Phosphorites and paleoceanography

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ABSTRACT

1) Phosphorite genesis correlates in a general way with elevated sea level and warm climate and is therefore influenced by plate tectonics and continental drift.

2) Phosphorite genesis correlates more specifically with transgression — a result of the interaction of continental hypsometry, tectonic perturbation and eustatic effects — whereby a small number of shallow slope and shelf sites are available for phosphate fixation. Such shallow transgressive seas are typically highly fertile, and tend to sequester nutrients, accounting for the common association of phosphorite with organic-rich black shales. Poorly-oxygenated shallow seas also provide a shorter transit for organic matter from productive surface waters to sediments, resulting in less oxidation and greater initial retention of organic phosphorus.

3) Phosphorite genesis correlates with warm climate, which may be related to a) increased flux of phosphorus to the ocean during time of increased chemical weathering on land ; and b) development of widespread oxygen-depleted waters because rates of oceanic circulation and O_2-solubility are reduced. Consistent with the hypothesis of increased nutrient supply to the oceans at, or just before, major Cenozoic phosphorogenic episodes, is the coeval development of widespread biogenic silica deposits.

4) Oceanic anoxic events (OAE's : episodes of world-wide deposition and preservation of organic carbon), which also correlate with particularly high sea level stands, generally do *not* coincide with major phosphorogenic episodes. This may be due to the fact that during OAE's abundant phosphorus is fixed in the deep sea with well-preserved organic carbon and is hence unavailable to form major shallow slope and shelf deposits. Furthermore when 'excessive' areas of shallow shelf exist in parallel with numerous potential sites of phosphate fixation, multiple small deposits tend to be produced rather than a few of economic importance : they thus may elude notice or classification. However, phosphatized seamount limestones and phosphatic hardgrounds in shelf carbonate sequences may be formed during OAE's.

5) In contrast to the assertions above, the permian Phosphoria Formation was deposited during a marked overall global low-stand of sea level. However, the phosphatic sequences were laid down during brief transgressive episodes. The anomalously high concentration of phosphorus in that unit probably exists because that part of North America provided one of the few available sites for the fixation of phosphate during the Permian. If global waters had withdrawn to the top of the continental slope, or if continental margins stood high, only a particularly low-lying continental area would be covered by the sea and could act as a sink for most of the ocean's available phosphate.

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RÉSUMÉ

Phosphorites et paléocéanographie.

1) La phosphatogenèse correspond dans ses grandes lignes à des périodes de transgression ou de climat chaud. Elle est donc influencée par la tectonique des plaques et la dérive des continents.

2) En période de transgression (combinaison du relief continental, des accidents tectoniques et des phénomènes eustatiques), le fond de la mer présente certains sites, tant sur le plateau que sur des pentes douces, qui permettent la fixation des phosphates. Les mers transgressives peu profondes sont très fertiles et tendent à retenir les sels nutritifs, expliquant ainsi l'association fréquente de phosphorites avec les vases organiques. De plus dans les mers peu profondes et appauvries en oxygène dissous, le transfert de la matrice organique des zones productives de la surface vers les sédiments, est plus rapide. L'oxydation y est réduite, ayant pour conséquence une rétention initiale plus grande du phosphate organique.

3) La phosphatogenèse, qui peut être mise en corrélation avec un climat chaud, peut s'expliquer soit par un accroissement de l'apport de phosphore à l'océan consécutif à une altération chimique plus intense à terre, soit à une généralisation de la diminution de teneurs en oxygène dans les eaux, liée au ralentissement de la circulation océanique ou à la baisse de solubilité de l'oxygène. La généralisation des dépôts de silice biogénique, qui va de pair avec les grands épisodes de phosphatogenèse au Cénozoïque, est compatible avec cette hypothèse d'un accroissement en sels nutritifs à ces mêmes époques.

4) Les épisodes anoxiques océaniques (OAE : période où le dépôt et la préservation du carbone organique constituent un phénomène général à l'échelle du globe), périodes qui sont en outre souvent corrélables avec un niveau élevé des mers, ne coïncident pas avec les grands épisodes phosphatés. Cela peut tenir au fait que durant les « OAE », une quantité importante de phosphore est retenue dans l'océan profond avec le carbone organique bien conservé ; le phosphore n'étant plus alors disponible pour constituer des accumulations importantes tant sur la pente que le plateau. Bien plus, quand la surface des eaux peu profondes est considérable, offrant ainsi de nombreux sites potentiels de fixation de phosphate, la tendance est à la multiplication de petits gisements plutôt qu'à la formation d'accumulations peu nombreuses et d'importance économique. Toutefois, durant les OAE, la phosphatisation de calcaires des seamounts et le développement des hardgrounds phosphatés dans les séries carbonatées du plateau continental peut se produire.

5) En contradiction avec ces hypothèses, on constate que la « phosphoria formation » du Permien s'est déposée à une époque caractérisée par un niveau général des mers particulièrement bas, bien que les niveaux de forte concentration à l'intérieur de cette unité se soient accumulés durant de brèves périodes de transgression. La concentration anormalement élevée de phosphore dans cette unité a dû se produire parce que cette partie de l'Amérique du Nord constituait un des rares sites de fixation pour le phosphate au Permien. En effet, si les eaux de l'océan global n'atteignent plus que le sommet de la pente, ou si les marges continentales sont trop élevées, seule une zone continentale exceptionnellement basse pourra être recouverte par la mer et agir comme un piège pour l'essentiel du phosphate océanique disponible.

INTRODUCTION

The availability of dissolved phosphate in the oceans in part controls primary productivity. At present, the concentrations of biologically useful nitrogen and phosphorus in the oceans relative to other elements suggest that these are the limiting nutrients in phytoplankton production (Broecker, 1974 ; Holland, 1978). Froelich *et al.* (1981 ; cf. Burnett, 1980) have quantified this present-day linkage between the oceanic phosphorus and carbon cycles (Fig. 1), although these fluxes are still only poorly known. In considering past variations in global oceanic productivity, and to estimate future trends, it is important to understand the possible effects of various paleoceanographic and climatic factors on the geochemical cycle of phosphorus. That significant variations in the phosphorous cycle have occurred in the geologic past is suggested by data compiled by Cook and McElhinny (1979), which show large differences in the mass of sedimentary phosphate deposits representing various parts of geologic time (Fig. 2 and 3). However, the reported absolute value of total phosphorus extracted could be as much as an order of magnitude in error for the following reasons : 1) these data are a record of what is *preserved* and *exposed* which may not adequately reflect what was initially
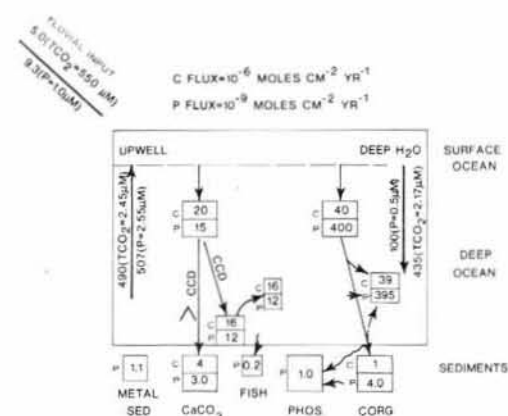

Figure 1

The interaction of the carbon and phosphorus cycles (modified after Froelich et al., 1981, cf. Burnett, 1980). Estimated fluxes and concentrations of P and C to and from various reservoirs are shown (see Table 1). Note that less than 10 % of the fluvial phosphorus flux apparently enters sedimentary phosphorite deposits worldwide under inferred present-day steady-state conditions. The proportionation of phosphorus into individual reservoirs might have been quite different at times in the past. TCO₂ denotes total dissolved carbon.

Figure 2

Late Mesozoic paleoceanographic parameters, geochemical accumulation rates, and generalized marine stratigraphy.

Column 1 : Jurassic and Cretaceous after van Hinte, 1976 a, b ; Column 2 : Jurassic modified after Hallam, 1978 ; Vail et al., 1977 ; Cretaceous after Hancock and Kauffman, 1979 ; Vail et al., 1977 ; Column 3 : after Arthur, 1981 ; Jenkyns, 1980 ; Schlanger and Jenkyns, 1976 ; Column 4 : after Scholle and Arthur, 1980 ; Column 5 : after Cook and McElhinny, 1979. (Abbreviations : Neocom = Neocomian ; Thit = Thithonian ; Trias. = Triassic).
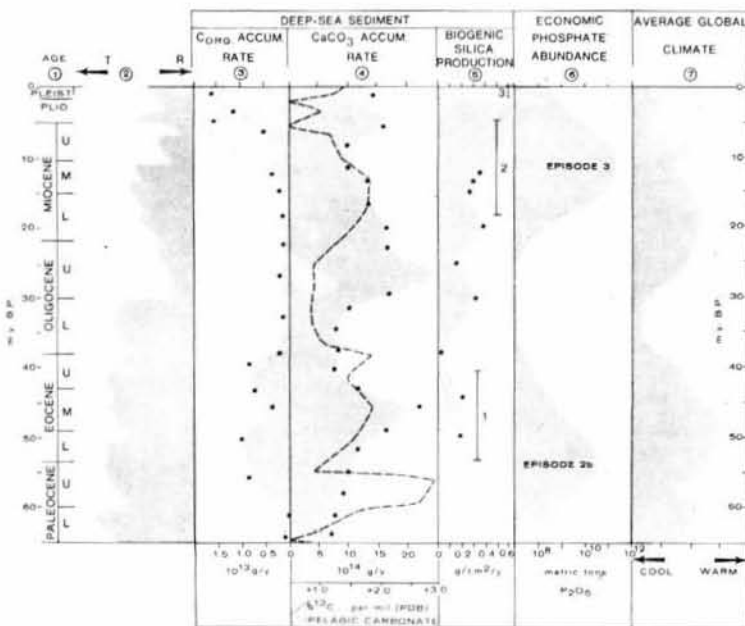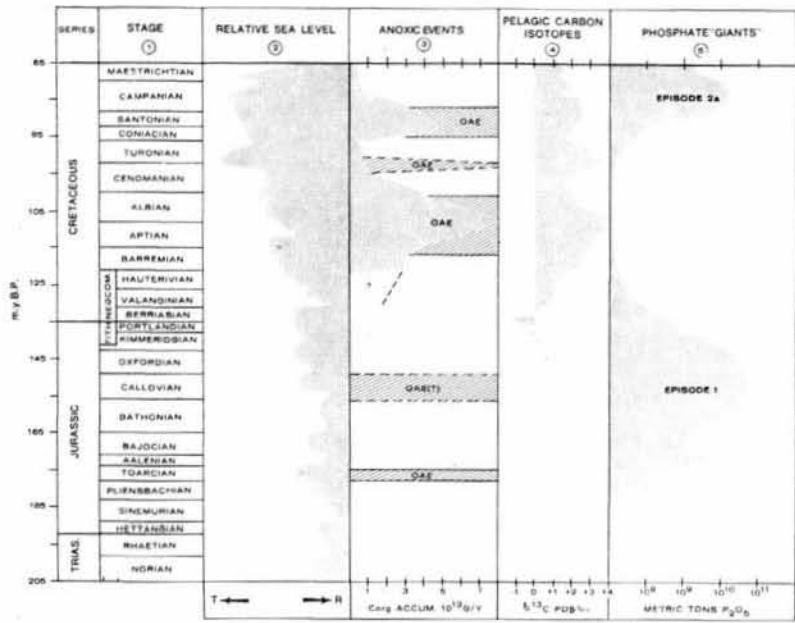

Figure 3

Cenozoic paleoceanographic parameters, geochemical accumulation rates, and generalized marine stratigraphy.

Column 1 : after Berggren, 1972 ; Column 2 : T, transgression ; R ; regression, indicate sea-level relative changes ; after Vail et al., 1977 ; Column 3 : after Arthur, 1981 ; Column 4 : after Worsley and Davies, 1981, and Arthur, 1981, compiled from numerous sources ; Column 5 : after Leinen, 1979, and other sources ; Column 6 : after Cook and McElhinny, 1979 ; Column 7 : after Savin, 1977 ; Frakes, 1979 ; and others. L = Late ; M = Middle ; E = Early.

deposited ; and 2) they represent only a tally of economic deposits and do not consider the amount of phosphate locked up in sedimentary organic matter or as absorbed phosphate or disseminated phosphate particles in other noneconomic sedimentary accumulations. Nonetheless, large relative differences in phosphate mass between sections of the geologic record (if they exist) should reflect real changes in rates of phosphate extraction from the oceans. If we accept that the mass of sedimentary phosphate deposits does change, then this implies that there have been changes in the concentration of dissolved phosphate in the oceans. The variations could have occurred because of changes in the rate of fixing of phosphate in sediments and/or in the flux of phosphorous to the oceans from various sources (see Table 1 and Fig. 1). The purpose of this paper is to consider possible past variations in the geochemical cycle of phosphorus, particularly during the Mesozoic-Cenozoic, and to suggest that a number of factors can account for the major changes in phosphate sedimentation. The general model developed here is intended to explain the episodicity of major phosphorite deposits, but is not intended to account for all large phosphorite accumulations.

A number of recent papers have thoroughly considered the 'phosphate problem' (e.g. Kolodny, 1980 ; Burnett, 1980 ; Sheldon, 1980 a, b ; Bentor, 1980 ; Cook, McElhinny, 1979 ; Slansky, 1980). We do not reiterate here any discussion of the fine-scale details of formation of these sediments. In general, we accept the idea that phosphatization is

Table 1

Major present sources and sinks in the geochemical cycle of phosphorous *

Estimated P residence time in oceans : 100,000 yr		
Sources		(average conc. 2.2 mM/kg)
1. Deep-water dissolved phosphate :	9×10^{16} gP	
2. Fluvial dissolved phosphate from rock weathering :	1.7×10^{12} gP/y	(range of estimates : 0.4-2.0×10^{12} gP/y) [atmospheric contribution negligible]
3. Volcanic emanations :	0.07×10^{12} gP/y	[Hydrothermal ridge circulation negligible]
4. Interstitial water reflux from sediments :	ca. 5×10^{12} gP/y	
5. Regeneration via C-org oxidation in water wolumn :		(> 90 % of downward flux)
Sinks		
1. Uptake in C-org by phytoplankton and zooplankton and burial in sediments	ca. 0.73×10^{12} gP/y	
2. Burial of apatitic bone teeth and scales :	ca. 0.04×10^{12} gP/y	
3. Burial in biogenic carbonates :	ca. 0.54×10^{12} gP/y	
4. Adsorption on iron-oxide-rich deep-sea sediments	ca. 0.2×10^{12} gP/y	
5. Incorporation in phosphatic sediment	ca. 0.17×10^{12} gP/y	

* Estimated steady-state values based on data from Froelich *et al.* (1981) ; Baturin, 1978 ; Morse in Burnett and Sheldon, 1979.

mainly a diagenetic process. Upwelling of relatively nutrient-rich deep waters leads to production of organic matter in near-surface waters and the increased downward flux of organic matter results in accumulation of organic carbon-rich sediment ; the release of phosphorus from this organic matter by oxidation and bacterial processes, and to some extent the phosphate supplied by dissolution of phosphatic fish and other bone debris, into the sediment pore waters causes phosphatization, either by replacement of carbonate, by replacement of fecal pellets, or by precipitation of carbonate fluorapatite within the sediment or at the sediment/water interface. The required conditions for phosphatization are therefore a fairly continuous supply of phosphorus to near-surface waters, the effective burial of organic matter in sediments, and the regeneration of sufficient phosphorus from organic matter in pore waters to allow precipitation of phosphate minerals at or near the sediment-water interface. However, we also acknowledge that some ancient phosphorites may be either primary precipitates, such as the oolitic phosphorites of part of the Phosphoria Formation (Sheldon, 1980 *b*), or replacements of carbonate sediments in certain regions, such as on seamounts or banks within the oxygen-minimum zone areas that were perhaps bathed in unusually phosphate-rich waters.

THE PHOSPHORITE PROBLEM : A CRITIQUE OF PREVIOUS MODELS

Other researchers have recognized that a large increase in the abundance of phosphate, as apparently represented by the Permian Phosphoria Formation of the western United States, might represent a significant increase in the oceanic phosphate concentration (e.g. Sheldon, 1980 *a* ; Bentor, 1980). The estimated mass of phosphorus (P) in the economic deposits of the Phosphoria Formation (7×10^{17} g) represents as much as that estimated to enter the oceans from land-derived fluvial supply in ca. 0.4×10^6 yrs (see Table 1) and contains nearly 10 times as much P as in the modern ocean. If the Meade Peak Member of the Phosphoria Formation represents deposition over about 4 m.y.

(Wardlaw, pers. comm., 1980) over ca. 0.2 % of the sea-floor, then more than 5 % of the steady-state fluvial P flux would have been stored there annually (this amount equals about 10 % of the annual riverine flux estimated by Burnett and Oas, 1979). At present, much less than about 10 % of annual P input to the oceans from rivers (based on steady-state considerations) is stored annually in sedimentary phosphate deposits all over the world (see Fig. 1 ; Froelich *et al.*, 1981). Clearly then, Phosphoria time was anomalous in terms of the marine phosphorus cycle. It is emphasized that these calculations do not take into account the amount of P contained in the noneconomic parts of the Phosphoria Formation or other age-equivalent rocks.

Previous models may well account for some of the variation in the mass of sedimentary phosphate deposited through geologic time. We are intrigued with the suggestion of Piper and Codispoti (1975) that the former presence of widespread anoxic oceanic deep-water masses could have led to increased rates of nitrate reduction and the consequent removal from the entire system of large amounts of combined nitrogen (nitrate) necessary for phyto- and zooplankton productivity ; this, it is hypothesized — given that biological uptake of N and P is in a constant ratio (the 'Redfield ratio' on average C:N:P = 106:16:1 — would lead to elevated phosphate concentrations and precipitation of marine apatite. Much of the phosphate would have to be incorporated in the hard tests of the phytoplankton in order to reach the sediment. We find two problems with this hypothesis : 1) there is a relatively poor correlation between inferred 'oceanic anoxic events' in the Mesozoic and times of known economic phosphate deposits as we discuss below (Fig. 2) ; and, 2) at present, phosphorite deposition appears to be closely related to production of organic matter and its burial in sediments ; thus any decrease in the flux of organic matter to sediments, such as that proposed by Piper and Codispoti (1975) would result in a decreased supply of phosphorus as well, and an increase in the oxygen concentration in deep-water masses, thereby decreasing the rate of nitrate reduction and reducing organic matter preservation, thus inhibiting phosphorite formation. Transport of phosphate to sediment via skeletal matter is not an efficient mechanism since much of this material is not rapidly

regenerated to liberate phosphate. Only if inorganic phosphorite formation occurred as in the Kazakov (1937) hypothesis after buildup of dissolved phosphate in the oceans to some critical level, would the 'nitrate-reduction' model lead to more widespread formation of phosphatic deposits. Consideration of apatite solubility in relation to the chemistry of seawater (particularly inhibition by Mg^{2+}) suggests that inorganic precipitation is exceedingly difficult, even at supersaturation (Atlas, 1979 ; in Sheldon, Burnett ; discussion in Bentor, 1980 ; Burnett, 1980). Therefore, we believe that although the 'nitrate-reduction' model describes a mechanism for increasing the phosphate content of the oceans it does not explain the sedimentary associations of phosphorites in the geologic record.

Sheldon (1980 b), following a suggestion of Berger and Roth (1975) and Fischer and Arthur (1977), proposed an 'episodic circulation' model in which generation of major phosphorite deposits is related to the residence time of oceanic deep water. He suggests that deep-water overturn might be more sluggish during warm climatic episodes, thus allowing deepwater phosphate contents to increase gradually. Sheldon's contention is that abrupt climatic-changes, specifically major global cooling, would result in more rapid deep-water turnover which would stimulate organic productivity and lead to the extraction of the large residual phosphate buildup into phosphorite deposits. This is a plausible mechanism, but there are problems with this fairly simple model. It does not seem to work, for example, at the Eocene/Oligocene transition which appears to be a time of a major readjustment of deep-water circulation (Benson, 1975 ; Shackleton, Kennett, 1975 ; Berggren, Hollister, 1977 ; Moore et al., 1978) : there are no known major Oligocene phosphorite deposits. Nor does the model explain the apparent episodicity of phosphorite formation during the Mesozoic when there were no major climatic perturbations and no significant glacial epochs. Another problem with the 'episodic circulation' model is that at present there are about 9×10^{16} gP in the deep-water reservoir and solubility considerations suggest that this is near the point of saturation with respect to apatite (Sheldon, 1980 b). It is certainly not likely that the ocean has maintained a deep-water reservoir of more than 2 or 3 times that amount, which is still 3 times less than that contained in the economic intervals of the Phosphoria Formation. It is, furthermore, unlikely that the ocean could be entirely stripped of its phosphate.

An idea of the maximum excursion of the deep-sea dissolved phosphate content during the Cenozoic may be provided by examination of $\delta^{13}C$ values of total dissolved carbon in the deep sea as recorded by benthic foraminifers of various ages. These values will only approximately represent the deep-sea total dissolved carbon $\delta^{13}C$ composition for a number of reasons which will not be dealt with here. A compilation of average benthic foraminifer $\delta^{13}C$ values for the Cenozoic (see Arthur, 1981) suggests that deep-water total dissolved carbon (TDC) was never much more negative than about $- 1$ ‰ which is only about 1 ‰ lighter than todays average TDC. Deep-water phosphate concentrations and $\delta^{13}C$ values of total dissolved carbon in the same deep-water mass are negatively correlated (e.g. Broecker, 1974). CO_2 is added to deeper water masses during organic carbon oxidation. The $\delta^{13}C$ values of organic carbon is much more negative (average $- 23$ ‰) than that of total dissolved carbon. As organic matter is oxidized then, both phosphate and isotopically light carbon are added to the water mass. The correspondence between phosphate and the $\delta^{13}C$ of the

TDC of average deep water is such that an average PO_4^{2-} concentration of about 2.2 µM/kg corresponds to a $\delta^{13}C$ value of about O ‰. Assuming that the average TDC in the deep sea does not change much through time and that organisms generally fix phosphorus to carbon in the Redfield ratio, then a 1 ‰ change in the deep-water TDC corresponds to about a 1 µM/kg change in the PO_4^{2-} concentration. If the record of $\delta^{13}C$ fluctuations given by an average benthic $\delta^{13}C$ signal is valid, then we may say that, at least during the Cenozoic, the deep-water phosphate concentration did not vary by more than a factor of two.

These arguments make the 'episodic circulation' model an unlikely explanation for all widespread phosphorite deposits. Another problem is that it is not certain that rates of deep-water turnover would necessarily decrease during times of warm, equable climate. At these times masses of dense saline water, derived from wide shelves in low latitudes or from restricted low-latitude basins, might slide basinward, stimulating rapid deep-water turnover.

It is therefore suggested that most previous models have been too simplistic. This paper discusses the factors which we think are the most important in consideration of long-term and short-term changes in the marine phosphorus cycle. These are : 1) the expanse of relatively shallow seas which is some function of global sea-level changes and continental hypsometry ; and 2) global climate which controls weathering rates and the input of phosphorus to the oceans. Both of these parameters vary in time, but do not necessarily vary together. They are also superimposed on the tableau of drifting continents which is an another significant factor (Cook, McElhinny, 1979). We have attempted to evaluate these parameters for the late Mesozoic-Cenozoic where the best record of changes in climate, oceanography, and sedimentation is preserved, and show how this model explains other phosphatic 'anomalies' in the geologic record. The emphasis is on explaining the time relations of large deposits, but other types of phosphate mineralization such as those of chalk hardgrounds (Kennedy, Garrison, 1975 ; Jarvis, 1980) are also briefly considered. We first describe the relationship between major 'phosphate events' or what we will term 'phosphorite giants' in the context of the paleoceanographic record. We next describe our model ; it is complex, but we believe that the interaction of several parameters best explains the variations in the marine phosphate cycle.

PHOSPHORITE 'GIANTS' AND PALEOCEANOGRAPHY

The distribution of 'phosphorite giants' of late Mesozoic-Cenozoic age (Cook, McElhinny, 1979) is shown in Figures 2 and 3. The compilation shows no important phosphorites formed in the Triassic, a mid-Jurassic increase in phosphorite formation, a major episode during the Late Jurassic-earliest Cretaceous, a relative low in the Early to mid-Cretaceous followed by a major Late Cretaceous-Paleocene 'phosphorite giant', a dearth of Oligocene phosphorite, a major Miocene peak in phosphorite accumulation, and a significant decline in formation through the Plio-Pleistocene. We believe, as do Cook and McElhinny, that these variations in amount of economic phosphorite deposits through time are significant age trends related to fluctuations in the conditions that favor phosphorite accumulation. Let us consider variations in a number of paleoceanographic parameters in order to see how they might bear on the formation of 'phosphorite giants'.

Sea level

The main Late Mesozoic-Cenozoic 'phosphorite giants' are labelled as follows (Fig. 2 and 3) : episode 1 (centered on Oxfordian-Callovian at about 149 m.y. BP) ; episode 2 (centered on the Cretaceous-Tertiary boundary at approximately 65 m.y. BP with two distinct peaks centered on Santonian-Campanian, about 77 m.y. BP, and Late-Paleocene-Early Eocene at about 54 m.y. BP) ; and episode 3 (Early to early Late Miocene, centered on about 14 m.y. BP). The major part of each episode lasted perhaps 30 m.y. or so with the exception of episode 3 which was relatively short-lived at perhaps 20 m.y. duration.

Each of the phosphorogenic episodes can be shown to have occurred during a period of relative highstand of sea-level (Fig. 2 and 3 ; based on Vail et al., 1977 ; Hancock, Kauffman, 1979 ; and Hallam, 1978). The correlation is good but not perfect. Episode 1 apparently began during a period of rising sea level during the Callovian and ended probably by Berriasian-Valanginian time with a lowstand. The Early to middle Cretaceous sea-level rise (Barremian through Turonian) was apparently not accompanied by major phosphorite deposition, although phosphatic levels occur locally in European chalks (e.g. Kennedy, Garrison, 1975). Episode 2, which began during the Coniacian-Santonian but peaked during the Campanian, corresponded to the highest Cretaceous stands of sea level. A decrease in the amount of economic phosphorite of early Paleocene age apparently corresponded to a lowering of sea level at the end of the Maestrichtian. The relatively high sea levels of the Late Paleocene-Middle Eocene were again in phase with formation of 'phosphorite giants'. The end of episode 2 occurred during the mid to Late Eocene, but this does not appear to have corresponded precisely to a global sea-level drop. A sea-level fall apparently occurred in the latest Eocene but the major drop occurred in mid-Oligocene time. The entire Oligocene is characterized by a lack of significant economic phosphorite deposits. Episode 3 occurred in conjunction with rising sea level ; the peak of this episode nearly coincided with the middle Miocene highstand. Falling or rapidly fluctuating sea level characterizes the more phosphorite-poor Pliocene-Pleistocene. Burnett (1980) has shown for the Peru-Chile margin that even though the relative amounts of phosphorite formed during the Pleistocene are low, the periods of formation coincide well with interglacial sea level highstands. Although there are periods of relatively high sea level during the Triassic, there are no known major phosphorites of that age. The exception that cannot be ignored is the Permian 'phosphorite giant' formed during a period of extremely low sea level (Vail et al., 1977). However, the main phosphatic members of the Phosphoria Formation may have formed during relatively brief transgressions within this predominantly regressive time (McKelvey et al., 1959).

Oceanic anoxic events

The 'phosphorite giant' episodes do not correspond well with so-called 'oceanic anoxic events' (OAE's of Schlanger, Jenkyns, 1976). These times of better preservation and more rapid accumulation of organic matter in deep marine settings (Fig. 2 and 3 ; after Arthur, 1981), related to times of apparent widespread deep- and intermediate-water oxygen deficits, are apparently not necessarily conducive to formation of major phosphate deposits. A possible Toarcian

(Early Jurassic) OAE (Jenkyns, 1980) does not correlate with a major 'phosphorite giant' episode although some phosphorite deposits of that general age are known. Episode 1 does not correspond to a well-developed OAE. The major OAE's of the Early to middle Cretaceous are also not accompanied by major phosphorite deposition. A less widespread (mainly epicontinental sea and deeper Tethyan-Atlantic-Caribbean) Coniacian-Santonian OAE was not entirely in phase with the early peak in episode 2, and the main part of the OAE precedes the main part of episode 2. The Late Paleocene-middle Eocene portion of episode 2 was accompanied by an increase in accumulation rates of organic carbon in marine basins according to a survey of DSDP sites (Fig. 3). The Oligocene was a time of very low accumulation rates of organic carbon and no major phosphorite accumulations. Episode 3 corresponds to widespread more or less shallow marine deposits (slopes and shallow basins) rich in organic carbon which were apparently deposited within well-developed oxygen-minimum zones (e.g. see Jenkyns, 1978 ; Arthur, 1979). There was also a slight increase in the global deep-sea accumulation rate of organic carbon at this time. Pliocene and Pleistocene time brought greatly increased rates of accumulation of organic carbon in deep-sea settings apparently without the development of widespread low-oxygen conditions or phosphorites. In this case the preservation of relatively more organic matter is probably related to greatly increased sedimentation rates of terrigenous detritus in the ocean basins because of increased glacial erosion on land. The 'phosphorite giant' episodes have only a moderate correlation with the average carbon isotope composition ($\delta^{13}C$) of coeval pelagic carbonates, which in part must reflect the relationship to carbon cycling and OAE's (e.g. Berger, 1977 ; Fischer, Arthur, 1977 ; Scholle, Arthur, 1980 ; Vincent et al., 1980). The 'phosphorite giants' tend to have corresponded to more positive $\delta^{13}C$ values in pelagic carbonates.

The 'phosphorite giants' are commonly associated with 'black shales' in a given depositional setting (e.g. Piper, Codispoti, 1975). However, widespread organic carbon-rich sediments formed during OAE's were not always associated in time or space with major phosphorite deposition. 'Phosphorite giants', in fact, tend to occur near the beginning or end of an OAE.

Climate

Climate is another variable that seems in some way to bear on the genesis of 'phosphorite giants'. The major episodes generally correspond to times of warm, equable global climate (as also pointed out by Slansky, 1980). This correlation works well for the Cenozoic, but changes in climate alone cannot explain the variability of phosphorite deposition during the warm, equable Mesozoic when overall climatic variations were apparently minor (e.g. Hallam, 1975). Colder, possibly dry intervals were, however, characterized by a lack of major phosphorite deposits as shown in Figure 3.

Carbonate accumulation and fluctuations in the CCD

Accumulation of carbonate in the deep sea (Fig. 3 ; after Worsley, Davies, 1981 ; compilation of DSDP results through Leg 44, biased towards the ocean floor below 3 km depth ; Whitman, Davies, 1979) is another parameter which

does not show a consistent relationship to 'phosphorite giants', at least in the Cenozoic where the most adequate data exist. However, in general, relatively high carbonate accumulation rates occurred in the deep-sea during non-phosphorogenic periods such as the Oligocene and Pleistocene and probably during the Early Cretaceous (pre-middle-Aptian) as well. The middle Cretaceous was characterized by low phosphorite and low deep-sea carbonate accumulation rates. A dip in the global rate of accumulation of deep-sea carbonate also occurred in the Early Paleocene, corresponding with a possible decrease in phosphorite accumulation during the middle of episode 2. Relatively low rates of accumulation of carbonate in the deep sea correlate with formation of 'phosphorite giants', with the exception of the Early to Middle Eocene which was characterized by an anomalously high carbonate accumulation rate.

Fluctuations of the Carbonate Compensation Depth (CCD) through time are now well established. In the Cenozoic a shallow CCD corresponded to formation of 'phosphorite giants' whereas a relatively deep CCD prevailed at other times. The Cretaceous, however, was characterized by a relatively shallow CCD throughout, except possibly during the Late Maestrichtian and during pre-Aptian time.

Association with siliceous sediments

Biogenic siliceous marine deposits appear to have been more widespread during deposition of 'phosphorite giants' (e.g., Fig. 4). Although the critical quantitative data remain unavailable, there appear to have been intervals of increased rate and area of accumulation of radiolarian, sponge, and diatom-rich strata during the Early to Middle Eocene (possibly beginning in the Late Paleocene) and the Early to early Late Miocene (e.g., LeClaire, 1974 ; Fischer, Arthur, 1977 ; Leinen, 1979 ; Ramsay, 1977). These periods correspond to part of 'phosphorite giant' episodes 2 and 3. The relatively phosphate-poor intervals of the Early Paleocene, the Oligocene, and Plio-Pleistocene are marked by apparent

decreases in the area and rates of accumulation of biogenic siliceous material. The Cretaceous, however, shows a relatively poor correlation between phosphorite and siliceous sediments. Deep-sea cherts and less altered siliceous biogenic sediments are common in pre-middle Aptian pelagic sequences and in Upper Albian through Conacian-Santonian deposits. The Campanian-Maestrichtian pelagic sequences contain relatively less biogenic siliceous material. Upper Jurassic Tethyan pelagic sequences are characterized by widespread radiolarian chert horizons ; however, it is not yet clear whether such siliceous rocks exist on Atlantic and Pacific deep-sea floors, although Jurassic radiolarites are prevalent in the Franciscan Complex of California. Obviously there is not a perfect correlation between 'phosphorite giants' and siliceous biogenic sediments in the Upper Mesozoic.

Interplay of variables

So far this discussion has considered mainly the relationship between deposition of phosphate and the pelagic deep-sea record. The possible correlations have been considered one at a time — an artificial way of examining the interaction between paleoceanography and sedimentation. In actuality there is a general interdependence of many of the variables considered (see Berger, 1977 ; Fischer, Arthur, 1977 ; Arthur, 1979 ; and references therein). For example, warm climate generally accompanies relatively high sea level. 'Anoxic events' occur during these times as well. Sea level and the area of shallow seas also, in part, determines the overall patterns of sedimentation, largely via so-called shelf-basin fractionation (e.g., Berger, Winterer, 1974 ; Hay, Southam, 1977 ; Worsley, Davies, 1979). These two factors are especially pertinent for carbonate accumulation as one expects deep-sea accumulation rates to increase during low sea-level and decrease during high stands in which larger carbonate platforms and/or extensive shallow chalk seas exist. The presence of abundant carbonate-rich shallow seas may also be reflected in an elevated CCD in the
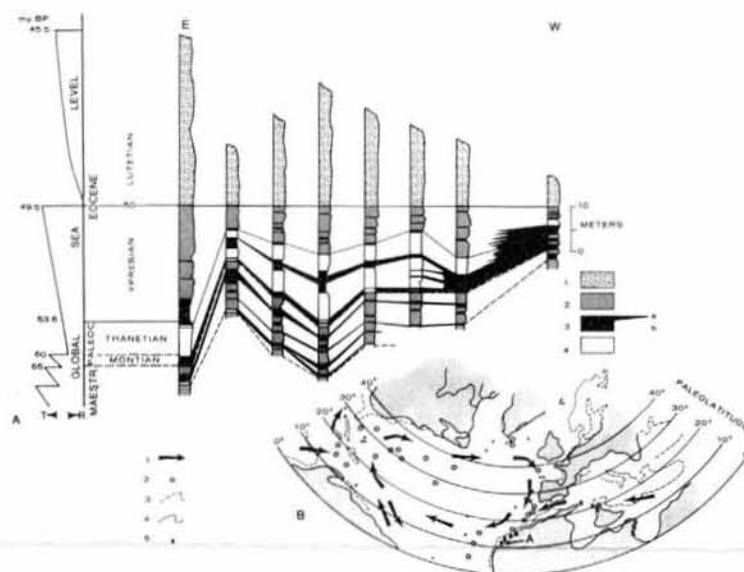
Figure 4

Stratigraphic and paleogeographic setting of phosphatic facies in North Africa.
A) *Stratigraphy of Moroccan Maestrichtian-Paleogene deposits (modified after Boujo, 1980 ; global sea level after Vail* et al., *1977). Note the general association of the richest phosphorite beds with low sea-level stands, probably representing reworking of previously-deposited phosphatic sediments. Phosphatic beds occur mainly in relatively poorly-oxidized marly units characterized by abundant associated biogenic silica. Sedimentation rates were low throughout deposition of the sequence, but increased greatly during deposition of Lutetian carbonates which are only slightly phosphatic.*
1. fossiliferous, slightly to non-phosphatic relatively shallow-water limestone
2. primarily marly, siliceous biogenic facies
3. phosphatic beds : a) > 28 P₂O₅, b) < 28 % P₂O₅.
4. primarily marlstone, claystone, and /or sandstone.
B) *Paleogeography of part of northern hemisphere for Ypresian time (after Firstbrook* et al., *1979) with generalized distribution of land and sea and postulated surface currents (after Riech, von Rad, 1979)*
1. hypothetical surface current pattern
2. DSDP sites with lower to middle Eocene biogenic siliceous facies
3. present-day continental outline
4. generalized Lower Eocene phosphate deposits
5. location of major Lower Eocene phosphate deposits.

world ocean. However, as shown in Figures 2 and 3 and discussed above, there are exceptions to many of these generalizations. We discuss in the next section the possible reasons for the correlations, both positive and negative, and present a somewhat complex but, we hope, realistic model to explain the apparent variations in phosphorite sedimentation through time.

A RATIONALE FOR 'PHOSPHORITE GIANTS'

The mechanisms for variation in phosphorite sedimentation and widespread phosphatization through time can be separated into first- and second-order effects (see Table 2). In addition to continental position ably argued by Cook and McElhinny (1979), a first-order control on the oceanic phosphate cycle is sea level (Fig. 2 and 3). This is because relative sea level controls supply of phosphate to the ocean and secondly because it determines, to a major degree, suitable sites for formation of phosphate-rich deposits

Phosphatic deposits are interpreted as having been formed under a generally low rate of sedimentation (particularly low detrital influx), a high rate of supply of phosphate to surface waters through some sort of upwelling, and a consequent large supply of phosphate-bearing organic matter to the sediment. Thus, the common model of upwelling zones along westward-facing coasts in the low-latitude Trade Wind Belts has evolved (e.g. Sheldon, 1980 a, b ; Cook, McElhinny, 1979). The coasts of ancient east-west seaways in equatorial zones were also common sites of phosphorite sedimentation, as revealed by paleocontinental reconstructions (e.g. Sheldon, 1964 ; 1980 a, b ; Cook, McElhinny, 1979). Veeh et al. (1973), Burnett (1977 and 1980), and Piper and Codispoti (1975) among others have suggested a relation between oxygen-minimum zones impinging on the continental slope and sites of phosphorite formation. This relationship implies that the low-oxygen conditions are necessary for the preservation of large amounts of organic carbon ; this carries in organic phosphorus compounds

which can be liberated in pore waters by microbial oxidation of the organic matter eventually to form interstitial diagenetic phosphate (usually carbonate fluorapatite) within the sediment. If too much organic matter is oxidized in transit through the water column, the necessary phosphorus is lost to deeper water masses or made available to the biomass. Much solid phosphate (fish debris and other vertebrate skeletal matter), which is also often a major source of phosphate in economic phosphorite deposits, might also be redissolved and either become available for inorganic fixation as carbonate fluorapatite or diffuse out of sediments if pore waters are not near to saturation with respect to carbonate fluorapatite. Skeletal phosphate is known to dissolve extensively in most oxidized or dysaerobic sediments (De Vries, 1979), but is often well preserved in anoxic environments, such as in the most intense oxygen deficits within the oxygen-minimum zone. Therefore, the distance from productive surface waters to the sediment/water interface and the oxygen levels in the water column through which the organic matter must fall is critical. Sholkowitz (1973) has demonstrated rapid phosphate depletion in organic matter falling through the water column and at the sediment water interface where the water is even only slightly oxygenated. Milliman (1977) has pointed out the same effect in a brief comparison of the present-day Namibian coastal area (e.g. Walvis Bay) of South Africa with that of the Spanish Sahara (NW Africa). According to his data the rate of upwelling (fertility) and productivity is similar at both places — classical upwelling coasts and candidates for formation of phosphorite deposits. However, much more organic carbon is apparently buried in the Nambian coastal region because the high productivity is centered over a broad, shallow shelf ; the shelf off Spanish Sahara is very narrow, and the major upwelling area is located over the slope. This causes the organic matter to fall through a deeper column of relatively oxygenated water, and there is more recycling of C, N, and P within the water column. Relatively less organic matter reaches slope sediment, and that which does fall is depleted in phosphorus. Thus only in the region around Walvis Bay are recent

Table 2

Main elements of the « Phosphorite Giant » model

First order effects	Second order effects
Continental position Major phosphorite deposits occur along coasts favorably oriented for significant upwelling and high surface fertility (equatorial and westward-facing coasts within trade wind belts).	*Rates of internal P cycling* (a) *Rates of oceanic overturn* : higher rates encourage more rapid P cycling to surface waters : changing rates may, in part, influence episodic phosphorite deposition. (b) *Deep-water P concentration* : elevated concentration may increase amount available for fixation in phosphatic sediments. Actual variations may be limited by a factor of 2 over the concentration of P in oceans today. (c) *Changes of P flux from external sources* : increased riverine flux may enhance phosphate fixation in sediments. Volcanic flux is presumed minor.

Extent of shelf seas
 Influences sites for phosphorite deposition
 Transgression (a) may bring upper part of O_2 minimum zone into shelf.
     (b) favors nutrient recycling and C-org burial on shelves and high rate of P delivery to sediments.
     (c) favors trapping of terrigenous sediment nearshore and low sedimentation rates offshore.
 Regression (a) following or within a transgressive episode it allows reworking and concentration of phosphatic sediment to form economic deposits.
     (b) increase area of weathering and erosion and allows eventual return of some fixed P to oceans.
     (c) denies major marine environmental sites for phosphorite deposition.
	Global climate
	 (a) *Weathering rate* ; warm, humid, equable global climate may favor more intense weathering and increased P supply to oceans.
	 (b) *Ocean circulation and deepwater oxygen deficits* ; expansion and intensification of oxygen deficits in deep-water masses appears related to warmer, more equable climates. These are generally conditions more favorable to phosphorite genesis.

phosphorites being generated (Baturin, Bezruhkov, 1979 ; Birch, 1980). Surface productivity in offshore Peru is about twice that of Walvis Bay and offshore Spanish Sahara surface productivity, and presumably the supply of phosphate to surface waters is about twice as high as well. Off Peru the oxygen-minimum zone is highly developed, abundant organic matter is preserved on the slope (especially between about 400-600 m below sea level), and phosphorite nodules form on the slope in that region (Burnett, 1977). The elevated productivity offshore Peru is presumably part of the reason for the difference between the Spanish Sahara slope and the Peru slope.

Very low oxygen conditions, such as those found in the midst of an oxygen-minimum zone, also tend to eliminate burrowing benthic macro-organisms (e.g. Rhoads, Morse, 1971 ; Calvert, 1964). Laminated carbonaceous muds associated with phosphorites are frequent in ancient deposits, and we suspect that the lack of 'irrigating' activities of an infauna allows buildup of phosphate in pore waters over that of bioturbated zones (e.g. Goldhaber et al., 1977 ; Aller, 1980). It is likely that major phosphorite formation is favored in regions of fluctuating redox conditions.

The influence of sea level

Relative sea level directly influences phosphorite deposition, in so far as it correlates with transgression and regression. Given favorable continental hypsometry, high stands favor 'phosphorite giants' by flooding available shelves, and allowing more upwelling localities to be centered over shelf seas. Thus, the organic matter and skeletal phosphate must fall only a short distance through the water column, suffering relatively less degradation than if upwelling was centered over the slope alone. During transgression terrigenous sediment is trapped in estuaries and nearshore regions, thus preventing extensive dilution of organic-carbon rich chemical sediments on the outer shelf by detrital material (Hay, Southam, 1977). This same phenomenon might also lead to localized phosphorus recycling in shallow seas by trapping the nutrient-bearing runoff from rivers as well as from upwelled dissolved phosphate in highly productive inner-shelf regions. Finally, rising sea level might also allow the oxygen-minimum zone to impinge on the outer parts of shelves and extend into epicontinental seas (Fis-

cher, Arthur, 1977 ; Jenkyns, 1980), thereby aiding in initial preservation of organic matter and phosphate in sediments (Fig. 5).

Burnett (1980) has noted the concentration of phosphatic material as fine-grained diagenetic apatite and as phosphatic crusts mainly near the top and bottom boundaries of the present oxygen-minimum zone. Studies of ancient deposits, such as the Upper Cretaceous and Paleocene phosphorites of North Africa, suggest an association of 'black shales' (organic-carbon rich sediment) with phosphorites (e.g. Garrison et al., in press ; Slansky, 1980). However, the most organic-carbon rich beds do not coincide with those of high phosphate content. In fact, from study of dinoflagellate cyst preservation (Fauconnier, Slansky, 1979) and of the character of amorphous marine organic matter (Belayouni, Trichet, 1980) in the Eocene phosphates of Tunisia, it appears that very slightly oxidizing environments favor the greatest mobilization and redeposition of phosphate. Cyst preservation is poorer and organic matter has a higher oxygen index and lower hydrogen index in the phosphate beds, whereas interbedded more organic-carbon rich beds show the opposite effects. Thus, it is likely that phosphorite formation is favored in slightly oxygenated environments (or alternating anoxic-slightly oxic zones) perhaps near the top or bottom of an oxygen-minimum zone (Fig. 5) where pH and Eh thresholds obtain (Veeh et al., 1973 ; Manheim et al., 1975 ; Burnett, 1980). These will be points at which drastic changes in the solubility of carbonate fluorapatite will occur, and where supply of phosphate from both upward-diffusing pore water and from within the water column will be significant.

Thus, transgressive seas favor initial formation of phosphorite deposits, while regressions generally do not : that is, much phosphate may be fixed in shelf sediments, but not necessarily concentrated into economic intervals during transgressions. Sea level changes have one further effect : shelf phosphates formed during highstands have a good chance of being reworked during drops in sea level (Fig. 4 and 5), whereas slope phosphorites do not. Therefore many 'phosphorite giants', that now appear as reworked conglomerates of phosphatic debris may have been initially formed during transgressions as organic-rich, phosphatic muds that were periodically winnowed and concentrated during one or more marine retreats during and following the transgres-

Figure 5

Effects of sea-level changes on phosphate deposition on generally low-latitude shelves (see also Garrison et al., 1981).
A) Transgression or general sea-level highstand. Note expanded oxygen-minimum zone and greater area of low-oxygen water mass impinging on a flooded shelf.
1. Zones of most intense diagenetic phosphorite formation (transitional Eh−pH conditions, see text)
*2. Oxygen-minimum zone*
a) $O_2 > 0.5 < 1.0$ ml/l
b) $O_2 < 0.5$ ml/l
3. Laminated black shale and siliceous biogenic facies
4. Current-reworked phosphorite deposits
B) Regression or sea-level lowstand. Note impingement of oxygen-minimum zone only on upper slope, minor penecontemporaneous phosphorite deposits, but possible major economic deposits formed by winnowing of older phosphatic material in shallow-water environments
C) Relationship between water-mass oxygenation and burrowing faunas (after Calvert, 1964) in muds rich in organic carbon and biogenic silica. Threshold for biologic activity is at about 0.5 ml/l O_2.
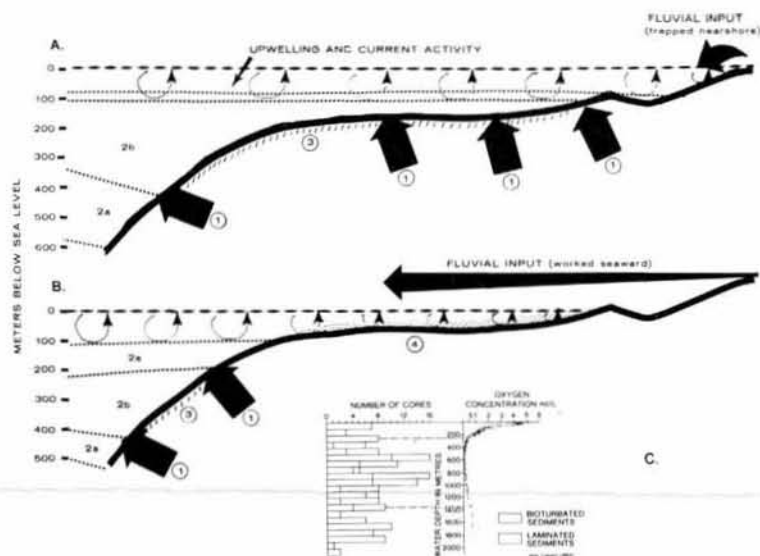
sion. This method of enrichment has been suggested for Namibian phosphorite deposits which were reworked during Pleistocene sea-level drops during glacials (Baturin, 1971), and for the Florida 'bone'-phosphates (Riggs, 1980) among others (Cook, 1967 ; 1976 ; Garrison *et al.*, in press). Locally, however, shelf bottom water concentrations of phosphate may build up to the point that primary precipitation of carbonate fluorapatite occurs, particularly where other phosphatic nuclei are exposed on the sea floor. This process could explain oolitic textures found in some ancient phosphorites.

The influence of global climate

As we described in a previous section, sea-level variations cannot explain the entire picture of Mesozoic-Cenozoic 'phosphorite giants', although it is certainly a first-order factor. Global climate seems also to have a strong effect on phosphorite sedimentation. Times of more equable, warm climates seem to correlate well with formation of 'phosphorite giants', as well as with relative highstands of sea level. We propose that globally warm climates promote phosphorite sedimentation in at least two ways : 1) by leading to an increase in chemical weathering on land and a consequent increase in supply of phosphorus to the ocean, and 2) by influencing the formation, oxygen content, and circulation of water masses thereby leading, in part, to the development of more intense oxygen-minimum zones which are known to be associated with sites of recent phosphorite formation.

The amount and distribution of rainfall was probably much different during times when global climate was warmer and more equable. Warm, humid climates were undoubtedly more widespread latitudinally during, for example, the Late Cretaceous, the Late Paleocene-Early Eocene, and the Early to Middle Miocene (Savin, 1977 ; Savin *et al.*, 1975 ; see also Frakes, 1979). Higher average global temperature is most likely accompanied by higher evaporation rates over the oceans and higher average rainfall on the continents (see Holland, 1978, p. 56-78). The combination of higher temperature and moisture most likely means increased chemical weathering rates, especially at higher latitudes, depending on vegetation cover. For example, oxysols (approaching laterites) of probable Lower Eocene age have been found at anomalously high latitudes in North America (Abbott *et al.*, 1976 ; Singer, Nkedi-Kizza, 1980). A similar increase in intensity of weathering occurred in the Southeastern United States during the Early to Middle Miocene (see Frakes, 1979, for review). We propose that this phenomenon is important for the phosphorus as well as other geochemical cycles. During such times of increased chemical weathering (relative to today), particularly that of widespread limestone, a larger supply of dissolved phosphorus, silica, calcium, magnesium, iron, and bicarbonate ions among others is probably carried to the ocean via rivers. Thus, in terms of supply the oceans were possibly more alkaline and more fertile during climatic optima such as during the Late Paleocene-Early Eocene. This increase in supply would allow a greater rate of sedimentation of phosphates, organic carbon, biogenic and inorganic silica, and carbonate in marine settings. Similar arguments were made by LeClaire (1974) to explain Late Cretaceous and Eocene expansions of silica productivity.

Let us consider the later part of "phosphorite giant" episode 2, in the Paleocene-Eocene. Figure 4 shows the stratigraphic setting, general sediment accumulation rates, and phosphatic zones in the "phosphorite giant" province represented by shallow-marine basins of north Africa during

the Paleocene. We may compare these relationships with the changes in deep-sea accumulation rates and generalized global stratigraphy of deep-sea sediments shown in Figure 3. The most intense period of phosphorite genesis in the Late Paleocene-Early Eocene coincided with the Paleocene climatic optimum. It also coincided with widespread transgressive shelf-sea marls and muds rich in bituminous matter as well as with maximum rates of accumulation of organic carbon in the deep-sea. Biogenic silica (now mostly chert) is also an important component of Upper Paleocene-Lower (and Middle) Eocene shelf and deep marine deposits (Slansky, 1980 ; see papers in BGRM, Doc. 24, 1980). New formed silica-rich minerals are also extremely common, particularly zeolites and montmorillonite (LeClaire, 1974 ; Slansky, 1980). Many of these are magnesium-rich ; in addition, dolomite is a common constituent of carbonate sequences. This suggests an enhanced supply of Mg^{2+}, which at the same time was being extracted into Mg-rich mineral phases. The association of Mg-rich phases and phosphorite deposits is a common one (Bentor, 1980). Removal of Mg^{2+} into other phases, including initial adsorption on biogenic opal (Donnelly, Merill, 1977), may be necessary in order to generate phosphatic sediments because the presence of Mg^{2+} has a deleterious effect on phosphate equilibria (Martens, Harris, 1970 ; Atlas, Pytkowicz, 1977 ; Atlas, 1979 ; cf. Burnett, 1980). This Mg^{2+} removal is apparently an important process, and it is now thought that dolomite can precipitate in anoxic sediments following removal of sulfate via bacterial sulfate reduction and formation of metal sulfides (Suess, 1979 ; Kelts, in press ; Baker, Kastner, 1980). This is yet another facet of the anoxia-phosphorite association.

The rock assemblages described above differ greatly from those of the Paleocene and the Late Eocene-Oligocene. Carbonate sedimentation peaked in the Middle Eocene (Lutetian) both on shelves and in deep-sea settings following the main phase of phosphorite formation. The anomalously high rates of accumulation of carbonate in both settings suggests a greater than normal supply of bicarbonate and calcium to the oceans. With constant input of Ca^{2+} and $HCO_3{}_-$ one would actually expect a decrease in deep-sea accumulation rates to accompany an increase in the area of carbonate sedimentation in shelf seas such as occurred in the Early Eocene (e.g., so-called shelf-basin fractionation ; Worsley, Davies, 1981). We believe that all of these relations suggest a link between global climate, rates of weathering on land, and supply of chemical elements to the sea. Cooling during the Late Eocene and Oligocene, especially at high latitudes, apparently led to more arid conditions and reduced weathering and erosion (Berger, 1979 ; Davies *et al.*, 1977). Warming in the Early to Middle Miocene again led to increased chemical weathering and greater flux of phosphorus and silica to the oceans. In addition, relatively little phosphate was deposited as rock phosphate from the Late Eocene through the Oligocene, a period of about 16 to 18 m.y. During much of this time large areas of the shelves were exposed to weathering and erosion. At least some of the phosphate deposited during episode 2 was exposed, possibly redissolved and returned to the sea. This could have led to a gradual increase in oceanic phosphate content until the Miocene episode 3. The combination of the undepleted oceanic and the weathering sources during the Miocene climatic optimum and transgression made this an extremely fertile phosphate-rich period. The "episodic-circulation" model may also partly account for the change in patterns of phosphorite sedimentation beginning in Miocene time, as it appears that coastal and

equatorial upwelling were intensified (Diester-Haass, Schrader, 1979 ; Leinen, 1979), perhaps related to high-latitude cooling, as argued by Sheldon (1980 a).

An addendum to the weathering model is that phosphate tends to form relatively insoluble complexes with iron, manganese and aluminum (e.g., Stumm, Morgan, 1970), so that oxysols might tend to hold a substantial amount of phosphate. However, when these are eroded and washed into low oxygen-high silica environments on flooded shelves where iron and manganese are reduced and aluminum enters into silicate mineral equilibrium, phosphate would be liberated to shelf waters (e.g. Patrick et al., 1973). This is a further mechanism for replenishing phosphate to the depleted oceans during and after a "phosphorite giant" episode, and particularly for enriching estuarine and inner shelf waters with phosphate.

There is a tendency for warm global climate to coincide with oxygen-deficiencies in oceanic deep-water masses. For example, the oxygen-minimum zones might expand and intensify (Schlanger, Jenkyns, 1976 ; Fischer, Arthur, 1977). This oxygen depletion may, in part, be due to the increased fertility and production of organic matter in surface waters. It is also probably due to the decrease in solubility of oxygen with increasing temperature (and salinity) of seawater (Kinsman et al., 1973 ; Berger, 1979). Thus, the oxygen demand is probably higher and available dissolved oxygen lower during generally warm, equable global climates, so areas of marine oxygen-deficits become more widespread. This deficiency aids in the preservation of organic matter and phosphate on their way to, and on, the seafloor. The accumulation rates of organic carbon for the Late Paleocene through Early Eocene interval show the possible effects of the generally lower dissolved oxygen levels (Fig. 3). However, the Miocene Episode differs greatly because the cold deep-water sphere had developed by then (Savin et al., 1975 ; Shackleton, Kennett, 1975), deep circulation may have been more rapid, dissolved oxygen levels higher, and therefore deep-sea accumulation rates of organic carbon lower than that during the Eocene (but higher than Oligocene rates). The main effects of the Miocene episode were probably seen as oxygen-deficiencies in midwater masses (expanded O_2-minimum zones) which impinged on the outer shelf and middle to upper slope. An example is the circum-Pacific Miocene continental margin deposits rich in organic carbon such as the Monterey Formation and equivalents (e.g. Jenkyns, 1978). The pre-Oligocene deep circulation was probably very different from that of the Neogene, and was largely dominated by salinity structure in the absence of temperature-induced density differences (Brass et al., 1981).

Although warm climates, flooded shelves, and marine oxygen-deficiency closely coincide, the periods of most intense deep-water oxygen depletion, or OAE's, do not seem to be consistently accompanied by deposition of "phosphorite giants". We propose that this is because under very widespread anoxic conditions, such as during the Early to mid-Cretaceous, organic matter is preserved over a much larger area of both the deep and shallow sea-floor. This effectively diminishes the amount of phosphate available to any one area. Therefore, although phosphatic crusts, hardgrounds, nodules, replacements, and skeletal material might be common to these intervals (e.g. Kennedy, Garrison, 1975 ; Jarvis, 1980), economic deposits are rare or absent. Perhaps, also, the excessive area of shallow seas and numerous available sites of fixation did not allow concentration of phosphate at a few specific loca-

tions ; hence substantial deposits could not be produced. In addition, if conditions were extremely anoxic, preservation of organic matter could have been enhanced in many areas to the point that insufficient phosphate was liberated to pore waters for formation of significant phosphate minerals. Thus, we favor times of waxing and waning of deeper-water oxygen deficits as candidates for "phosphorite giants", just as precipitation of carbonate fluorapatite is probably favored in areas of fluctuating redox potential, such as at the margins of the O_2-minimum zone.

CONCLUSIONS

It has been shown that there is no one-to-one correlation between the major episodes of phosphate deposition and any single variable such as climate, oceanic circulation patterns, sea level, anoxic events, or continental position, at least for the Late Mesozoic-Cenozoic. Instead, these parameters together determine the supply of phosphate to the ocean and its rate of extraction to the sediment reservoir. These factors are shown in Table 2 and Figure 5.

Major phosphorite deposits do not necessarily result whenever continents are situated favorably. The paucity of Pleistocene and Holocene phosphorite attests to this. However, it is probably true that continental position is important in relation to other factors, and given that favorable sites are available for phosphorite formation, other variables must come into play. Most important of these is the relationship between sea level, continental hypsometry and tectonics in controlling the area of epicontinental seas, in part expounded by Riggs (1980). This determines the availability of sites for production, preservation and burial of organic matter including phosphorus. Low sea-level stands limit the area of slope under the oxygen-minimum zone and increase the vertical distance that organic matter produced in surface waters must fall through the water column. Therefore, all other things being equal, more organic matter would be oxidized in the water column before burial and the flux of phosphorus to the sediment would be lowered. High sea level and greater expanse of shelf and epicontinental seas provides a greater area for organic matter preservation and phosphate deposition on the outer shelf and slope, a shorter distance and, in some regions, a less-well oxygenated water column for organic matter in transit to the bottom, and, furthermore, a tendency to lock-up the nutrient flux to the oceans from land in estuaries and on the shelves and upper slope. Thus transgressions favor more widespread deposition of major phosphorite deposits while lowstands are less likely to produce widespread phosphorite horizons. If, however, a period of relatively high sea level coincides with major "oceanic anoxic events", such as occurred in the Early to middle Cretaceous, the widespread oxygen deficiencies in oceanic deep water masses would lead to preservation of organic matter over a much greater area of the sea floor, thereby possibly diminishing the amount of organic matter and related phosphate available at any one site. At these times we might expect more numerous small phosphate deposits, but much of the phosphorous might remain locked up in buried organic matter. In the same vein, during low sea-level stands there may still be one or more ideal settings for phosphorite formation. Any one of these, over a period of a few million years, might extract all "excess" oceanic phosphate available ; we envision the Permian Phosphoria sea in Western North America as an example of such an anomaly.

Although a rise in the CCD and a consequent decrease in the area of carbonate sedimentation on deep-sea floors might release some phosphorus from the deep-water carbonate sink (e.g. Bentor, 1980), it is likely that the phosphorus would be transferred either to the shallow-water carbonate sink, since an elevated CCD generally occurs with high sea-level stands, and/or more phosphorus would be absorbed on the greater expanse of red clays or metalliferous clays below the CCD (e.g. Berner, 1973 ; Froelich *et al.*, 1977). Thus, it is difficult to envision an entirely carbonate control of phosphate deposition.

The aforementioned controls notwithstanding, the amount of phosphate being sequestered in phosphorite deposits at any given time is more or less a balance between input and output. Therefore any controls on input would also act to limit the system. Since the amount of phosphorus supplied to the ocean through weathering and fluvial transport allows a net storage of phosphorus in marine sediments, any variation in this flux would have the greatest long-term effect on the amount of phosphorite deposited over a given time interval. Climate (temperature and rainfall/humidity), in part controls rates of weathering. Thus, during times of more equable global climate the increased temperatures and probably increased rainfall would lead to greater rates of chemical weathering, especially at low but extending to higher latitudes. The late Paleocene-middle Eocene and Early to Middle Miocene global climates, for example, were characterized by spread of warm, humid conditions to higher latitudes and more intense lateritic weathering to higher paleolatitude. These were probably times of greater chemical flux through rivers to the ocean, and there is evidence during these times for much higher than average rates of accumulation of carbonate and silica in the deep-sea and on shelves and also for concomitant accumulation of major phosphorite deposits. These were also times of relatively high sea-level stands. Here the significance of continental position becomes apparent. If continents are clustered in lower latitudes a greater supply of phosphate through chemical weathering might be expected. However, the existence of large "supercontinents", such as Pangaea during the Permo-Triassic might also allow for greater continental aridity and internal drainage systems. During these times a lower fluvial phosphorous flux to oceans might obtain. This, in part, might explain the paucity of Triassic phosphorites, although it is difficult, in this regard, to account for the Permian phosphorites. More widespread Tethyan shallow-water limestones may have acted as the main sink for P during the Triassic.

The lack of exact correlation of "phosphorite giants" with any one or even several factors is undoubtedly due to the complex interplay of these variables. In addition we expect some time lags in, for example, the response of phosphorus input by weathering during climate change and its cycling through the ocean and biota. This may amount to several million years. Furthermore, many major phosphorite deposits are mechanical concentrates, for example the Pliocene phosphates of Florida. Though much of the phosphate minerals and other phosphatic biogenic debris were proba-

bly formed during a stage of relatively high sea level in one of our "phosphorite giant" epochs — the Miocene — concentration of this material is of younger age and related to winnowing and sorting during a lowstand of sea level. Thus the majority of major phosphorite deposits are probably mechanical concentrates related to relative sea level changes that occurred during and after the main episode of phosphatization.

We have attempted, in our model, to account for the major variability in phosphorite deposition through time, at least in the late Phanerozoic. There are, of course, other plausible models for the genesis of phosphate deposits, such as those resulting from bird guano or from phosphatization of hiatus surfaces (see Sheldon, Burnett, 1980, for outline of possible models). Yet, we are impressed by the great fluctuations in volume of "economic" deposits through time. In our model we have not considered possible hydrothermal or volcanic flux of phosphate to the oceans (e.g. Riggs, 1980) because this flux is very poorly known and is probably minor (Baturin, 1978 ; see Table 1). Global changes in rates of sea-floor spreading may also be a factor in the phosphorus cycle because the area of metalliferous clays probably varies directly as a function of spreading rates, and because these clays are an important sink for P. However, if there is a relation between sea level and spreading rate, as proposed by numerous researchers (e.g. Pitman, 1978 ; Vogt, 1979), then we doubt that past variations in the area of metalliferous clays could have been significant, because "phosphorite giants" often occur with transgression times of proposed as fast spreading and increased area of metalliferous clays. The sea-floor spreading rate and hydrothermal circulation through the mid-ocean ridge might be important to the phosphorus cycle in another way, however. Mg^{2+} is selectively scavenged during this process, thereby possibly lowering the Mg^{2+} concentration in the oceans and the inhibition of carbonate fluorapatite precipitation. We have not considered possible variations in the return flux of phosphate from sediment pore waters as important, since this is probably related to the same factors that determine "phosphorite giant" episodes. Obviously, we have only outlined the general patterns of global phosphate sedimentation here. Much more detailed sedimentological, geochemical, and paleoenvironmental study of ancient phosphorites is certainly necessary.

Acknowledgements

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