased burial) of P relative to C during formation of sapropel S1 and the Pliocene sapropel i-282c. This is the result of (1) enhanced release of P from organic matter during sapropel formation, (2) limited burial of

Fe-bound P and (3) only limited increased burial of biogenic P and CFA. For sapropel S1, retention of both P_{org} and P_{reac} relative to C_{org} was found to increase with increasing sedimentation rate and exposure to oxygen. Inorganic P_{reac} may be an important source of P at two sites. This suggests that the general assumption that P_{org} is the primary source of P_{reac} to sediments (e.g. Berner et al., 1993; Filippelli, 2001) may not hold in all sedimentary environments. Our results are in line with the major role of sediment accumulation (Filippelli, 1997) and bottom water oxygenation (Ingall and Jahnke, 1994, 1997) for P burial in marine sediments demonstrated previously.

Whether the water column is dysoxic/semi-euxinic or euxinic does not appear to affect the burial efficiencies of P_{org} and P_{reac} . Enhanced C_{org} burial under the euxinic water column explains the extremely high $C_{\text{org}}/P_{\text{org}}$ and $C_{\text{org}}/P_{\text{reac}}$ ratios in the Pliocene sapropel. As was shown previously for sapropel S1 (Slomp et al., 2002), the enhanced regeneration of P in combination with circulation changes will have contributed to a significant increase in deep-water concentrations of HPO_4^{2-} during Pliocene sapropel formation. The stronger decoupling of the burial of C and P during euxinia (Pliocene) compared to dysoxia/semi-euxinia (S1) will have resulted in a stronger positive feed-back loop between water column anoxia, primary productivity and C_{org} burial (Van Cappellen and Ingall, 1994, 1996).

Our results indicate that authigenic apatite formation is quantitatively unimportant during S1 and Pliocene sapropel formation relative to the enhanced release from organic matter. This result is seemingly in contrast with the efficient transformation of P_{org} to authigenic P reported for modern anoxic sediments (e.g. Ruttenberg and Berner, 1993). The unusual combination of very low sedimentation rates and bottom water dysoxia/anoxia during sapropel formation (which does not occur in any present-day sedimentary environment) apparently precludes such a transformation. Calculated paleogradients of pore water PO_4 in the surface sediment during sapropel S1 formation ($0.7\text{--}1.0 \mu\text{M}$ over a 1-cm depth interval in core BC19) suggest that porewater PO_4 concen-

trations may have been too low for CFA formation (Slomp et al., 2002).

If we view sapropels as a modern analog of black shales (e.g. Thomson et al., 1999; Nijenhuis et al., 1999; Erbacher et al., 2001), these results may also have wider implications. In their model calculations for global ocean C, P and O cycling, Van Cappellen and Ingall (1994, 1996) assumed that CFA formation and burial increased substantially during ocean anoxia as a result of increased primary production. At steady-state, this fully compensated for the decreased burial of organic and Fe-bound P. If our results for Mediterranean sapropels are extrapolated to times of world-wide ocean anoxia (Ocean Anoxic Events or OAE, e.g. Wignall, 1994; Kuypers, 2001), substantial CFA formation and burial of biogenic Ca-P did not take place in the deep-sea (i.e. in pelagic environments). Increased burial of CFA and biogenic P may have occurred in the coastal zone, however, upon (periodic) upwelling of P-rich bottom water on to the shelves either during or after an OAE (Cook and Shergold, 1984; Donnelly et al., 1990).

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