Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environments

KATHLEEN C. RUTTENBERG* and ROBERT A. BERNER
Department of Geology and Geophysics, Yale University, New Haven, CT 06511, USA

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Abstract—Evidence for precipitation of authigenic carbonate fluorapatite (CFA) in Long Island Sound and Mississippi Delta sediments suggests that formation of CFA is not restricted to environments of active coastal upwelling. We present porewater data suggestive of CFA formation in both these areas. Application of a sequential leaching procedure, designed specifically to separate authigenic carbonate fluorapatite from other phosphorus-containing phases, including detrital apatite of igneous or metamorphic origin, provides strong supporting evidence for authigenic apatite formation in these sediments. The size of the authigenic apatite reservoir increases with depth, indicating continued formation of CFA during early diagenesis. This depth increase is mirrored by a decrease in solid-phase organic P at both sites, suggesting that CFA is forming at the expense of organic P. Mass balance considerations, application of diagenetic models to interstitial water nutrient data, and the saturation state of the interstitial water are consistent with this interpretation. Diagenetic redistribution of phosphorus among the different solid-phase reservoirs is observed at both sites, and results in near perfect retention of P by these sediments over the depth intervals sampled. Formation of CFA in continental margins which do not conform to the classically defined regions of phosphorite formation renders CFA a quantitatively more important sink than has previously been recognized. Including this reservoir as a newly identified sink for reactive P in the ocean, the residence time of P in the modern ocean must be revised downward. The implication for ancient oceans of CFA formation in continental margin sediments other than phosphorites is that phosphorite formation may be less a representation of episodicity in removal of reactive P from the oceans than of localized concentration of CFA in phosphatic sediments by secondary physical processes.

INTRODUCTION

PHOSPHORUS (P) IS AN essential nutrient and is believed to limit marine productivity, especially on geologic time scales (HOLLAND, 1978; SMITH, 1984; HOWARTH, 1988). Burial with sediments is the mechanism for ultimate removal of P from the oceans, and as such is a key factor controlling the inventory of oceanic P over geologically significant time periods and, hence, the amount of biological production which can be sustained in the oceans. Attempts to quantify P burial fluxes have generally been motivated by two objectives. The first, to assess the fraction of P reaching the sediment-water interface which is subsequently recycled back into the water column for renewed participation in biological cycling, is geared toward understanding the phosphorus cycle in the modern ocean and often forms the subject of regional or ecosystem studies (for example, KLUMP and MARTENS, 1981, 1987). The second, to quantify the burial flux of P to sediments in order to draw inferences about paleo-ocean carbon cycling, has its impetus in understanding the effects on atmospheric CO₂ and O₂ of a changing oceanic P inventory, which would then modulate photosynthetic productivity (for example, SANDSTROM, 1982; MACH et al., 1987; MOODY et al., 1988). This latter process has been termed the nutrient-CO₂ connection (BROECKER, 1982a,b) and has been considered as a possible mechanism for inducing climate change.

Both of these objectives, but especially the second, are generally pursued for the ultimate purpose of extrapolating to a global marine P budget which can then be used to formulate quantitative predictive models of the marine P cycle, the related carbon cycle, and atmospheric chemistry (HOLLAND, 1978; BROECKER, 1982a,b; SARMIENTO and TOGGWEILER, 1984; BOYLE, 1990).

Organic P is quantitatively one of the most important reservoirs of P in marine sediments, and organic matter is often the principle carrier of P to sediments (FROELICH et al., 1982; RUTTENBERG, 1990). Most of the organic matter (and associated P) which ultimately reaches the ocean bottom is deposited in continental margin sediments (BERNER, 1982). Whereas primary production in deep sea regions is largely regenerated in the water column by the action of bacteria, with only about 1% buried in the sediments (SUSS, 1980; BROECKER and PENG, 1982), up to 50% reaches the bottom in continental margin sediments (MÖLLER and SUSS, 1979; SUSS, 1980; JÖRGENSEN, 1983). Continental margin sediments are therefore key sites for remineralization processes and the primary sinks for P and other bioactive elements following early diagenesis (HOLLAND, 1978; BERNER, 1982; JÖRGENSEN, 1983; MARTENS, 1987; BATURIN, 1988, RUTTENBERG, 1990).

The burial flux of P to sediments is governed by the input flux to sediments and the fraction of this input flux which is retained by the sediments. Factors influencing the ability of a sediment to retain P include: (1) the nature of the input source material, e.g., is it labile or refractory? (2) sedimentation rate, e.g., how rapidly is the input material buried below
the depth at which diffusional escape of remineralized P is possible? (3) the occurrence and intensity of porewater irrigation and of sediment reworking, whether biogenic or abiotic, and (4) formation of secondary authigenic phases due to diagenetic immobilization reactions such as precipitation and adsorption. Because these factors vary as a function of depositional environment, it is clear that phosphorus retention by sediments is also a function of depositional environment. For example, the ability of organic matter reaching the sediment-water interface and the presence and reactivity of inorganic phosphatic phases, coupled with the sediment burial rate, will directly control the rate and extent of dissolved P build-up in porewaters. Particle transport processes and biogenic irrigation can affect the rate and extent of porewater phosphate build-up by altering the depth distribution of metabolizable organic matter and the concentration of oxidants in the sediments (e.g., Aller, 1980). The nature of the sedimentary matrix (for example, grain size and chemistry) with which dissolved P interacts can influence the types of secondary P phases which form under elevated porewater phosphate conditions. Iron cycling, a process in which ferric iron scavenges dissolved P from porewater withinoxic regions of the sediment column, and subsequently releases it when transported into reducing regions, provides an example of the sediment-water interface and the presence and reactivity of inorganic phosphatic phases, coupled with the sediment burial rate, will directly control the rate and extent of dissolved P build-up in porewaters. Particle transport processes and biogenic irrigation can affect the rate and extent of porewater phosphate build-up by altering the depth distribution of metabolizable organic matter and the concentration of oxidants in the sediments (e.g., Aller, 1980). The nature of the sedimentary matrix (for example, grain size and chemistry) with which dissolved P interacts can influence the types of secondary P phases which form under elevated porewater phosphate conditions. Iron cycling, a process in which ferric iron scavenges dissolved P from porewater withinoxic regions of the sediment column, and subsequently releases it when transported into reducing regions, provides an example of the sediment-water interface and the presence and reactivity of inorganic phosphatic phases, coupled with the sediment burial rate, will directly control the rate and extent of dissolved P build-up in porewaters. Particle transport processes and biogenic irrigation can affect the rate and extent of porewater phosphate build-up by altering the depth distribution of metabolizable organic matter and the concentration of oxidants 

In order to construct quantitative, predictive models of the marine P (and related carbon) cycle, and to interpret paleo ocean chemistry of phosphorus through study of sediments or the rock record, it is necessary to understand the depositional environmental controls on both the recycling efficiency of P (e.g., the fraction of initially deposited P which re-enters the water column) and the burial efficiency of P (e.g., the amount of initially deposited P which is ultimately buried). The work presented here focuses on two continental margin environments, the Mississippi Delta and the FOAM site in Long Island Sound. We have focused on continental margin sediments to Redress the bias of existing marine P studies due to high net accumulation rates of mostly terrigenous debris, is a distinct phenomenon which has not been reported previously. The concentration of CFA in sediments from the FOAM and Mississippi Delta sites is considerably diluted to well below levels which would constitute a phosphorite deposit, due to high net accumulation rates of mostly terrigenous debris. For this reason CFA has not previously been recognized as a distinct phase in these sediments. Despite low concentrations, the high net sediment accumulation rates of these sites result in a significant P burial flux in association with CFA. The occurrence of CFA formation in depositional environments such as FOAM and the Mississippi Delta raises the possibility that CFA is an important sink for reactive P from the oceans not only in environments which conform to the classical upwelling-associated phosphorite formation environments, but in “normal”, terrigenous-dominated sediments in non-upwelling environments as well. Authigenic precipitation of CFA is known to occur in other environments which differ from the classical upwelling-associated phosphorite formation environments, such as seamounts (Barnett et al., 1983, and references therein) and the non-upwelling environment of the East Australian continental margin, which is characterized by low sediment accumulation rates and active winnowing and erosion (O’Brien et al., 1981, 1986, 1990; Heggie et al., 1990). The occurrence of CFA formation in environments such as FOAM and the Mississippi Delta, which are characterized by relatively rapidly accumulating sediments dominated by terrigenous debris, is a distinct phenomenon which has not been reported previously. The concentration of CFA in sediments from the FOAM and Mississippi Delta sites is considerably diluted to well below levels which would constitute a phosphorite deposit, due to high net accumulation rates of mostly terrigenous debris. 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For this reason CFA has not previously been recognized as a distinct phase in these sediments. Despite low concentrations, the high net sediment accumulation rates of these sites result in a significant P burial flux in association with CFA. The formation of CFA in environments such as FOAM and the Mississippi Delta is a widespread phenomenon, the implications for both the modern ocean and for ancient oceans, as represented by the sedimentary rock record, are
signficant. For the modern ocean, formation of authigenic CFA in non-upwelling continental margin sediments represents an important sink, previously unrecognized, for reactive P. This is one of two authigenic phases (the other is detrital ferric iron bound-P) which are potentially important sinks for reactive P from the oceans which have not been included in previously constructed marine P budgets. Taken together with the larger burial flux of organic P observed for continental margin sediments relative to the deep sea (Ruttenberg, 1990), we conclude that continental margins are quantitatively more important sites for P burial than the deep sea. Inclusion of the continental margin burial flux of P in a revised budget for the marine P cycle will undoubtably necessitate new estimates of oceanic residence time for P in the modern ocean. These will be lower than currently accepted estimates.

The implications for paleoceanographic interpretations of the marine P cycle of the observation that CFA forms in continental margin environments of the type discussed here are of two kinds. First, although there is a definite episodicity in the occurrence of phosphorite deposits (Cook and McElhinny, 1979), this may not translate directly to a difference in the quantity of reactive P being removed from the oceans in times of phosphorite deposition. The possibility that authigenic carbonate fluorapatite forms ubiquitously in normal, terrigenous-dominated sediments in non-upwelling environments, sediments which are precursors for black or gray shales in the sedimentary record, raises the question of whether removal of reactive P from the oceans as CFA during non-phosphogenic periods may be of comparable magnitude to that during episodes of phosphorite formation. The second implication is not specific to authigenic CFA formation, but applies to any secondarily precipitated phase which derives its phosphorus from the remineralization of organic matter, and is illustrated clearly by the data on CFA formation presented here. This is that models which extrapolate from bulk sedimentary organic P ratios to fluxes of P removal to sediments will underestimate the removal term if remineralized P is retained in sediments by secondary immobilization reactions. The extent to which the removal term may be underestimated can be quantified, as illustrated in this work, by mapping out the diagenetic redistribution occurring in sediments as reflected by depth changes in porewater and solid phase chemistry. 

**METHODS**

**Core Sampling and Sediment Processing**

In order to obtain deeply buried sediment samples, the sediment core from the FOAM site in Long Island Sound was collected using a vibrcorer. The core, which was fitted with a core cutter to support acetate-butyrate liners of 6.67 cm i.d., was lowered to the sediment surface on a boom line and positioned with the aid of a diver; deep penetration into the sediment was facilitated by vibration. Cores three times the length of ordinary gravity cores were collected (3 m). Porewater profiles measured for vibrocore samples compare well with those from gravity cores (K. C. Ruttenberg, unpubl. data), suggesting that porewater disturbance and compaction resulting from vibration is not significant over the sampling intervals used (10 cm). The sediment surface appeared undisturbed, suggesting that using a diver to insert the core prior to initiating the vibration/penetration stage of coring minimized disturbance of the interface. Bottom water was diver-collected in acid-washed polypropylene bottles at the time of coring. Processing of cores was initiated within 6 h of sample collection. Sediments were processed at room temperature, which, at the time of core collection, was within 5°C of bottom water temperatures. Visual descriptions of cores were recorded and then desired sampling depth intervals below the sediment-water interface were ruled on the outside of the core liner. Core liners were then cut into 10-20 cm lengths, immediately capped, and placed in a N-filled, collapsible glove bag. Inside the glove bag, sediment was collected from core liners by extruding with a plunger fitted to the core liner, briefly homogenized, and packed into screw-capped, sterile polypropylene centrifuge tubes. Sediment immediately adjacent to the cut ends of the core liner was discarded. Tubes were either frozen for future solid phase analysis or centrifuged for 5-10 min at 3900 x g in a refrigerated centrifuge, maintained at 15°C, and returned to the glove bag. Inside the glove bag, porewater was extracted into sterile plastic syringes and filtered through 0.45 μm Millipore filters into acid-washed scintillation vials. Two vials were collected for each interval; one acidified to pH 1 and the other left unacidified. Porewater vials were wrapped in paraffin and stored refrigerated in Zip-lock plastic bags until analysis.

The sediment core from the Mississippi Delta site was collected in an acetate-butyrate liner (4.5 cm i.d.) fitted within a stainless steel gravity corer topped with lead weights. The gravity corer was lowered on a boom line to within a few feet of the sediment surface, and then allowed to free fall and sink under its own weight into the sediment. The interface appeared undisturbed. The core was taken immediately to a refrigerated lab on board ship (the RV Gyre) and stored until processed. Bottom water was collected from water overlying the sediment in the core tubes and filtered into acid-washed polypropylene bottles. Core processing was initiated within 4 days after collection and was conducted in a cold lab kept at ca. 3°C. The bottom core cap was removed and replaced with a plunger fitted to the core liner. The top of the core was sealed inside a N-filled, collapsible glove bag, and sediment was extruded in 2 cm intervals and packed into polypropylene screw-cap centrifuge tubes. Tubes were either frozen for future solid phase analysis or centrifuged for 2-3 min at 15,000 rpm in a gimballed Sorvall SS-3 centrifuge located in the cold lab. Porewater was collected as described for the FOAM core, except that it was performed outside the glove bag. The acidified aliquot (final pH of 1) was rapidly dispensed directly into a vial containing 12 M HCl to minimize loss of phosphate due to adsorption.

**Porewater Analyses**

Dissolved fluoride concentrations were determined with a precision of ±2% using a fluoride-specific electrode. The potentiometric and spike methods for concentration determination were employed (Warner, 1971). Precision was estimated on the basis of replicate electrode analyses, by comparing results from the previously mentioned electrode methods with the slope method used by Froelich et al. (1983) and with results obtained using the colorimetric technique of Greenhaugh and Riley (1961). Dissolved phosphate and ammonium were determined using the molybdate blue method and the indophenol method of Koroleff (1976), with precisions of ±3% and ±3%, respectively, based on replicate analyses. Chloride was measured using the Mohr titration (Strickland and Parsons, 1972), with a precision of ±3% based on replicate analyses. Fluoride, chloride, and ammonium analyses were performed on unacidified samples, and phosphate on acidified samples. Sediment pH for FOAM sediments was measured during core processing under nitrogen by the punch-in method. In this method, the pH electrode is inserted into a section of sediment prior to homogenization and transfer to centrifuge tubes in order to minimize degassing. The electrode is standardized before the first measurement and after the final measurement to monitor electrode drift; based on the observed drift, an accuracy of ±0.1 pH unit is estimated.

**Solid Phase Analyses**

Detailed solid-phase P speciation of the sediments was obtained using a selective, sequential chemical extraction technique (hereafter referred to as the SEDEX method) for P. The SEDEX method is illustrated schematically in Fig. 1. The five sedimentary P reservoirs
The wet chemical sequential extraction scheme (SEDEX) for quantification of five sedimentary P reservoirs: (I) exchangeable or loosely sorbed P; (II) ferric iron bound P; (III) authigenic apatite + biogenic apatite + CaCO₃ bound P; (IV) detrital apatite; and (V) organic P. Details of the development and standardization of this method can be found in RUTTENBERG (1990, 1992). The SEDEX method is capable of measuring concentrations as low as 0.005 wt% P with a reproducibility, based on analysis of replicates, of +4%. A detailed description of the SEDEX method is given elsewhere (RUTTENBERG, 1990, 1992). Three salient features which distinguish the SEDEX method from other selective extraction methods are briefly summarized here. First, a means for the chemical separation of authigenic apatite from detrital apatite of igneous or metamorphic origin has been devised. This is an important distinction since authigenic apatite represents an oceanic sink for reactive P, whereas detrital apatite does not. Second, it has been demonstrated that the matrix effect, or the redistribution of P onto residual solid surfaces during a given extraction step, can be extreme and result in large errors in the identification and quantification of sedimentary P reservoirs. The use of a MgCl₂ wash following those extraction steps for which secondary re-adsorption onto the residual sedimentary matrix is a problem reverses most of it. Finally, each extraction step has been standardized individually to ensure the selectivity and specificity of the extractants, using phases and materials which are analogous for naturally occurring sedimentary P phases. The SEDEX method was applied to freeze-dried sediment which had been ground to <125 μm. It is also important to note that, due to the very low phosphorus content of most marine sediments, indirect operationally defined methods such as the SEDEX method are the only available means for determining detailed solid-phase speciation information on sedimentary phosphorus.

SITE DESCRIPTIONS

The FOAM site in Long Island Sound is located in 9 m water depth in the vicinity of the Thimble Islands off the coast of Connecticut, 41°14.5' N lat., 72°44.8' W long. The sediment at this site is intermittently oxygenated via irrigation and bioturbation to depths of 10-15 cm, an oxic cap of sediment is observed (1-3 cm) at most times of the year, and shallow porewater and solid phase
FIG. 2. Location maps showing core locations at (a) the FOAM site in Long Island Sound, and (b) site CT15 on the Mississippi Delta in the Gulf of Mexico.

chemistry are perturbed as a result of infaunal activity (ALLER, 1977; WESTRICH, 1983; CANFIELD, 1988; RUTTENBERG, 1990). As noted by CANFIELD (1988), below the zone of bioturbation, porewater and solid phase profiles approximate a system at steady-state. Porewater gradients appear to be controlled by molecular diffusion in this depth region, despite evidence from x-radiographs that sedimentation at FOAM may be interrupted by periodic storm events which resuspend sediments and leave shell lag deposits and imperfect sediment laminations. These laminations and lag deposits are preserved because of the small size and intermittent activity of the benthic fauna at FOAM (ALLER, 1977). Porewater sulfate concentrations drop to zero at depths of 100-130 cm, and sulfate reduction rates reach 80-100 mM/yr in the top 5 cm during late summer and early fall (WESTRICH, 1983). Porewater nutrient concentrations are high, reflecting remineralization of relatively labile organic matter, reaching levels of 2-3.5 mM ammonium and 200-300 μM phosphate at depths of 1-3 m (GOLDHABER et al., 1971; ALLER, 1977; RUTTENBERG, 1990). Sedimentation rates are estimated at between 0.1 and 0.3 cm/yr on the basis of radiometric and geochemical analyses (BERNER, 1978; GOLDHABER et al., 1977; KRISHNASWAMI et al., 1982).

Mississippi Delta core CT15-GC4 was collected in 110 m water depth on the lower Mississippi Delta-upper Mississippi Cone east of the Mississippi Trough and the mouth of Southwest Pass, 28°47.75’ N lat., 89°19.11’ W long. (Fig. 2b). Burrows were observed and core color was a mottled brown and gray to a depth of 10 cm. Below 10 cm, the uniform gray color of the sediment indicates little or no burrowing. Integrated sulfate reduction rates of 7.7 mmol/m²/day were measured for the top 26 cm, and porewater sulfate concentration is constant at between 31 mM and 32 mM to a depth of 19 cm (LIN, 1990). Porewater ammonium and phosphate reach values at 700 μM and 86 μM, respectively, at a depth of 1 m. The shape of the nutrient profiles and the vertical porewater sulfate profile suggest that the sediment has been disturbed, either by bioturbation or slumping, to a depth of 45 cm. Below this depth, porewater nutrient profiles appear diffusional. Sedimentation rate is estimated to be 0.8 cm/yr from the 137Cs depth profile (RUTTENBERG, 1990).

RESULTS

Porewater profiles of fluoride, chloride, phosphate, and ammonia are presented in Fig. 3 for both the FOAM and Delta sites. The arrows denote bottom water fluoride concentration. The fluoride profile from the FOAM site displays a concentration maximum above that of the bottom water, near the sediment-water interface, and a subsequent drop to below bottom water concentration in the depth region below 10 cm. The increase in dissolved fluoride near the sediment-water interface reflects the presence of a source of fluoride to porewater within this depth range, and the subsequent drop reflects removal of fluoride from porewater to the solid phase deeper in the core. The processes responsible for these features are discussed in the following text. The fluoride profile from the Mississippi Delta core is negatively offset from bottom water fluoride concentration, by roughly 25 μM. Fluoride concentration is relatively constant at a value of 45-46 μM in the top 65 cm (excepting the first two depth intervals). Below 70 cm, fluoride concentrations drop below this level to a minimum of 37 μM at 89 cm. The salinity profiles (derived from chloride concentration measurements) at both the FOAM and Delta sites are invariant with depth, suggesting that the variations in fluoride concentration observed at these sites result from processes other than those which would also perturb chloride, such as freshwater incursion. Several other cores taken at the FOAM site and the Mississippi Delta display features similar to those discussed here (RUTTENBERG, 1990).

The porewater nutrient profiles from both sites display steep positive gradients above bottom water concentrations near the sediment-water interface. Below this, the ammonia profile at the FOAM site increases fairly monotonically throughout the depth of the core. The phosphate also increases, although there is a negative concentration gradient over the 10-40 cm depth interval. Both the ammonia and phosphate profiles in the Mississippi Delta core can be divided into two distinct depth regions which result from different physico-chemical processes. The region below 50 cm reflects undisturbed build-up of porewater metabolites, whereas in the 0-50 cm region, the absence of a monotonically increasing concentration profile, normally produced by diffusional smoothing of the concentration gradient, indicates some physical disturbance of the sediment due either to sediment slumping, deep sediment mixing, or irrigation by benthos.

The solid-phase phosphorus data obtained using the SEDEX method are given in Table 1 for the FOAM site and
the Mississippi Delta site, respectively. The quantity of P in each of the five reservoirs separated by the SEDEX scheme is given as the fraction of the total sedimentary P in percent. The total P concentration in μg P/g dry wt is also given. The solid-phase profiles of organic P and of authigenic P are plotted together for both sites in Fig. 4 to illustrate the near mirror-image relationship between these two P reservoirs. The significance of this relationship is discussed next.

**DISCUSSION**

**The Case for Authigenic Carbonate Fluorapatite Formation at the FOAM and Mississippi Delta Sites**

**Diagnostic indicators of authigenic carbonate fluorapatite formation**

It is necessary to use indirect diagnostic indicators of CFA when the quantity of solid-phase P present as CFA in sediments is below the detection limit of direct identification methods, such as X-ray diffraction or petrographic analysis.

The majority of marine sediments fall in this category, as they contain <0.1 wt% total P, already an order of magnitude lower than the detection limit of X-ray diffraction. Three of these diagnostic indicators use porewater chemistry to infer the presence of CFA in sediments. These are porewater fluoride profiles, porewater phosphate profiles (which are decoupled from porewater ammonia profiles), and saturation state of the porewater with respect to the authigenic mineral phase, CFA. These indicators are described in the following text. The fourth diagnostic indicator is indirect identification of CFA in the solid phase using the SEDEX method.

Downward decreasing porewater fluoride concentration indicates removal of fluoride to the solid phase. The most common explanation for removal of fluoride to the solid phase is incorporation into CFA (e.g., FROELICH et al., 1983; JAHNKE et al., 1983; BURNETT et al., 1987; FROELICH et al., 1988; SCHUFFERT, 1988). Results of recent work on early diagenetic fluoride chemistry suggest that phases other than CFA, such as nonphosphatic carbonate minerals (RUDE and ALLER, 1991) and ferric iron phases (RUTTENBERG and

![Figure 3](image-url)
Authigenic apatite from continental margins

Table 1a. Solid-Phase Phosphorus Speciation for FOAM-W-D.*

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>STEP I</th>
<th>STEP II</th>
<th>STEP III</th>
<th>STEP IV</th>
<th>STEP V</th>
<th>STEPS I-IV</th>
<th>STEPS I-V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exch. &amp; Loosely sorbed P (%) of Total-P</td>
<td>Iron ox/oxyhydrox. bound P (%) of Total-P</td>
<td>Authigenic-P (%) of Total-P</td>
<td>Inorganic-P (%) of Total-P</td>
<td>Organic-P (%) of Total-P</td>
<td>Inorganic-P (µgP/g)</td>
<td>Total-P (µgP/g)</td>
</tr>
<tr>
<td>0-10</td>
<td>8</td>
<td>&lt; d.l.</td>
<td>29</td>
<td>41</td>
<td>22</td>
<td>78</td>
<td>436</td>
</tr>
<tr>
<td>50-60</td>
<td>7</td>
<td>&lt; d.l.</td>
<td>36</td>
<td>45</td>
<td>12</td>
<td>88</td>
<td>450</td>
</tr>
<tr>
<td>100-110</td>
<td>4</td>
<td>&lt; d.l.</td>
<td>39</td>
<td>44</td>
<td>13</td>
<td>87</td>
<td>448</td>
</tr>
<tr>
<td>150-160</td>
<td>5</td>
<td>&lt; d.l.</td>
<td>37</td>
<td>47</td>
<td>11</td>
<td>89</td>
<td>456</td>
</tr>
<tr>
<td>200-210</td>
<td>6</td>
<td>&lt; d.l.</td>
<td>39</td>
<td>41</td>
<td>14</td>
<td>86</td>
<td>449</td>
</tr>
<tr>
<td>250-260</td>
<td>8</td>
<td>&lt; d.l.</td>
<td>40</td>
<td>41</td>
<td>11</td>
<td>89</td>
<td>429</td>
</tr>
<tr>
<td>290-300</td>
<td>5</td>
<td>&lt; d.l.</td>
<td>39</td>
<td>36</td>
<td>19</td>
<td>81</td>
<td>417</td>
</tr>
</tbody>
</table>

* All values are the average over duplicate analyses; reproducibility errors are discussed in the text.
† Inorganic-P is the sum of Steps I-IV.
‡ Total-P is the sum of Steps I-V, reported in units of concentration.
§ < d.l indicates concentration is below the detection limit.

CANFIELD, 1988; RUTTENBERG, 1990), may play an important role in controlling interstitial water fluoride profiles, as well. This additional aspect of early diagenetic fluoride chemistry and its bearing on interpreting fluoride profiles as indicators of CFA precipitation are discussed in the following text.

Porewater phosphate concentrations are the result of the balance between input from microbially mediated organic matter decomposition, anoxic reduction of ferric iron phases and liberation of associated phosphate, and fish-bone dissolution; and removal by diffusional loss or by secondary immobilization reactions, of which formation of authigenic carbonate fluorapatite is one. When the rate of removal to an authigenic phase exceeds the input rate, the dissolved phosphate profile will show a reversal in gradient from positive to negative. This has been observed in classical upwelling sites where CFA has been directly identified in sediments, such as the Peru and Baja California shelf regions (FROELICH et al., 1983, 1988; JAHNKE et al., 1983; SCHUFFERT, 1988). When a gradient reversal is not apparent, it is possible to detect removal of phosphate from porewater using ammonia as a conservative tracer of organic matter decomposition. This is a variant of the stoichiometric nutrient regeneration model for anoxic sediments described by BERNER (1977). These models have been employed to ascertain the C:N:P ratio of organic matter undergoing decomposition from the ratio of metabolites in the interstitial water, or to predict the ratio of porewater metabolites from measured solid-phase C:N:P (HARTMANN et al., 1973, 1976; BERNER, 1974, 1977; MARTENS et al., 1978; KROM and BERNER, 1981; ROSENFELD, 1981), and also to estimate fluxes of nutrients out of the sediment (KLUMP and MARTENS, 1987). Deviations from stoichiometric release of phosphate are explained as being due to removal via adsorption or precipitation of authigenic minerals (MARTENS et al., 1978; KLUMP and MARTENS, 1981, 1987). In the current treatment, we assume stoichiometric release of phosphate and ammonia from organic matter decomposition, and steady state deposition and burial. We also take into account differential diffusion and adsorption, and use an empirical fit of the ammonia profile to predict the shape of the phosphate profile. If porewater phosphate and ammonia profiles are decoupled such that the prediction based on the fit to the ammonia profile overestimates the measured phosphate profile, the deficit is interpreted to be the result of removal to an authigenic solid phase.

The third porewater indicator is the calculated saturation

Table 1b. Solid-Phase Phosphorus Speciation for Mississippi Delta core CT15-GC4.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>STEP I</th>
<th>STEP II</th>
<th>STEP III</th>
<th>STEP IV</th>
<th>STEP V</th>
<th>STEPS I-IV</th>
<th>STEPS I-V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exch. &amp; Loosely sorbed P (%) of Total-P</td>
<td>Iron ox/oxyhydrox. bound P (%) of Total-P</td>
<td>Authigenic-P (%) of Total-P</td>
<td>Inorganic-P (%) of Total-P</td>
<td>Organic-P (%) of Total-P</td>
<td>Inorganic-P (µgP/g)</td>
<td>Total-P (µgP/g)</td>
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<tr>
<td>0-2</td>
<td>8</td>
<td>30</td>
<td>23</td>
<td>11</td>
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<td>30</td>
<td>13</td>
<td>20</td>
<td>80</td>
<td>598</td>
</tr>
</tbody>
</table>

* Inorganic-P is the sum of Steps I-IV, reported in units of concentration.
† Total-P is the sum of Steps I-V.
K. C. Ruttenberg and R. A. Berner

FIG. 4. Solid-phase profiles of authigenic P and organic P vs. depth at the FOAM and Mississippi Delta sites. Data are from STEP III and STEP V, respectively, of the SEDEX method (Table 1). The curves drawn through the data points are empirical best-fit curves which are given explicitly in the notes accompanying Table 2 and are discussed in the text.

state with respect to the authigenic mineral. Where the ion activity product (IAP) is equal to or exceeds the solubility product ($K_{sp}$) for CFA, the porewaters are saturated or supersaturated with respect to CFA, respectively, and precipitation is thermodynamically favored. This indirect approach to inferring the presence of authigenic minerals in sediments has been widely used (Berner, 1974; Emerson, 1976; Emerson and Widmer, 1978; Martens et al., 1978; Murray et al., 1978; Möller and Suess, 1979; Aller, 1980; Jahnke et al., 1983; De Lange, 1986; Canfield, 1989). Because the solubility of CFA is a sensitive function of the activity of dissolved carbonate (Jahnke, 1984; Glenn and Arthur, 1988), a single $K_{sp}$ does not adequately reflect the saturation conditions at all depths. To account for changes in porewater chemistry with depth, separate values for $K_{sp}$ must be calculated at each depth.

These indirect diagnostic indicators provide the most convincing argument for the presence of CFA in sediments when they are used in concert. For example, we have quantified the removal flux of fluoride over a given depth interval and compared it to the quantity of CFA in that depth interval as measured by the SEDEX method. A deficit in porewater phosphate has been identified using the measured ammonia profile and a stoichiometric nutrient regeneration model, indicating removal of dissolved phosphate to the solid phase. The increase in CFA has been compared to the decrease in organic P measured by the SEDEX method. When these various indicators of CFA formation yield consistent results, a convincing argument is made for formation of CFA in a sediment.

Formation of authigenic CFA at the expense of organic phosphorus: Solid-phase diagnostic indicators

A large fraction of the total P at both the FOAM and the Mississippi Delta sites is in the authigenic CFA + biogenic apatite + CaCO$_3$ reservoir (Table 1). All three of these phases, extractable in STEP III of the SEDEX scheme, are authigenic because they represent removal of reactive P from either the water column or from porewater. For the purposes of this discussion, the term authigenic P will be used to denote all three. Authigenic P, present in appreciable quantities at all depths at both the FOAM and the Mississippi Delta sites, displays a depth trend that indicates an increase in the size of this reservoir with depth (Fig. 4). Evidence suggests that the decrease in organic P at the FOAM site and 0–2 cm at the Delta) is actually a non-CFA background phase. Candidates for this background phase are suggested on the basis of results obtained during standardization of the SEDEX method. Sedimentary P phases identified as being soluble in pH 4 acetate buffer (STEP III) during specificity standardization experiments are CaCO$_3$ bound P, biogenic apatite (fish bones, teeth, and scales), and P associated with smectite (Ruttenberg, 1990, 1997). Of
these possible non-CFA background phases, finely divided biogenic apatite and/or P associated with smectite are considered the most likely. Phosphorus associated with CaCO₃ is ruled out at the FOAM site because, although some sediment layers contain significant shell material, this material was found to contain only minor P. This is consistent with the findings of SHERWOOD et al. (1987), who also found that shell material contains very little P. CaCO₃ is ruled out as a non-CFA background phase at the Delta site because these sediments contain negligible amounts of CaCO₃ (<0.5 wt%). Biogenic apatite debris, which was not readily visible upon microscopic analysis, may be present in very finely divided form. The presence of P associated with a smectite-like clay in these sediments is possible. If the background phase is biogenic apatite, the entire authigenic P reservoir is truly authigenic, in the sense that it represents removal of reactive P from seawater. If smectite is the background phase, whether it is truly authigenic or not depends on whether the P became associated with the clay before or after the clay entered the marine system.

An alternative explanation for the presence of appreciable authigenic P at the sediment-water interface is that it reflects virtually instantaneous formation of authigenic CFA within the first 2–10 cm of sediment below the sediment-water interface. This is believed to be the case for CFA forming in sediments on the Mexican (JAHNKE et al., 1983) and Peru margins (BURNETT et al., 1988; FROELICH et al., 1988; GLENN and ARTHUR, 1988). Although rapid, near-interface precipitation of CFA at FOAM and the Mississippi Delta is not supported by the quantitative arguments based on porewater and other solid-phase data presented in the following text, it cannot be ruled out, since near-interface processes cannot be resolved by the current data sets, which provide only cm-scale depth resolution. Collection of porewater and detailed solid-phase phosphorus data over finer depth scales (e.g., mm) may reveal that CFA formation is occurring at accelerated rates very near the sediment-water interface.

Assuming that the background phase at FOAM and the Delta is not CFA, the increase above background levels reflects authigenic formation of CFA within these sediments. The depth trends of authigenic P and organic P clearly mirror each other (Fig. 4), and we suggest that authigenic carbonate fluorapatite is forming from the organic P which has been liberated to porewater as a result of microbial remineralization of organic matter. Comparison of the integrated amount of authigenic P represented by the increase above background to the integrated amount of organic P decrease gives a measure of the degree to which the transfer of phosphorus from one reservoir to another (sink-switching) can explain the mirrorimage depth profiles of these two reservoirs. Best-fit curves were drawn through the data for authigenic and organic P at both sites, and the area under these curves was obtained by integration. Logarithmic functions yielded the best fit for both authigenic and organic P at both sites. At the FOAM site, these curves were integrated from the interface to 110 cm depth (the region of the largest gradient). At the Delta these curves were integrated over the full data set as the gradients appear to persist throughout the depth of the core. The integrated values for both sites are listed in Table 2. The organic P deficit matches the authigenic P increase at the FOAM site to within the calculated error, and the match for the Mississippi Delta core falls just outside the calculated error. The fact that the profiles do not perfectly mirror each other indicates that the transfer of phosphorus from the organic to the authigenic P reservoir is not the only process operating, or that the two processes operate at different rates. In addition, sources of P other than organic matter, such as ferric iron associated P or biogenic apatite (fish debris), could be important, especially near the interface.

Near-quantitative transfer of dissolved P from remineralized organic matter to CFA implies that loss of dissolved phosphate by diffusion out of the sediment prior to precipitation as CFA is minimal. Although there is significant diffusive flux out of the upper 10–15 cm of sediment at the FOAM site during most of the year, as documented by previous workers (ALLER, 1980; KROM and BERNER, 1981) and indicated by the upper 20 cm of the FOAM phosphate profile discussed here (Fig. 3), the essentially quantitative transfer of solid-phase P from the organic to the authigenic reservoir suggests that beneath this horizon diffusive loss is insignificant. Near-coincident minima in the dissolved phosphate and fluoride profiles at 40–60 cm depth provide supporting evidence for this interpretation, implying diffusion of phosphate and fluoride into the sediments and subsequent removal to the solid phase in this depth interval. We note also that it is not uncommon for minima in phosphate profiles to be observed in sediment cores from the FOAM site (see, for example, GOLDBERG et al., 1977; ALLER, 1980). The largest increase in the authigenic P reservoir, and therefore the most CFA precipitation, occurs in the top 60 cm. The coarsely spaced
depth intervals of the solid-phase data prevent us from as-
certaining whether precipitation occurs throughout this inter-
val or is localized in a discrete depth horizon; however,
the minima in the porewater phosphate and fluoride profiles
suggest that formation of CFA occurs predominantly within
the 40–60 cm depth interval. (We restrict our discussion of
porewater to the FOAM site, since the Mississippi Delta
porewater profiles show evidence of recent disturbance.)

It is the observed mirror image of the organic P and au-
thigenic P profiles, and the match between integrated loss of
organic P and gain in authigenic P, which compels us to
argue that authigenic P is forming at the expense of organic
P. Diffusive loss of phosphate from surficial sediments does
not invalidate this conclusion. Calculated diffusive loss of
phosphate based on near-interface porewater data will have
limited bearing on diagenetic transfer of phosphorus occurring
at depth. In addition, surficial porewater profiles at the FOAM
site are known to display seasonal variability. A diffusive flux
calculated from a single porewater profile represents an in-
stantaneous flux and will not necessarily reflect past input
and perturbation of porewater which may have been recorded
in the solid phase.

Formation of authigenic CFA: Porewater diagnostic
indicators

The use of porewater chemical profiles to infer processes
occurring in the solid phase is widespread (GOLDBAER et
al., 1977; MARTENS et al., 1978; MURRAY et al., 1978; FROE-
LICH et al., 1982, 1983; JAHNKE et al., 1989). The main
advantage offered is that changes in porewater chemistry are
sensitive indicators of changes in the solid phase, due to much
lower concentrations in porewaters. Most models which use
porewater profiles to infer solid-phase processes require an
assumption of steady state. This requirement presents the
most serious limitation to solid phase arguments based on
porewater chemistry. Especially in regions of dynamic phys-
ical processes, which characterize most continental margin
areas, the steady state assumption often cannot be made.
This is so in the Mississippi Delta site discussed in this study.
The FOAM site appears to be in steady state, as evidenced
by the shape of the porewater nutrient profiles presented here
(Fig. 3), as well as other porewater chemical profiles for this
same core (SO4; H2S; CANFIELD, 1988), and by the success
of steady state models presented in this and in previous studies
at describing both solid-phase and porewater data (BERNER,
1977; ALFAR, 1977; GOLDBAER et al., 1977; MARTENS et
al., 1978; KROM and BERNER, 1981; BOUDREAU and CAN-
FIELD, 1988). In contrast, porewater profiles from the Mis-
sissippi Delta site show clear evidence of disturbance, as dis-
cussed in the Results section. The following discussion of
CFA formation based on porewater data will be made, there-
fore, exclusively for the FOAM site. We note, however, that
porewater profiles from the Delta are qualitatively consistent
with the solid-phase evidence for CFA formation at this site:
fluoride profiles indicate removal to the solid phase, and
phosphate profiles increase with depth up to nearly 100 µM.
The similar porefluid chemistries of the two sites suggest that
interstitial water should be at saturation or greater with respect
to CFA in the Delta core.

In general, the fluoride profile at the FOAM site displays
a negative concentration gradient (Fig. 3), consistent with
removal to the solid phase. In the region of steepest negative
slope, between 0 and 60 cm depth, mass balance calculations
suggest that this removal is the result of authigenic CFA for-
mation.

The amount of fluoride removed from porewater, approx-
imated by the negative dissolved fluoride concentration gra-
dient over the 0–60 cm depth interval and its change to a
roughly constant fluoride concentration below 60 cm, is cal-
culated using Fick's first law of diffusion. The removal flux
of fluoride to the solid phase within a box defined by this
depth interval is assumed to be equal to the amount of CFA
buried at 60 cm depth, and the system is assumed to be at
steady state. In other words, essentially all dissolved fluoride
entering the top of the box by diffusion is removed at the
bottom of the box as CFA buried with sediment. This cal-
culated removal flux of fluoride is then compared to the in-
crease in the size of this reservoir, as determined by the
SEDEX method. The amount of fluoride removed from
porewater to the solid phase is calculated using Eqn. 1:

$$\frac{\partial C_F}{\partial X} = J_F,$$

where

$$\phi = 0.7 \text{ (KROM and BERNER, 1980),}$$
$$D_F = 200 \text{ cm}^2/\text{yr (VAN CAPPELEN and BERNER, 1988),}$$
and

$$\frac{\Delta C_F}{\Delta X} = -14 \text{ µmol/L/60 cm}.$$  

The mass of CFA-P per unit area leaving the bottom of the
box is obtained by multiplying the observed flux of fluoride,
calculated using Eqn. 1, by a P/F ratio of 2.5, which is typical
for authigenic marine CFA (FROELICH et al., 1988). Division
by a sediment accumulation rate appropriate for the FOAM
site (0.075 g/cm² yr) yields a value of 0.0034 wt% authigenic
P. The measured increase of authigenic P above background
in the 0–60 cm depth interval is 0.0032 wt%.

There is additional structure in the porewater fluoride pro-
file, however, which merits discussion both to ensure that
the processes responsible for these other features are not at
odds with the interpretation rendered thus far (e.g., that
fluoride removal from porewater in the upper 60 cm of the core
is due to incorporation into CFA), and to address the question
of general fluoride reactivity during early diagenesis. The sub-
surface maximum observed in the FOAM core has been ob-
served in other cores taken at this and other sites (Sachem,
NWC) in Long Island Sound (RUTTENBERG, 1990). We have
observed that this concentration maximum is coincident with
the redox boundary, and that it coincides with a maximum in
porewater [Fe²⁺] and with the most rapid decrease in solid-
phase reactive ferric iron (RUTTENBERG and CANFIELD, 1988;
RUTTENBERG, 1990). These observations, coupled with re-
results from laboratory adsorption experiments (RUTTENBERG,
1990) which indicate that fluoride adsorbs readily onto ferric
oxyhydroxides at porewater pH (7.4 to 7.6), suggest that the
observed sub-surface maximum in porewater fluoride is re-
related to redox chemistry in the sediment. Fluoride is adsorbed
onto reactive ferric iron phases in the surficial oxidized layer
of the sediments, and when these phases are buried below the redox boundary, the fluoride is released to porewater upon reduction of the ferric iron. Significant levels of fluoride adsorption onto other phases was also observed in laboratory adsorption experiments, especially clays (smectite and kaolinite, but not illite) and humic acid (RUTTENBERG, 1990).

Because the sub-surface maximum in porewater fluoride concentration implies a source of fluoride to porewater, however, it is most readily explained by association with redox-sensitive reactive iron phases. The structure of the fluoride profile below the top 60 cm may, however, be the result of adsorption or desorption reactions involving non-iron phases, or indeed may be due to continued CFA formation. A gradual increase in fluoride concentration occurs immediately below the 0–60 cm zone of CFA formation, and below 100 cm concentrations drop once again, with a negative slope much shallower than that observed in the upper 60 cm of the core. The increase observed between 50 and 100 cm implies input of fluoride from the solid phase. The fact that the size of the CFA reservoir continues to increase within this depth interval (Table 1a) argues against dissolution of CFA as the process responsible for the increase in fluoride concentration. Other phases which are possible candidates as the source of this fluoride input, based on the adsorption experiment results previously discussed, are clays or organic matter, although more work on the early diagenetic chemistry of fluoride is required before a more definite interpretation can be made. The return to a negative concentration gradient below 100 cm indicates removal from porewater to the solid phase is occurring below 100 cm depth. As there is no systematic change in the CFA reservoir in this interval, the solid-phase chemical data do not provide an unequivocal indication that this is the result of continued CFA formation. The possibility exists that another phase is responsible for removing fluoride in this region of the core, or that CFA formed in the upper regions of the sediment column is recrystallizing with a more fluorne-rich stoichiometry.

The negative offset of porewater from bottom water fluoride concentration observed in the Mississippi Delta core (Fig. 3) is believed to be the result of fluoride adsorption onto reactive ferric oxyhydroxides which are present in sediments throughout this 100 cm core (RUTTENBERG, 1990). There is a trend of more gently decreasing porewater fluoride concentrations superimposed on the more dramatic negative offset of porewater from bottom water, indicative of removal of dissolved fluoride from porewater by a separate mechanism. Solid-phase sedimentary phosphorus data from this site support the argument that this removal is the result of incorporation into carbonate fluorapatite.

There is an interesting link between the processes of sorption of fluoride onto ferric-oxyhydroxides and of authigenic carbonate fluorapatite formation. The results of the FOAM site will be used to illustrate this link, but the argument can be generalized. Ferric-oxyhydroxides are capable of adsorbing both fluoride and phosphate from seawater. There is a sub surface maximum in porewater fluoride as a result of reduction of these ferric phases, as previously discussed, and there is a similar spike in porewater phosphate near the sediment-water interface as a result of reduction of ferric-oxyhydroxides and release of associated phosphate to porewater (KROM and BERNER, 1981). The spike in concentration of fluoride and phosphate which results from release of these two solutes at or below the redox boundary in sediments may provide the necessary conditions of supersaturation required for the precipitation of authigenic carbonate fluorapatite (RUTTENBERG, 1990). This has been proposed for the phosphorites forming on the East Australian continental margin (HEGGIE et al., 1990) and may be important at FOAM and the Mississippi Delta, as well. A more detailed treatment of the early diagenetic chemistry of fluoride in terrigenous sediments will be presented elsewhere (K. C. Ruttenberg, unpubl. data).

To assess whether the porewater phosphate profile is decoupled from the ammonia profile at the FOAM site, an empirically derived best-fit curve was drawn through the ammonia data. The equation for this curve was used to predict the porewater phosphate profile using a stoichiometric nutrient regeneration model (Fig. 5). The details of the model are given in the Appendix. There is clearly a deficit of porewater phosphate relative to the model-predicted concentrations. This result illustrates that the process of P removal from porewaters to form secondary phases can be identified in a depth zone where porewater phosphate concentrations are increasing as a result of release of remineralized organic P. A quantitative comparison of the porewater phosphate deficit to the solid-phase CFA increase is complicated by the fact that the upper limit of integration for the porewater curves was taken at 25 cm to avoid bioturbation effects, and that due to the coarse sampling intervals used in this core, diffusional loss of phosphate cannot be adequately estimated from the profile. The much coarser sample intervals in the solid-phase profile also make a detailed comparison difficult. Given the limitations of the data set and of the model, this should be viewed as a qualitative comparison, the results of which are consistent with removal of porewater phosphate to form authigenic CFA.

The saturation state of porewaters at the FOAM site with respect to CFA was calculated using the ion activity product (IAP) derived from porewater data for apatite of stoichiometry $\text{Ca}_{10.24}\text{Na}_{0.33}\text{Mg}_{0.13}(\text{PO}_4)_{6.12}(\text{CO}_3)_{2.7}(\text{F})_{2.86}$, normalized to the solubility product ($K_{\text{sp}}$) for the authigenic phase (IAP/ $K_{\text{sp}}$). The solubility product was calculated in the same manner described by JAHNKE et al. (1983), where $K_{\text{sp}}$ is evaluated for each depth interval using the experimental relationship between carbonate activity and $K_{\text{sp}}$, shown in JAHNKE et al. (1983, Fig. 5) and the corresponding carbonate activity obtained from the measured alkalinity and pH at each depth. Porewater data are tabulated in RUTTENBERG (1990). We chose the stoichiometry for carbonate fluorapatite used by JAHNKE in his experimental and field work characterizing the solubility of carbonate-rich apatites in marine systems (JAHNKE et al., 1983; JAHNKE, 1984). The interstitial water is supersaturated by a factor of $10^4$ to $10^6$ throughout the length of the core, indicating that precipitation of the authigenic phase is thermodynamically favored. The extensive and complex substitution chemistry displayed by apatite (McCLELLAN, 1980; JAHNKE, 1984; LEGEROS, 1965; LEGEROS et al., 1967, 1980; McARTHUR, 1985), however, results in a large degree of uncertainty in the parameter $K_{\text{sp}}$. Also, any effects of recrystallization of authigenic CFA with depth, or any continued uptake of fluoride through exchange processes (e.g., without additional growth or formation of new material), are excluded from this simple interpretation.
Such processes could result in a situation where the porewater derived \((\text{IAP}/K_{sp})\) relation does not necessarily reflect the solubility of the solid phase. In spite of these uncertainties, the saturation state calculation results are consistent with the conclusion that CFA is forming in these sediments.

In sum, all four diagnostic indicators show positive, internally consistent evidence of CFA formation at the FOAM site. Mass balance arguments coupling porewater fluoride to solid-phase CFA and the match between SEDEX-determined solid-phase CFA and solid-phase organic P provide a quantitatively coherent argument for authigenic CFA formation in these sediments. Evidence for a deficit in porewater phosphate as predicted by the ammonia curve and the saturation state of porewaters with respect to CFA are consistent with this interpretation. At the Mississippi Delta site, the match between SEDEX-determined solid-phase CFA and solid-phase organic P is strongly suggestive of authigenic CFA formation, and the fact that the porewater fluoride profile indicates removal of fluoride to the solid phase is consistent with this argument. However, because the physical disturbance of this core makes the assumption of steady state untenable, porewater arguments cannot be used in a straightforward way to supplement the solid-phase evidence for CFA formation. This particular case illustrates the point that solid-phase chemistry can be a more accurate, integrated measure of early diagenetic processes than is porewater. Porewater can be useful as a very sensitive indicator of solid-phase processes, but it is also much more easily perturbed than the solid phase. For this reason, it is crucial that porewater chemistry be viewed in conjunction with solid-phase chemistry. Using this combined porewater/solid-phase approach to characterizing early diagenetic chemistry, the risk of incorrectly inferring solid-phase processes from porewater profiles alone is greatly reduced.

That the comparison of integrated areas of the decrease in organic P and the increase in CFA for both the FOAM and Delta should yield such good agreement is surprising, given that non-steady state effects of any significance should promote irregular solid-phase profiles. At the FOAM site, we conclude that either sediment deposition has occurred in a steady state manner, or that bioturbational smoothing has effectively overprinted any non-steady state signal. At the Delta, the smoothly varying solid-phase profiles provide evidence that the porewater disturbance reflected in the nutrient profiles is due either to physical pumping or to biological irrigation and not to sediment slumping. At this site the solid-phase is a more accurate integrated measure of early diagenetic processes than is the porewater.

**Diagenetic Redistribution of Phosphorus**

The formation of CFA at the expense of organic P at the FOAM and Mississippi Delta sites is a clear example of diagenetic redistribution of P in sediments (Fig. 4). The five
individual reservoirs separated by the SEDEX method display
depth variations ranging from 8–25% at FOAM and from
9–17% at the Delta, whereas the depth variation of total P
at each site is only 4% and 5%, respectively. This indicates
that, within the resolution of the solid-phase sampling inter-
vals, the sediments are nearly 100% retentive of P. The evi-
dence for growth of CFA at the expense of organic P indicates
that the mechanisms of retention include diagenetic redis-
tribution among reservoirs. Direct measurement of phosphate
diffusive flux and estimates based on porewater phosphate
profiles document a flux of phosphate from surficial sediments
to bottom water during most times of year (ALLER, 1980;
KROM and BERNER, 1981). Finer sampling intervals near
the sediment-water interface should therefore reveal net loss
of solid-phase P near this interface at the FOAM site. Diffusive
loss in surficial sediments, however, need have little bearing
on subsequent diagenetic transfer that occurs at greater depth,
as argued previously for the FOAM site. Reconciling diffusive
loss of phosphate from FOAM surficial sediments with re-
tention via diagenetic redistribution at depth, we place the
horizon below which maximum retention occurs at 20 cm.
The porewater phosphate gradient below this depth is in fact
supplying phosphate to the zone of P removal and does not
ultimately result in loss to overlying water. The impact of
enhanced retention on P recycling back into the water col-
umn, and more precise determination of the depth below
which diffusive loss of phosphate becomes insignificant, will
require finer depth-scale sampling near the sediment-water
interface. Since short-term perturbation of porewater profiles
will not necessarily disrupt the time-integrated record pro-
vided by the solid phase, detailed P speciation of the solid
phase sampled on a fine depth-scale will be particularly useful
in cases, like the Mississippi Delta core discussed here, in
which porewater has been disturbed. Despite the limitations
imposed by the coarse depth intervals employed in the cores
studied, the impact of enhanced sediment retention of P via
diagenetic redistribution on the ultimate burial of P can be
addressed with the current data set.

An important consequence of the diagenetic redistribution
of P is the ultimate burial of P in association with phases
different from its initial association, or sink-switching. The
case discussed here, that of formation of CFA at the expense
of organic P, has important ramifications for the use of sed-
imentary organic C:P ratios to link marine productivity
to atmospheric CO2 and O2, as a result of changes in the
balance between biological production, respiration, and burial
of reduced carbon (BROECKER, 1982a,b; McELROY, 1983;
Use of coupled water column–sediment models which em-
ploy sedimentary organic C:P ratios to link marine produc-
tivity to atmospheric CO2 and O2 will be useful only if this
parameter is carefully evaluated. Quantification of secondary
minerals (e.g., CFA) formed from remineralized P may pro-
vide a means for estimating the C:P ratio of organic matter
initially buried, unless sources other than organic P are sig-
nificant.

Implications of Authigenic CFA Formation in
Non-upwelling Environments

The observation that authigenic carbonate fluorapatite
forms in non-upwelling environments such as those repre-
sented by the FOAM and Mississippi Delta sites indicates
that conditions necessary for CFA formation are not restricted
to upwelling areas. The key characteristic of deposits formed
beneath upwelling currents may be that CFA concentrations
are less diluted by continentally derived terrigenous sediment
flux (MANHEIM et al., 1975; CALVERT and PRICE, 1983; BA-
TURN, 1983; RIGGS, 1984). We suggest that authigenic CFA
is forming at FOAM and the Mississippi Delta, but that the
concentration of P as CFA in these sediments is well below
that which defines a phosphorite deposit. The distinguishing
features of CFA formation in environments such as these
from environments of phosphorite formation may not imply
a difference in the mechanism of formation of the authigenic
mineral, but of the general sedimentary environment. The
feature of minimal dilution of CFA can be enhanced if the
sediment is exposed to the winnowing action of currents, a
generally accepted phase in the genesis of phosphorite deposits
(KOLODNY, 1981, and references therein; although reworking
is not a necessary factor in concentration of CFA, e.g., BUR-
NETT et al., 1988). The possibility that CFA forms by a dif-
ferent mechanism in upwelling environments cannot be ruled
out, however. The data presented here indicate that CFA
formation occurs dispersed in the sediments of the non-up-
wellings environments studied, whereas CFA occurs in discrete
layers in many upwelling environments (JAHNKE et al., 1983; VAN
CAPPENELLEN and BERNER, 1988; SCHUFFERT, 1988). In
addition, remineralized organic P appears nearly sufficient
as a source for authigenic CFA at FOAM and the Mississippi
Delta, whereas other sources are required to explain CFA
formation in Peru margin sediments (FROELICH et al., 1988).
There have been other observations of CFA formation in
non-upwelling environments, but these have usually been
attributed to special, possibly site-specific formation mech-
nisms (e.g., McKELVEY, 1967; GAUDETTE and LYONS, 1980, O’BRIEN et al., 1981; HEGCIE et al., 1990). Unlike
these specialized environments, the formation of dispersed
authigenic apatite in non-upwelling environments such as
those represented by the FOAM and Mississippi Delta sites
based on concentration measurements of organic P at depth
in sediments may seriously underestimate the true quantity
of organic P that was originally deposited. This will also have
implications for paleoceanographic and paleoclimate models,
which are based on the premise that oceanic biological cycles
affect atmospheric CO2 and O2 as a result of changes in the
balance between biological production, respiration, and burial
of reduced carbon (BROECKER, 1982a,b; McELROY, 1983;
Use of coupled water column–sediment models which em-
ploy sedimentary organic C:P ratios to link marine produc-
tivity to atmospheric CO2 and O2 will be useful only if this
parameter is carefully evaluated. Quantification of secondary
minerals (e.g., CFA) formed from remineralized P may pro-
vide a means for estimating the C:P ratio of organic matter
initially buried, unless sources other than organic P are sig-
nificant.
and mass balance models indicate that authigenic carbonate represents a potentially large burial flux for phosphorus which has previously gone unrecognized. These moderately organic-rich (~1 wt% C\textsubscript{org}) sediments, dominated by terrigenous debris and characterized by high sediment accumulation rates, are representative of an important fraction of continental margin sediments. If CFA formation is a general occurrence in sediments of this type, the burial flux of reactive P as authigenic CFA will be significantly larger than estimated in previous budgets (FROELICH et al., 1982) which considered burial of P as CFA in upwelling regions only.

The deltaic ferric iron P reservoir is another potential sink for reactive P which has only been identified through use of the SEDEX method (Table 1b). Considering this reservoir in conjunction with the CFA reservoir in non-upwelling continental margin environments, it is clear that the burial flux of P to continental margins has been underestimated in previous studies. It is necessary to obtain a larger, more representative solid-phase P data set before a well-constrained budget can be constructed. Preliminary estimates of the effect of continental margin burial fluxes of P on the oceanic residence time of P are that it may drop by as much as 50% of the currently accepted value (RUTTENBERG, 1990).

If formation of CFA in sediments similar to those represented by the FOAM and Mississippi Delta is a ubiquitous phenomenon in the modern ocean, it is likely that this was also the case in the geologic past. Due to the small quantity and dispersed nature of CFA in these sediments, this phase is not readily apparent through normal mineral identification techniques. It seems likely, therefore, that many if not most black or gray marine shales host dispersed CFA in quantities similar to those found in the FOAM and Mississippi Delta sites. In view of this possibility, the notion that the episodic formation of phosphorites throughout geologic time (COOK and McELHINNY, 1979) is of importance to the marine P cycle may require reassessment. The phenomenon of episodicity may hold true for phosphorite deposits, but not for authigenic CFA formation which occurs dispersed in organic-rich sediments. Although the average P content of shales is less than that of phosphorites (0.07 wt% P in shales, TURKIAN, 1972; vs. 2-18 wt% P in phosphorites, e.g., COOK, 1984), the greater abundance of shales over phosphorites throughout geologic time (RONOV, 1976) indicates that far more P is present in shales. If the fraction of the total P as authigenic CFA which is present in average shale is similar to that found in sediments from FOAM and the Delta (e.g., 13% to 9% of the total P, respectively), the quantity of P buried as CFA in shales is equally as important or more important than P buried as CFA in phosphorites as a marine sedimentary sink for reactive phosphorus. The significance of this distinction is that times of phosphorite deposition may reflect less a change in marine sedimentary conditions favorable to precipitation of authigenic CFA than a change in depositional environmental conditions to a regime conducive to segregation and concentration of authigenic CFA into discrete horizons.

CONCLUSIONS

Porewater fluoride and nutrient data, solid-phase P data, and mass balance models indicate that authigenic carbonate fluorapatite is currently forming in sediments from the FOAM site in Long Island Sound and the shallow Mississippi Delta. The size of the authigenic CFA reservoir increases with depth at both sites and is mirrored by a decrease in size of the organic P reservoir, implying that authigenic CFA is being formed at the expense of organic P. This scenario of sink-switching, from organic P to authigenic CFA, is supported by the fact that the calculated integrated amount of the CFA increase matches the integrated amount of the organic P decrease at both the FOAM site and the Mississippi Delta site. Furthermore, the amount of CFA formation predicted on the basis of the porewater fluoride gradient observed at the FOAM site is quite close to the measured value of CFA at this site. One consequence of diagenetic redistribution of P from organic P to CFA is that organic P burial efficiency will not be accurately quantified by sedimentary organic C:P ratios in cases where P initially deposited as organic P is ultimately buried in association with CFA.

In both study sites, the amount of total P is virtually constant with depth, whereas the proportion of P contained in the different solid-phase P reservoirs is quite variable. This indicates that the sediments are retentive of P over the depth intervals sampled, and that one of the mechanisms which enhances retention is transformation of P from one reservoir to another.

The identification of authigenic CFA formed in non-upwelling environments raises the question: What is the difference between precipitation of CFA in terrigenous dominated sediments in non-upwelling environments vs. biogenic sediments in classical phosphate deposit environments? Authigenic CFA precipitation may proceed by different chemical mechanisms in the two depositional environments. It is equally possible, however, that phosphorite deposits are distinctive simply due to the fact that the classical environments in which they form are impoverished in terrigenous detritus and are subject to winnowing events, resulting in both primary and secondary concentration of the authigenic phase, whereas CFA in non-upwelling environments is diluted by terrigenous debris to the point that it is only identifiable with difficulty. In the latter case the mechanisms of precipitation need not be different. The question of the relative quantitative importance of the two environments as sites for removal of reactive P from the oceans can be addressed despite the fact that the mechanism of formation in the two environments remains unresolved. The well-known episodicity curve for phosphorites through geologic time (COOK and McELHINNY, 1979) is based on the number and size of economically important deposits. Inclusion of P as CFA in normal sedimentary rocks for which terrigenous dominated sediments in non-upwelling environments are the precursors, e.g., black or gray shales, in a curve of phosphorus burial through time, may reveal that although episodicity in formation of phosphorite deposits occurs, this does not translate directly to a difference in the quantity of P being removed from the oceans.

The identification of authigenic CFA formed in non-upwelling environments as a previously unrecognized sink for reactive P requires that a revised budget for marine P which includes this continental margin sink be constructed. Preliminary burial flux calculations indicate that the currently accepted residence time for P may be as much as 50% too high.
if continental margins are not included as sites of P burial (Ruttenberg, 1990). This would place the residence time of P on the time scale of global-glacial transitions.

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Hartmann M., Muller P., Suess E., and Van der Weijden


SANDSTROM M. W. (1982) Diagenesis of organic phosphorus in ma-
The principal assumption required when use is made of a stoichiometric nutrient regeneration model is that regeneration rates of N and P bear a constant ratio to one another. Other required assumptions are: steady state deposition and burial; first order decomposition kinetics; rapid, reversible adsorption of phosphate and ammonia which follows simple linear isotherms; negligible compaction and porewater flow; simple molecular diffusion below the mixed zone. The ammonia profile was fit to the equation (BERNER, 1980)

\[ C = C_0 + A (1 - \exp(-Bx)) \]

where \( A = F N_{\text{max}}/D_{\text{ku}} + (1 + K)\omega^2 \) and \( B = (kN/\omega) \).

For the FOAM site, the sedimentation rate \( \omega = 0.1 \text{ cm/yr} \); \( F = [(1 - g)/\sigma] = 1.35 \text{ g/cm}^3 \); the molecular diffusion coefficient \( D \) for ammonia = 309 cm\(^2\)/yr (KROM and BERNER, 1980); the reversible adsorption constant for ammonia \( K = 1.3 \) (ROSENFELD, 1979). From the fit the constants were evaluated as \( A = 3200 \text{ mmol/L} \); \( B = 0.0065 \text{ cm}^{-1} \). Evaluation of the first order rate constant \( kN \) from \( B \) and \( \omega \) yields a value of 0.00065 yr\(^{-1}\). Evaluation of \( N_0 \) from \( A \) yields a value of 53.1 \( \mu \text{moles N/g} \). This compares favorably to measured organic nitrogen values obtained for the FOAM site (ROSENFELD, 1980) of 52.3 \( \mu \text{moles N/g} \).

The rate constant obtained above for ammonia regeneration \( kN \) should be equal to the rate constant for phosphate regeneration according to the assumption of stoichiometric nutrient regeneration, e.g., \( kN = kP \) (BERNER, 1977). The pre-exponential constant \( A \) was evaluated for phosphate using Eqn. A2, the value for \( kP \) calculated from the empirical fit to the ammonia data, and the appropriate constants for phosphate: the molecular diffusion coefficient \( D \) for phosphate = 100 cm\(^2\)/yr (KROM and BERNER, 1981); the reversible adsorption constant for phosphate \( K = 2.0 \) (KROM and BERNER, 1981); the initial concentration of solid-phase organic P \( P_0 = 3.1 \mu \text{moles P/g} \) (value is from the 0–10 cm interval SEDEX organic-P). The pre-exponential constant is evaluated as \( A = 435 \). The resulting predicted profile is shown in Fig. 5.