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A sediment–nutrient–oxygen feedback responsible for productivity variations in Late Miocene sapropel sequences of the western Mediterranean

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Abstract

Cyclic sediments observed throughout the Mediterranean during the Late Miocene have been related to precessional forcing of ocean stratification. Individual couplets, typically 2-m-thick sequences of sapropels and diatom-rich marls, can be reliably traced from western Spain to Crete, and were formed in restricted marginal basins. Micropaleontological evidence indicates paradoxically that the organic carbon-rich sapropels were formed under low productivity conditions marked by surface water stratification and deep anoxia, whereas the diatom-rich marls were formed under high productivity conditions marked by upwelling. Here we present geochemical evidence, mainly from detailed phosphorus determinations and paleo-redox proxies, indicating that a sediment–nutrient–oxygen feedback (herein dubbed the SNO Effect) is in part responsible for driving the observed productivity variations. During stratification, anoxic conditions in these basins cause the release of the limiting nutrient phosphorus from reducible oxide phases in the sediments. Basin stagnation causes the buildup of phosphorus below the photic zone. Subsequent overturn driven by precessionally-driven winds injects phosphorus-rich bottom waters into the photic zone. The biotic response to this overturn is high productivity in marls directly overlying the sapropels culminating in diatom mat formation. Exhaustion of the stored excess phosphorus results in lower productivity marls, which grade back into sapropels due to lower wind stresses and the return of stagnant basin conditions. These findings indicate that the SNO Effect may in part be responsible for precessional-scale productivity variations observed in parts of the Mediterranean, and perhaps present in other restricted ocean basins, like the Miocene Monterey Formation and the modern Santa Barbara Basin.

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1. Introduction

Phosphorus and nitrogen are key macronu-

trients for carbon fixation in organic matter. In normal marine organic matter, the ratio of C:N:P is 106:16:1 (the Redfield ratio; Redfield et al., 1963), but in sediments this ratio is typically changed due to preferential diagenesis of organic matter after burial. For example, the typ-

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ical C:P ratios average about 400–500 (e.g. Ramirez and Rose, 1992). Some workers indicate that this ratio is particularly elevated in anoxic settings due to preferential regeneration of P in these conditions (e.g. Ingall et al., 1993; Van Cappellen and Ingall, 1996; Schenau et al., 2000; Slomp et al., 2002), whereas others note little or no difference (Colman et al., 1997; Colman and Holland, 2000; Anderson et al., 2001; Filippelli, 2001). Perhaps depositional environment is the key to controlling this preferential regeneration from organic matter, with sedimentation rate perhaps the master variable in this (e.g. Filippelli, 1997). Notably, a recent study of Devonian black shales (Murphy et al., 2000) used nutrient regeneration from organic matter along with bulk sediment accumulation, oxygen dynamics, and climatically-driven overturn to drive a 100-kyr eutrophication cycle in a shallow epicontinental sea.

In most marine systems, the main shuttle of phosphorus to the seafloor is via photosynthetic incorporation in organic matter and transport via settling and aggregation (e.g. Delaney, 1998). This organic phosphorus can be released during organic matter degradation and released to interstitial waters and fluxed to bottom waters. The released phosphorus may also be adsorbed onto or co-precipitated with oxide minerals (e.g. goethite), which have an extremely high affinity for phosphate. Further, the released phosphate may be authigenically precipitated as disseminated carbonate fluorapatite (CFA) within interstitial spaces; in fact, this may be the 'ultimate' pool of marine reactive phosphorus. Once precipitated as CFA, phosphorus is extremely unreactive. Based on the definitions above, the retention or release of organic phosphorus is sensitive to the net rate of organic matter degradation, whereas the retention or release of adsorbed/oxide-bound phosphorus is sensitive to redox conditions. Questions still remain, however, about the relationship between organic matter degradation rates and redox state (Pederson and Calvert, 1990; Calvert et al., 1992; Canfield, 1994) – our data here in ancient sediments cannot address this issue, but other work on phosphorus geochemistry of recent sediments (e.g. Colman and Holland, 2000; Filippelli, 2001;

Anderson et al., 2001) begin to address this issue for phosphorus at least.

A number of marginal basins surrounding the proto-Mediterranean in the latest Miocene have yielded outstanding records of precession-controlled cyclic sediments, with individual sedimentary couplets traceable in sedimentary sequences from southern Spain to Crete (Hilgen et al., 1995; Sierro et al., 1997; Sierro et al., 1999; Krijgsman et al., 1999). These papers use detailed bio- and magneto-stratigraphy for basic stratigraphy, then use stratal number and thickness combined with spectral analysis to indicate that precession forcing (~ 23 kyr) is the dominant factor controlling deposition of these cyclic sediments. The sediment couplets themselves are composed of sapropels and marls. The sapropels exhibit organic carbon contents between 0.2 and 2%, strong lamination indicating anoxic depositional conditions, and microfossil assemblages indicative of warm, stratified, oligotrophic surface conditions (e.g. Sierro et al., 1999). The marls are homogeneous, and are marked by microfossil assemblages indicative of high productivity and cold surface water conditions (Sierro et al., 1999; Vázquez et al., 2000). In the middle of many of the marl layers are diatomites, indicating extremely high nutrient supply (e.g. Kemp and Baldauf, 1993).

The driving force for the Mediterranean sapropel sequences is debated (e.g. Rossignol-Strick et al., 1982; de Lange and ten Haven, 1983; Howell et al., 1988; Thunell et al., 1984; Meyers, 1993; Van Os et al., 1994; Rohling, 1994; Passier et al., 1999; Kemp et al., 1999). It is still unclear whether sapropels formed under conditions of enhanced productivity, enhanced preservation, or both. It has been difficult, however, to reconcile evidence for high organic matter flux to the seafloor with evidence for a highly stratified ocean with little supply of nutrients to the surface, although some modelling work indicates that this may be feasible if the nutrient content of deep water is extremely high (Van Cappellen and Ingall, 1994). Sachs and Repeta (1999) forwarded a compromise hypothesis: increased river runoff driving surface stratification did not supply new nutrients, but instead led to specialized nitrogen-fixing phytoplankton populations (mat form-

ing diatoms), the sinking of which into the anoxic deep basins provided the organic matter flux for sapropel formation.

Although this scenario might explain Pleistocene Mediterranean sapropels, the presence of diatom mats within the middle of the marl layers (not the sapropels) and several sedimentary geochemical proxies for phosphorus (P) cycling indicate that this process could not have driven the cyclic sedimentation found in the Late Miocene. We forward a different hypothesis for the Late Miocene sapropel/marl sequences in the western Mediterranean, based on a detailed study from the Sorbas Basin in southeast Spain, wherein P regenerated from oxide phases accumulated in the anoxic deep water during stratified sapropel conditions. Upon precession-driven overturn of the basin, this accumulated P fueled high surface productivity as well as marl and diatomite sedimentation. This sediment–nutrient–oxygen feedback (the SNO Effect) is supported by observations of enhanced release of oxide-bound phosphorus from the water column and surface sediments in other anoxic settings (e.g. Krom and Berner, 1980; Gächter et al., 1988; Froelich, 1988; Sundby et al., 1992; Lucotte et al., 1994; Filippelli, 2001). The eventual depletion of this stored P source led to lower productivity conditions toward the top of the marls, and the onset of stratified conditions resulted in the return of sapropel deposition in the deep basins. Aspects of this hypothesis are supported by the micropaleontological data, which indicate relatively low productivity and warm/oligotrophic conditions during sapropel deposition, and relatively high productivity and cold/eutrophic conditions during marl and diatomite deposition (see Sierro et al., 2003, and Pérez-Folgado et al., 2003, for detailed descriptions of these data).

2. Site description, sampling, and methods

Marls and sapropels of the Abad Member (Völk and Rondeel, 1964) were deposited in the Sorbas Basin of southern Spain during the Late Miocene, and represent relatively high deposition rate (e.g. 10 cm/kyr; Sierro et al., 2001a) marine

sediments deposited in a tectonically produced marginal basin within the greater proto-Mediterranean Sea. These marl+diatomite/sapropel sequences are well exposed in the arid environment of southern Spain. The Abad Member is separated into the Lower Abad and the Upper Abad, with the Upper Abad marked by particularly good preservation of diatomites and well-developed brown, laminated organic-rich shales intercalated with the homogeneous marls. The distinct layering in the Upper Abad has been suggested to be the result of increased restriction of the Sorbas Basin from the main Mediterranean, perhaps due to tectonic isolation (Sierro et al., 1997), and a shallowing of water depths to about 150 m (Troelstra et al., 1980). Individual couplets have been correlated to couplets in other sections situated across the Mediterranean (Krijgsman et al., 1999; Sierro et al., 2001a; Sierro et al., 2003), and are suggested to result from precession-scale variability in insolation and wind stress amplified in these restricted marginal basins.

We sampled intensively four couplets from the Upper Abad Member (UA5–8), representing ap-

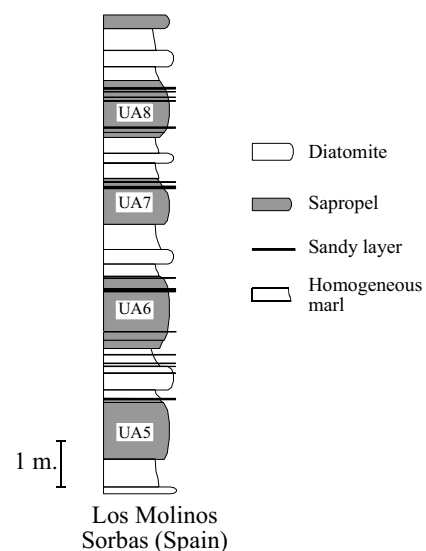


Fig. 1. Stratigraphic column of four couplets from the Los Molinos section of the Upper Abad Formation, Sorbas Basin, southern Spain. This 10-m section, marked by laminated sapropels and homogeneous marls, with diatomite layers within the marls, was deposited between 6.62 and 6.50 Ma (based on astronomical calibration; e.g. Sierro et al., 2001a).

proximately 100 kyr of time centered around 6.6 Ma (using the astronomically-calibrated ages of Sierro et al., 2001a). A total of 104 samples were collected and analyzed for geochemistry, with an approximate sample resolution of about 1 kyr, including sapropels, homogeneous marls, and diatomites (Fig. 1). All samples were taken after surface cleaning of the section, and the lack of iron or clay drapes as well as penetrative roots (not particularly common in this arid region) ensured unweathered samples.

3. Geochemical techniques

All samples were analyzed for bulk geochemistry, including percentage of opal, carbon geochemistry and total nitrogen, as well as minor and trace element geochemistry via inductively coupled plasma–atomic emission spectroscopy after total sediment digestion, at the Earth Science Institute in Barcelona (see Vázquez et al., 2000, for technique descriptions). A subset of samples (60) were also analyzed using sequential extraction techniques for phosphorus at IUPUI, following the techniques utilized extensively in our laboratories (e.g. Filippelli and Delaney, 1996; Filippelli and Souch, 1999; Filippelli, 2001) and employing the modification by Anderson and Delaney (2000) of Ruttenberg (1992). The purpose of this detailed analysis was to examine the role that this nutrient element had on productivity in the Sorbas Basin, and is outlined below.

Sequential extraction analysis of phosphorus has been used to elucidate phosphorus diagenesis (Ruttenberg and Berner, 1993; Sundby et al., 1992; Filippelli and Delaney, 1996; Anderson and Delaney, 2000) and mass balances (Ruttenberg, 1993; Ruttenberg and Berner, 1993; Filippelli and Delaney, 1996; Filippelli and Souch, 1999). The sequential extraction technique yields chemical information about the reactivity of phosphorus within sediments; the geochemical fractionation leads to the apportionment of phosphorus in several operationally-defined pools (e.g. Ruttenberg, 1992; Anderson and Delaney, 2000). Reactive phosphorus pools, so-called because the phosphorus has the geochemical po-

tential for release to the environment, include organic phosphorus, adsorbed and oxide-bound phosphorus, and authigenic–biogenic phosphorus.

4. Results and discussion

The integration of lithologic variations with geochemical and micropaleontological proxies yields a consistent picture of productivity, oxygenation, and sediment/water feedbacks in the Sorbas Basin just over 6 million years ago. In the following, we outline first the geochemical record obtained for the four couplets, then the micropaleontological data supporting our interpretation of benthic recycling and productivity history.

4.1. Geochemical productivity proxies

The ratio of phosphorus/titanium (determined after whole-sediment digestion) is a useful proxy for the sedimentation of phosphorus independent of terrigenous input; this ratio has been employed by several of us recently to assess paleoproductivity in Pleistocene (Latimer and Filippelli, 2001) and Early Cenozoic (Latimer and Filippelli, 2002) settings. This ratio approach has the advantage over simple concentration or percent of total values of being independent of sedimentation rate, and thus not impacted by dilution or concentration effects of bulk sedimentation. In opal-rich settings, this ratio is perhaps better than P/Al given the potential scavenging of Al in opal. Another useful proxy for P deposition is the detailed P chemistry itself as determined by sequential extraction analyses. For the purpose of this particular study, this has the greatest power in being a measure of oxide-P interactions and thus the effects of sedimentary anoxia (discussed below). But the reactive phosphorus content (determined as the sum of non-detrital P components from a sequential extraction analysis) together with the P/Ti can help to elucidate the main sources and fluxes of bioreactive P to marine sediments.

The reactive P concentration and the P/Ti ratio correlate with each other (Fig. 2), even across the range of lithologies encountered here. Thus, the bulk concentration of reactive and the terrige-

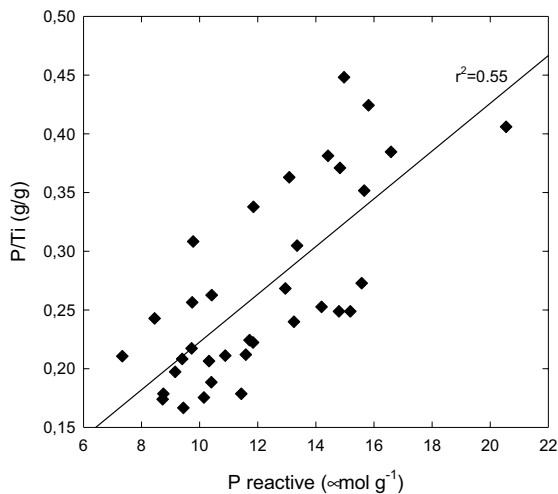


Fig. 2. Cross plot of the P/Ti ratio and total reactive P (determined by sequential extraction analysis), revealing a correlation between these two factors. Both are productivity proxies, with the P/Ti ratio revealing P export in excess of terrigenous sedimentation, and total reactive P related to the bioavailable P in surface waters.

nous-normalized concentrations of P are in general agreement. Although this correlation is not perfect (nor should it be expected to be given the different geochemical approaches used to derive each proxy), the general correspondence lends support to the use of these two factors as measures of bioactive P deposition in the Sorbas Basin, with a close link to the P availability and flux to surface waters fueling productivity.

The P/Ti ratio varies systematically through the couplets sampled from the Sorbas Basin (Fig. 3). Although of lower resolution and focused on several of the marl intervals, the reactive P content also varies systematically. Peaks in both proxies center around diatomite layers. The P/Ti is about 0.15 in sapropel layers (Fig. 3), about as expected for marine shales (0.15; Taylor and McLennan, 1985), but peaks to values about three times normal in marl and particularly diatomite layers, indicative of high export production during these intervals. A more detailed sequential extraction analysis of phosphorus supports the interpretation of high marl productivity. Peak values of reactive phosphorus reach 18 $\mu\text{mol/g}$, a value characteristic of moderately productive continental margins, whereas values in sapropel sequences

are significantly lower ($\sim 8 \mu\text{mol/g}$) than most continental margin sediments and approach those found in low productivity open-ocean settings (Filippelli, 1997). This result is surprising, given that other organic rich sequences in anoxic settings have significantly higher reactive phosphorus contents (18–26 $\mu\text{mol/g}$ for Saanich Inlet, British Columbia, Filippelli, 2001; 23–33 $\mu\text{mol/g}$ for the California margin, Ingall and Jahnke, 1997), but may be the result of different sedimentation rates in these areas.

Two factors indicate that the source and flux of terrigenous input (i.e. nutrients from river runoff) have not significantly impacted the productivity variations we observe. First, the P/Ti ratio removes terrigenous contributions of P from the record, and the fact that P/Ti is high during marl and diatomite deposition indicates that the excess P is not from terrigenous input (which would also contribute the ubiquitous terrigenous element Ti, thus lowering this ratio instead of raising it). Furthermore, the Al/Ti ratio remains relatively constant throughout the record (Fig. 4), indicating that terrigenous source areas have not changed on timescales of couplet deposition. The values reflect normal continental crust values for the terrigenous input, as expected in this setting, even in the face of large changes in sediment types and bioproductivity (e.g. the opal-rich diatomite layers; Fig. 4). This is important, as it confirms that although external factors are certainly affecting stratification of the Mediterranean at this time, they are not impacting productivity variations via nutrient input from riverine input.

4.2. Geochemical vs. micropaleontological proxies of productivity

As noted above, geochemical proxies indicate enhanced P fluxes and utilization during marl and particularly diatomite deposition, with very low values during sapropel deposition. How does this compare to the paleontological record of productivity? In fact, the two proxies agree quite well. For example, the percentage of benthic foraminifera (on a benthic/benthic+planktic basis) may be a useful measure of organic carbon flux to the seafloor (Kuhnt et al., 1999; Rathburn et al.,

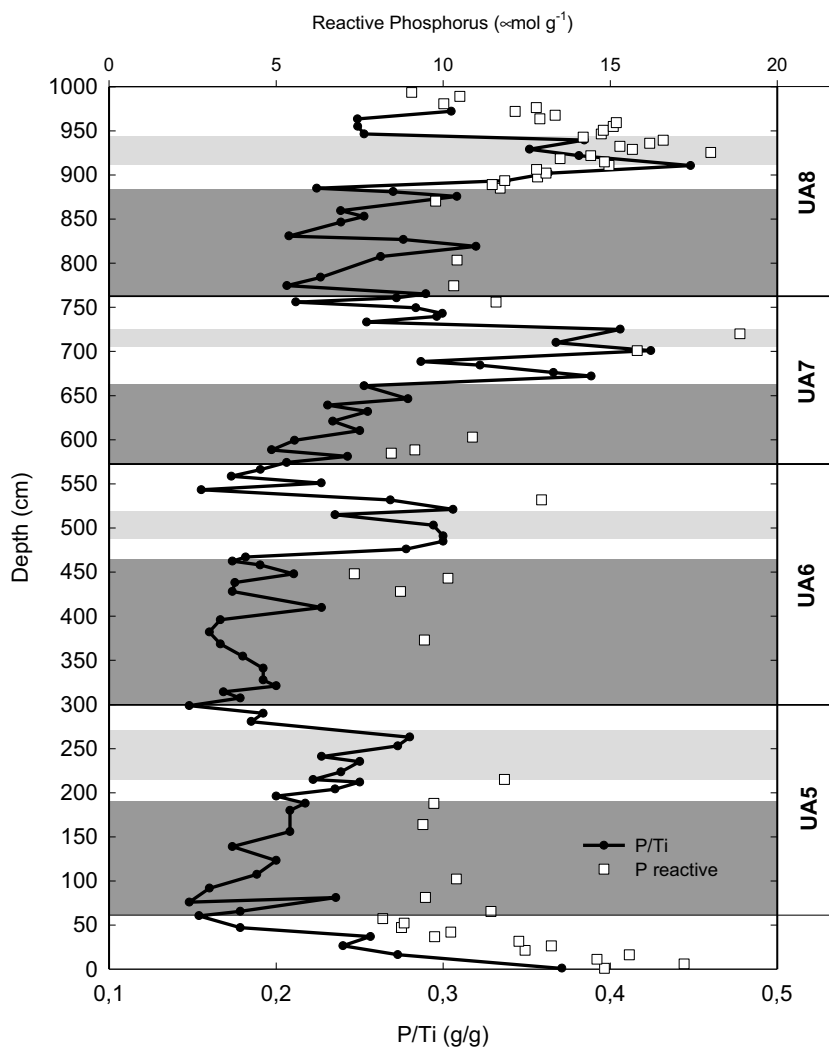


Fig. 3. Nutrient proxy records (reactive P: open squares; P/Ti: closed symbol with connecting line) vs. depth across the four sapropel/marl couplets studied here. Dark shading represents sapropels and lighter shading diatomites; marls are unshaded. Proxy records reveal high nutrient availability and flux during marl, and especially diatomite, deposition, and low availability during sapropel deposition. In detail, the nutrient proxies steadily increase during sapropel deposition, peak during diatomite deposition, and decrease steadily to their lowest values during the deposition of the overlying homogeneous marls.

2000; Wollenburg and Kuhnt, 2000), and thus surface water productivity. In the Sorbas Basin, this measure increases sharply during marl and diatomite deposition, mimicking the P/Ti ratio proxy of nutrient availability (Fig. 5). The abundance of benthics, however, is also affected by bottom water oxygenation (e.g. Kaiho, 1999), which is clearly about zero during the deposition of the laminated sapropels. Two other micropa-

leontological proxies support lower productivity during the sapropels and higher productivity during marl/diatomite deposition. First, the ratio of warm-oligotrophic/cold-eutrophic foraminifera is very high during sapropel deposition, and drops to nearly zero during marl and diatomite deposition (see Pérez-Folgado et al., in press). Second, the same ratio in calcareous nannoplankton shows an identical pattern of high values (oligo-

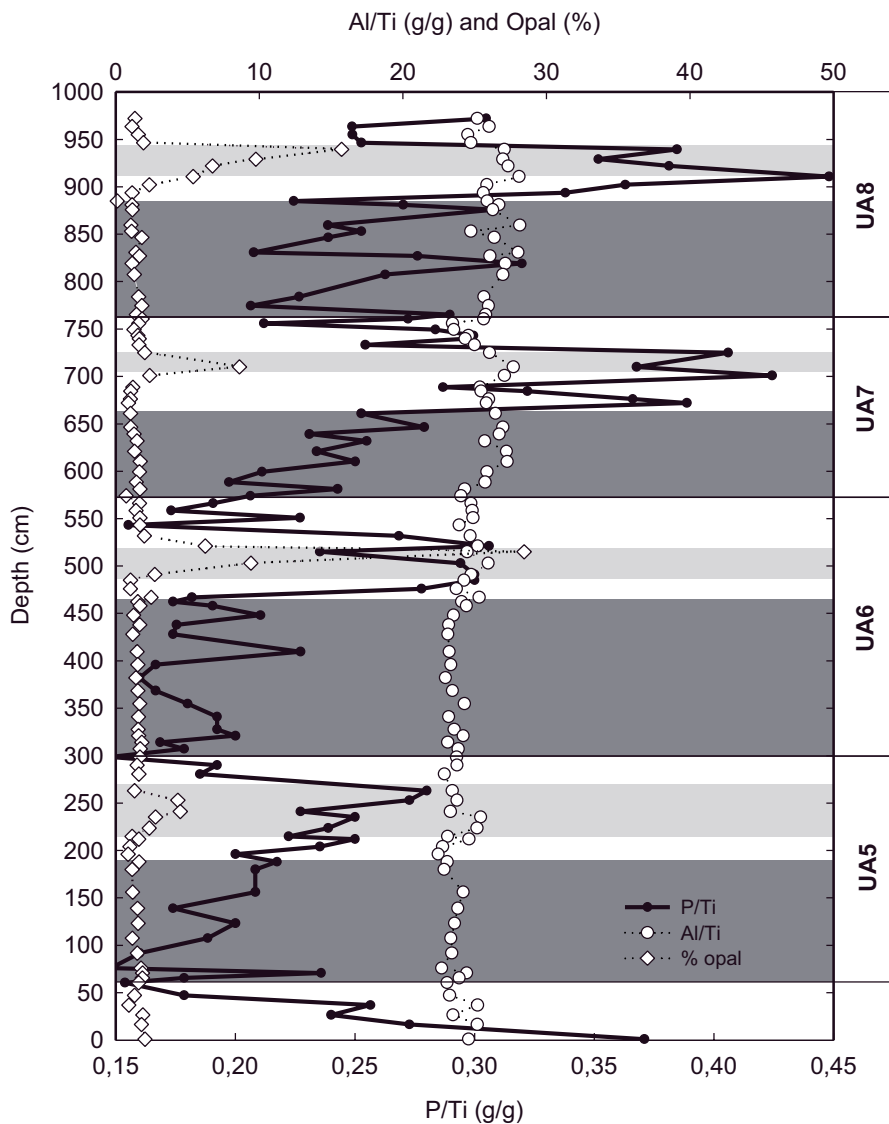


Fig. 4. The nutrient proxy P/Ti, the record of terrigenous sources and input (Al/Ti: open circles) and opal concentration (open diamonds) vs. depth. Dark shading represents sapropels and lighter shading diatomites; marls are unshaded. These records reveal that little change in terrigenous source areas and fluxes are observed, even in the face of large changes in nutrient availability and diatom productivity. This indicates that variations in a terrigenous source (i.e. river input) are not responsible for supplying the nutrients that drove observed productivity variations, and thus an internal nutrient source is a more likely candidate.

trophic) during sapropel deposition and extremely low values (eutrophic) during marl and diatomite deposition (Vázquez et al., 2000) for these same cycles. Furthermore, the diatomite itself represents conditions of extreme eutrophication and nutrient flux to surface waters. Thus, a variety of geochemical proxies and a variety of micropa-

leontological proxies agree that (1) the sapropels were deposited during conditions of low nutrient fluxes to the surface waters and low surface productivity, (2) the intercalated marls were deposited during conditions of high nutrient fluxes to the surface water and high surface productivity, and (3) the diatomite layer in the middle of the

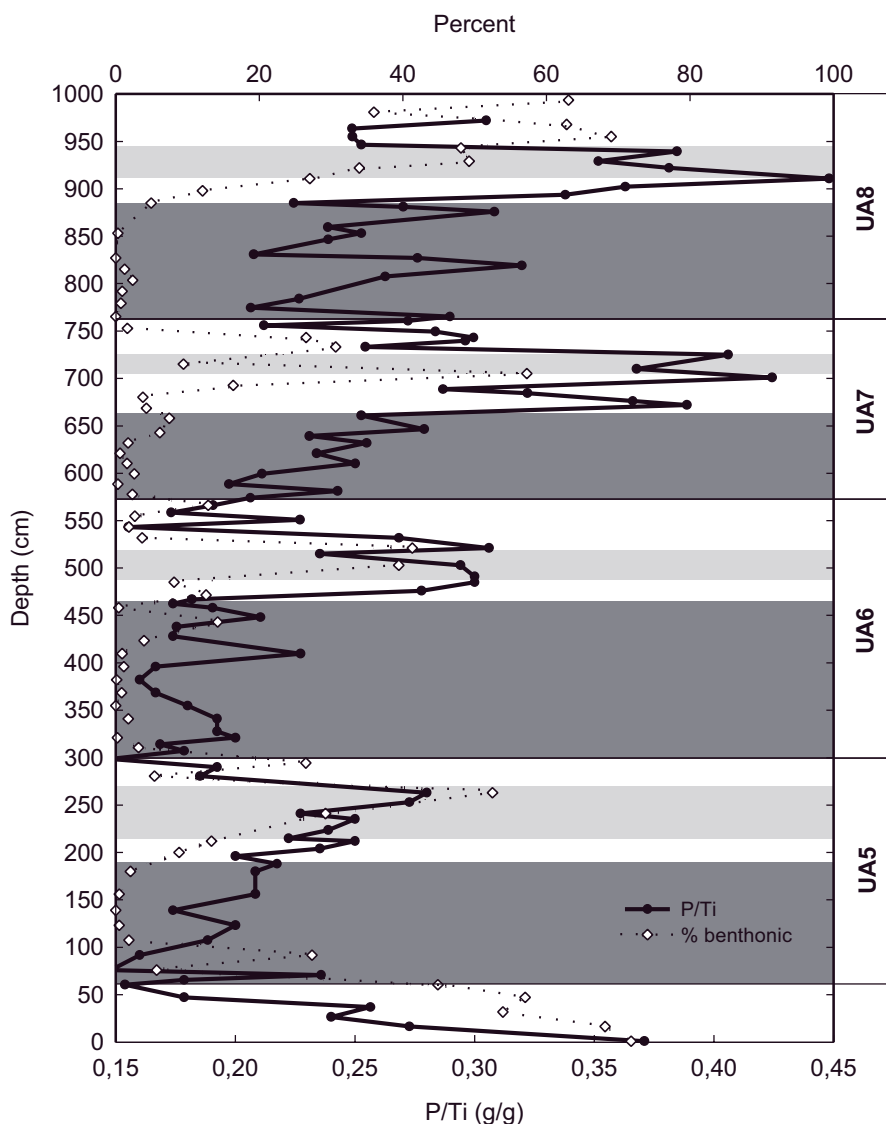


Fig. 5. The nutrient proxy P/Ti and the record of percentage benthic foraminifera (as a percentage of benthic+planktic foraminifera; open diamonds) vs. depth. Dark shading represents sapropels and lighter shading diatomites; marls are unshaded. These records indicate a tight temporal connection between nutrients and organic matter production and delivery to the seafloor. Benthic foraminifera are also susceptible to bottom oxygen conditions; independent micropaleontological proxies recording the ratio of warm-oligotrophic/cold-eutrophic foraminifera (Pérez-Folgado et al., in press) and nannofossils (Vázquez et al., 2000) reveal an identical pattern of oligotrophic low productivity conditions during sapropel deposition and eutrophic high productivity conditions during marl deposition. The correlation between nutrient proxies and productivity proxies, as well as the details of iron cycling in this basin (described in the text), indicate that nutrient cycling is in part driving the lithologic and biologic response to precession-related upwelling in the western Mediterranean.

marls represents a eutrophic acme of extremely high nutrient fluxes to the surface waters. These suggestions leave us with a question, however. If the flux of nutrients during marl and diatomite

was high and the source was not external, what process could provide an adequate and sustained load of nutrients to the surface waters, and explain the observed succession of marl–diatomite–

marl? A look at iron cycling and the interactions between iron and phosphorus may in part address this question.

4.3. Iron cycling in the Sorbas Basin

Iron records from the sequences indicate that this oxide phase is largely responsible for controlling phosphorus cycling and regeneration from the sediments. Oxide-bound phosphorus typically accounts for 10–30% of total phosphorus in marine sediments (Ruttenberg, 1993; Filippelli and Delaney, 1996). In the anoxic Saanich Inlet, for example, the oxide-bound phosphorus accounts for 30% (averaging $\sim 6 \mu\text{mol/g}$) of total reactive phosphorus (Filippelli, 2001), indicating very little phosphorus loss under the strongly anoxic conditions at this site. In comparison, oxide-bound phosphorus here (determined via inductively coupled plasma analysis of reduction step in the phosphorus extraction) is below detection limit ($\sim 1 \mu\text{mol/g}$), and thus unreportable, in both the sapropel and marl sediments from the Sorbas Basin in the Mediterranean. Given a total reactive phosphorus value from 8 to 18 $\mu\text{mol/g}$, this indicates that the oxide-bound component likely accounts for less than 10% of total reactive phosphorus in this setting. The difference in oxide-related phosphorus cycling between these two sites is probably due to iron supply and sedimentation rate. The Saanich Inlet is a narrow embayment surrounded by mountainous terrain on both sides, and has extremely high sedimentation rates (1–1.8 cm/yr) with high reducible iron contents (100–200 $\mu\text{mol/g}$). This combination of a high available pool and inadequate time for oxide dissolution results in relatively high oxide-bound phosphorus contents. In contrast, the deeper basins surrounding the Mediterranean have a much lower sedimentation rate (~ 0.01 cm/yr), allowing more time to overcome kinetic obstacles to iron oxide reduction. The reducible iron content is also much lower in the Sorbas Basin, with typical values ranging from 1–60 $\mu\text{mol/g}$. Although this might reflect lower original reducible iron content, it might also be the result of dissolution of oxides after prolonged reaction with anoxic waters.

The absolute lack of oxide-bound phosphorus

in both the sapropel and marl layers suggests the loss of a significant pool of phosphorus from the sediments. It is unlikely that the loss of oxide-bound phosphorus occurred sometime well after sedimentation (i.e. as a weathering process) because these sediments show little signs of weathering, with delicate carbonate and siliceous plankton well-preserved. Furthermore, post-depositional processes and oxidative weathering tend to add Fe, and not remove it. Thus, the oxide-bound phosphorus was likely stripped from the sediments soon after deposition. Because the reactive phosphorus content is relatively low in these sediments, phosphorus released from oxides does not seem to have been retained by other authigenic forms, and was likely fluxed from the sediments into the anoxic deep basin waters. The lack of oxide-bound phosphorus in both sapropel and marl sediments indicates that partial reduction of the oxide minerals during anoxic conditions extended down into marl layers, with a front of oxygen-depleted interstitial waters penetrating the underlying ~ 1 -m marl layers and rapidly stripping the P from easily reduced oxide forms (supported by other work on marl layers within sapropel sequences; Passier et al., 1996; Slomp et al., 2002).

Another factor could play a role in the benthic release of P during anoxic basin conditions. As noted earlier, several authors suggest preferential release of P (compared to C) from degrading organic matter in anoxic environments (Ingall et al., 1993; Van Cappellen and Ingall, 1996; Schenau et al., 2000). Although not all studies show this to be the case (Colman et al., 1997; McManus et al., 1997; Anderson et al., 2001; Filippelli, 2001), Slomp et al. (2002) suggested this as a driving mechanism for observed productivity variations related to the deposition of eastern Mediterranean marl–sapropel sequences. In the Sorbas Basin, we find molar Corg:Porg ratios between 200 and 500 (Sierro et al., 2001b), not particularly high compared to average marine sediment values of 400 to 500, and similar to that observed in recent sediments from another anoxic basin – the Saanich Inlet in British Columbia (Filippelli, 2001). The Corg:Preactive ratio, perhaps a better comparison of net P in the sediments (Anderson et al., 2001)

averages about 20 (Sierro et al., 2001b), and, like the Corg:Porg ratio, shows no systematic variation between the lithologies and little indication of preferential release of P during organic matter degradation. Thus, the data from this study indicate that sedimentary conditions in this restricted margin in the western Mediterranean may not be the same as in the eastern Mediterranean, perhaps due to the amplification of the anoxic signal in the Sorbas Basin or differences in sedimentation rate. Therefore, a search for a comprehensive explanation of benthic cycling and the role of P in surface water productivity, as pursued by Schenau et al. (1999), must continue. However, at least for the Sorbas Basin, an interesting chain of biogeochemical, oceanographic, and climatic effects may be reflected in the sapropel/marl couplets.

5. The SNO Effect and surface productivity

The geochemical evidence, mainly from detailed phosphorus determinations and paleo-redox proxies, presented here supports a hypothesis that a sediment–nutrient–oxygen feedback (herein dubbed the SNO Effect) is in part responsible for driving the observed productivity variations. This feedback is strongly related to stagnation and overturn events driven by climatic variations on precessional timescales, and represents an intriguing interplay between climatic, oceanographic, biogeochemical, and net control on lithologic composition of this marginal basin. The SNO Effect is best described for each couplet beginning at the sapropel layer, and is diagrammed in Fig. 6. Water column stratification, due to lower wind stresses at insolation minima, results in reduced oxygen ventilation to deep waters, eventual depletion of deep water oxygen due to organic matter consumption, and the deposition of laminated sapropels. Anoxic conditions at these times lead to the release of the biologically limiting nutrient P from reducible iron phases in the sediments as these phases are dissolved. Water column stagnation causes the buildup of P below the photic zone. If these conditions were to last several times the residence time of P with respect to removal (about 20–40 kyr, but calculated for a steady-state

whole-ocean scenario; Ruttenberg, 1993; Filippelli and Delaney, 1996), the lowered vertical water flux would be mitigated by high P concentrations, and thus the net flux of P to surface waters would again increase (e.g. Broecker and Peng, 1982). However, this stagnation period persists for less than 10 kyr, and is disrupted by increased wind stresses as the climate state moves toward insolation maximum. Wind-driven mixing and overturn driven injects P-rich bottom waters into the photic zone. The biotic response to this overturn is high productivity in marls directly overlying the sapropels, culminating in diatom mat formation as the peak in P fluxes is reached. The end of the bloom events may have been forced by the depletion of this deep source of P, resulting in the return of normal productivity conditions and marl deposition. Eventually, a decrease in wind stress resulting from the climatic trend toward insolation minima begins the process of decreased ventilation and eventual stagnation, resulting in the deposition of the next sapropel layer. At least some aspects of these results are similar to those for other sapropel sequences in the Mediterranean and the organic-rich layers in the Arabian Sea (Van Os et al., 1994; Schenau et al., 2000), and indicates that sedimentary recycling of nutrients may be a widespread process driving surface productivity in other regions. Clarification of the timing of events in this model is necessary, however. First, the release of nutrients to deep water would eventually result in increased productivity even in a stagnant environment (e.g. Van Cappellen and Ingall, 1994), since stagnation is not total and even the minimal water flux to the surface ocean would be nutrient enriched. Second, why does the diatomite, indicating an acme bloom under eutrophic conditions, take several thousand years to occur even after the initiation of upwelling? Third, what is the mass balance of phosphorus (inventories, fluxes, and residence times) in this semi-open marginal basin? Fourth, what must the release rate of phosphorus from oxides and perhaps organic matter have been to allow build-up of phosphorus in deeper water on this spatial and temporal scale? Most of these questions revolve around a comprehensive understanding of the phosphorus mass balance in not

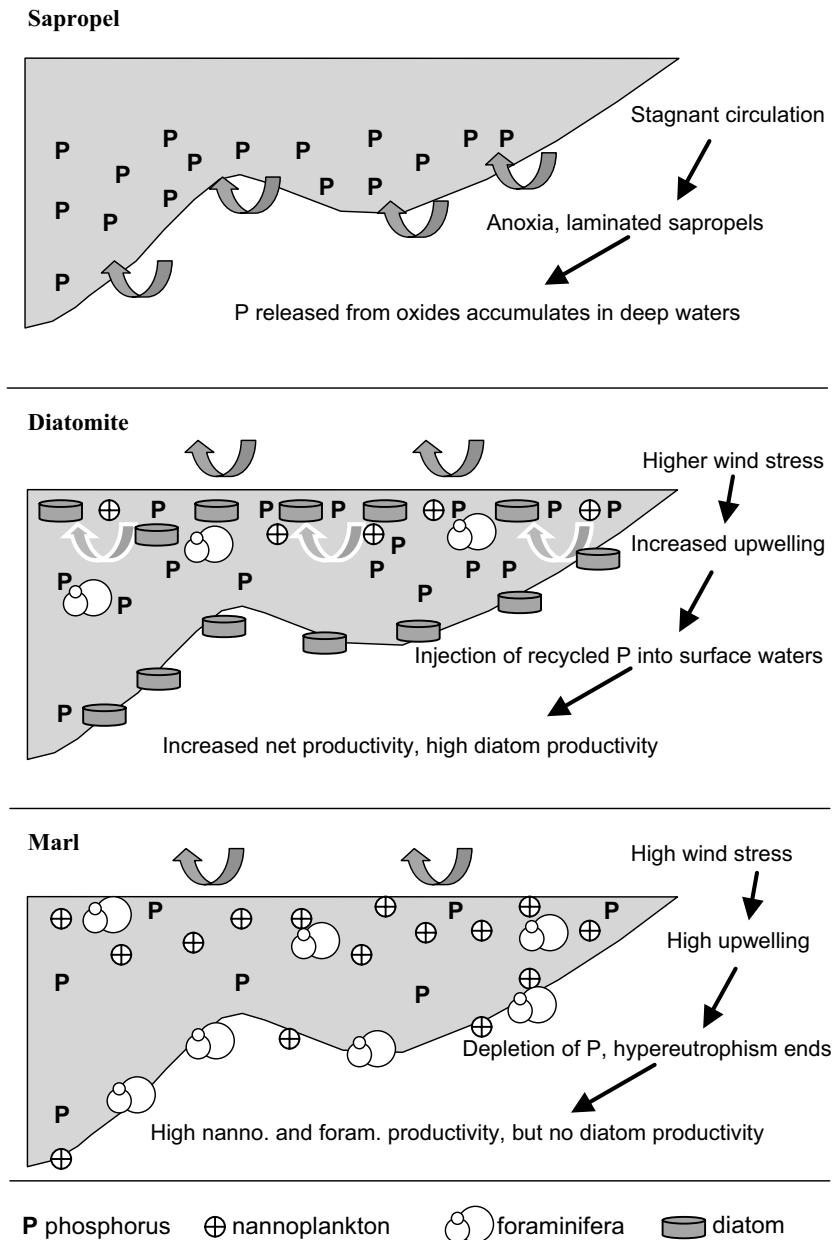


Fig. 6. A model of cyclic sedimentation in the Sorbas Basin. This model invokes the buildup of P in deeper waters caused by the release of P associated with iron oxides during sapropel formation and ocean stagnation, injection of P into surface waters due to wind-driven ocean ventilation culminating in hypereutrophic conditions and diatomite deposition, then subsequent depletion of these excess nutrients and return to 'normal' productivity conditions during marl deposition. The actual couplet cycle contains a marl layer forming after sapropel deposition but before diatomite formation, which can be considered to represent the beginning of P injection into surface waters as winds increase heading towards insolation maxima.

only the Sorbas Basin but also in the deeper sections and the eastern Mediterranean, as well as a better understanding of the similarities and differences in nutrient cycling, oxygenation, sedimentation, and climate that somehow drive cyclical sedimentation in the Mediterranean across large temporal and spatial scales.

6. Implications

Two important features arise from these results. First, the sediment dynamics in this region may have been controlled in large part by the availability of an internal pool of nutrients. Second, external factors beyond upwelling intensity (i.e. nutrient input from rivers) are not necessary to drive the sapropel/marl cycles seen in these sequences. This in no means rules out external factors in driving these cycles, but simply reveals that an internal mechanism is a viable competing hypothesis. Several important questions also arise from this research. What controls the preferential P release from organic matter in anoxic settings? Although documented in several settings, it is in no way a universal process and thus should be used with care in models of ocean and atmosphere biochemical processes until more is known about this. Sedimentation rate, type of organic matter, presence or absence of other substrates (e.g. reducible oxides, sulfate) are among several factors that should be tested to further understand the coupling between anoxia and P and C cycling in the ocean. How comparable are these short-lived cyclic events to widespread and prolonged Oceanic Anoxic Events (OAEs)? The temporal and spatial scales of these two processes are quite different, but can any of these processes of nutrient cycling and biogeochemical feedbacks observed in the western Mediterranean help to explain OAEs? How does this SNO Effect impact the deeper Mediterranean? The effect is clearly amplified in the restricted Sorbas Basin, and may in fact occur in other restricted basins like the Santa Barbara Basin and the marginal basins in which the Miocene Monterey Formation was deposited. But do the sediment–water interactions occurring in shallower waters of these restricted basins im-

act the whole ocean in a substantive way? If so, then these basins do not just amplify climatic processes, but may be a vehicle by which these climatic processes impact the whole ocean.

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