

DIAGENETIC CONTROLS OF PHOSPHORUS IN OUTER CONTINENTAL-SHELF SEDIMENTS FROM THE GULF OF MEXICO

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ABSTRACT

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A sequential extraction scheme was used to isolate organic P and inorganic P associated with various forms of Fe, Mn and major cations in two low-carbonate cores from the outer Texas shelf, in which sulfate reduction is minor. Although total extractable P does not change significantly with depth, there is a strong shift in the phase associations. At the surface and the subsurface oxidation maximum of both cores, inorganic P is associated mainly with oxidized Fe. Oxidation of organic matter by reduction of the hydrous Fe-oxides causes a rapid decrease in both the hydrous-Fe-oxide-related P and organic P in the more reducing parts of the cores. The P released during these reactions becomes associated with Mg, Al, K and reduced Fe in one or more highly reactive [1 M acetic acid (HOAc)-soluble] phases with an average Mg:K:Fe:P molar ratio of ~ 16:6:6:1. Although the exact nature of the HOAc-soluble P phase is unknown, it appears to control pore-water concentrations of P, precluding formation of struvite or vivianite. $(C/P)_{org}$ ratios in both cores tend to increase with depth in the sediment column, which suggests preferential breakdown of organic P. The shallower station 19 (32 m) has an average molar $(C/P)_{org}$ ratio of 190, whereas station 9 (112 m) has an average ratio of 253.

Accumulation rates of hydrogenous P at station 19 are between 40 and 140 $\mu\text{g P cm}^{-2} \text{ yr}^{-1}$, while rates at station 9 are 20 $\mu\text{g P cm}^{-2} \text{ yr}^{-1}$. These rates are 5–35 times greater than average accumulation rates of P along ridge crests, where high concentrations of P are associated with hydrogenous Fe. Flux calculations indicate ~ 0.2 $\mu\text{g P cm}^{-2} \text{ yr}^{-1}$ of dissolved reactive P is released from sediments at the deeper station, while 6–55 $\mu\text{g P cm}^{-2} \text{ yr}^{-1}$ is released from the sediments at the shallower station.

INTRODUCTION

Knowledge of the diagenesis of P in the marine environment is important because P is an essential micronutrient and is often the limiting factor for biological growth. In some anoxic nearshore sediments, pore-water data on phosphate and sulfate have been sufficient to model early P diagenesis because the major processes involving P included only organic-matter decomposition via

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sulfate reduction and reversible linear adsorption of released phosphate (Berner, 1977). However, P diagenesis is not always this simple. For example, in certain estuarine environments where pore-water sulfate concentrations are insufficient to oxidize all the reactive organic matter (Bray et al., 1973; Martens et al., 1978), distributions of dissolved P and Fe suggest the formation of Fe(II)-orthophosphate (vivianite). This mineral is also believed to be present in anaerobic lacustrine sediments where sulfide ion concentration is low and phosphate is high (Nriagu, 1972; Emerson and Widmer, 1978). In oxidizing sediments most of the P released into interstitial water during organic matter decomposition is adsorbed by Fe-oxides, carbonates and clay minerals (Price, 1976) in processes similar to those in the overlying oxygenated waters. Further in areas of high CaCO_3 , P may precipitate as apatite (Calvert, 1976).

Because the partitioning of P in the sediment environment is affected by so many geochemical variables, study of the solid-P phases is difficult. Some work has been done to investigate the geochemical partitioning of P in lacustrine sediments. Williams et al. (1971, 1976) used a sequential extraction scheme to separate apatite P, non-apatite inorganic P and organic P. They determined that Fe controlled inorganic P in both oxidized and reduced sediments, and postulated the formation in anoxic sediments of a reduced-Fe gel of the form $\text{Fe}(\text{OH})_2$ which is capable of adsorbing large quantities of P (Fe/P molar ratio $\sim 6:1$). Their method was employed by Morse and Cook (1978) to investigate the different forms of P in continental slope and deep-sea sediments. These investigators reported that apatite P was the most abundant form and that its concentration closely followed that of CaCO_3 in deep-sea sediments. Nonapatite inorganic P correlated with acid-leachable Fe and Mn, while organic P was closely related to organic-C content (Morse and Cook, 1978). Other than the above-mentioned work and two studies relating high P concentration in metalliferous sediments to precipitation of hydrogenous Fe (Froelich et al., 1977; Bloch, 1978), little has been done to investigate the partitioning of P in marine sediments.

The purpose of the present work is to investigate early diagenesis of P in low-carbonate outer continental-shelf sediments where sulfate pore-water gradients are very gentle. The distributions of dissolved P and solid organic and inorganic P in sediment cores are determined using a sequential extraction scheme, originally developed to investigate heavy-metal-phase partitioning (Gupta and Chen, 1975; Filipek and Owen, 1978). This scheme has the advantage that it is more selective than that of Williams et al. (1971, 1976), especially in a low-carbonate environment where apatite is not expected to be a major phase (Berner, 1974). It also allows direct determination of Fe and other elements extracted with the P phases. Statistical techniques are then employed to deduce the diagenetic interrelationships among the organic and inorganic forms of P and other sediment components, especially Fe, Mn, K, Mg, S, Ca, carbonate C and organic C. Finally, rates of solid-P accumulation and fluxes of dissolved reactive P from the sediments are estimated.

The outer continental-shelf environment was chosen for study because it

is a potentially important sink for P in the oceans. It is a complex environment representing the transition between two diagenetic extremes: (1) slowly-deposited, organic-poor pelagic sediments with sparse benthic populations, in which the organic matter decomposition involves reduction of O_2 , nitrate and hydrous Fe-oxides over a large depth range in the sediment column (e.g., Froelich et al., 1979); and (2) rapidly deposited, organic-rich nearshore sediments with large benthic populations, in which sulfate is the major oxidant and the majority of pyrite production occurs within the uppermost few centimeters (e.g., Goldhaber et al., 1977).

SAMPLING AND ANALYTIC PROCEDURES

Sampling sites

During May and June, 1977, members of the U.S. Geological Survey at Corpus Christi, Texas, participated in a cruise aboard the R.V. "Decca Profiler" to recover sediment samples from the outer Texas shelf in the Gulf of Mexico. In the present study, core and grab samples were analyzed from three locations sampled during that cruise (Fig. 1). Core 19 ($28^{\circ}0'N$, $96^{\circ}34'W$), from a water depth of 30 m, consists of sandy silt containing discrete sand lenses due to hurricane activity. This location has a large benthic population (Berryhill, 1977). Core 9 ($26^{\circ}53'N$, $96^{\circ}33'W$), from a water depth of 112 m, is a fairly homogeneous mud with few organisms (Berryhill, 1977). Core 32 ($26^{\circ}54'N$, $96^{\circ}52'W$), from a depth of 61 m, is a fairly homogeneous dark-gray silt. The cores were sectioned in the ship's laboratory, where the temperature was approximately equal to the in situ temperature of the sediments (25° – $28^{\circ}C$). The interstitial water was expressed using N_2 pressure in a Reeburgh-type squeezer with a $0.45\text{-}\mu\text{m}$ filter. The first milliliter or so of each water sample was discarded. Between 25 and 50 ml of pore water was collected from most sediment sections. The water samples were immediately acidified and frozen, and the sectioned sediment was placed in plastic bags and refrigerated.

In all three cores, a subsurface oxidation maximum at ~ 10 cm was determined on the basis of interstitial sulfate concentrations, porosity and other sediment parameters. This maximum is believed due to an activity, such as irrigation, of some form of benthic organism or to the existence of a preferred feeding depth. The sulfate maximum was discussed in detail in an earlier paper (Filipek and Owen, 1980; see also Table I). Below this oxidation maximum, sulfate pore-water gradients were very gentle (Table I). In addition, the presence of abundant live worms at depths of 35 cm in core 19 indicated the existence of oxidizing niches at depth in the core. No H_2S odor was detected in any core interval.

TABLE I

Concentration of elements in dissolved and solid phases in three cores from the Gulf of Mexico shelf (labels for solid phases are defined in text)

Depth (cm)	Diss-P (μM)	Diss-Fe (μM)	Diss-SO ₄ ²⁻ (mM)	Diss-K (mM)	Diss-Mg (mM)	Solid phases in $\mu mol/g$ dry sediment			
						pyrite S	Org-C	Carb-C	HOAc- Ca
<i>Core 9</i>									
0-1	1.1	2.7	29.0	17.9	50.4	6.2	575	642	561
1-2	1.2	13.4	24.7	6.6	41.4	10.3	525	742	554
2-4	1.7	4.5	24.4	8.7	47.1	13.2	617	617	536
4-7	1.9	2.5	27.2	10.2	49.8	14.1	508	992	511
7-11	2.3	26.0	26.8	9.6	49.1	14.1	417	975	477
11-16	5.2	8.1	29.9	10.2	52.4	18.8	617	567	501
20-25	8.0	6.6	27.5	9.6	50.4	21.6	417	688	634
30-35	8.3	2.5	27.7	10.2	49.8	25.1	533	550	492
45-50	10.0	12.4	28.2	9.9	49.8	34.4	483	592	482
70-75	14.4	3.8	27.6	9.6	49.1	49.9	550	492	414
95-100	11.0	2.1	27.4	9.6	49.1	67.3	542	608	534
120-125	15.4	3.8	25.2	9.6	47.8	55.0	558	492	467
145-150	13.0	6.3	22.9	9.6	47.5	79.5	425	433	387
170-175	17.5	3.2	24.0	9.6	48.2	68.8	442	633	467
195-200	14.2	5.4	21.0	9.6	50.4	59.5	525	467	441
<i>Core 19**</i>									
0-1	3.2	4.8	29.5	9.9	51.7	9.4	450	350	274
1-2	3.5	6.1	27.0	8.6	51.7	30.2	442	317	309
2-4	3.9	2.9	24.0	8.3	47.8	36.8	258	783	297
4-7	5.5	1.8	27.6	8.3	50.4	35.6	183	925	242
7-11	4.9	1.8	27.4	9.0	-	44.3	183	292	245
11-16	4.7	2.7	27.1	9.0	51.7	57.5	267	333	220
20-25	5.7	2.6	26.1	8.3	51.0	56.1	242	283	302
30-35	5.9	1.8	26.4	8.3	50.4	77.4	242	367	232
45-50	9.4	17.9	26.3	8.3	51.7	90.4	233	117	210
70-75	12.8	2.1	26.3	8.3	50.4	103	375	267	210
95-100	15.9	2.0	25.1	8.3	50.4	116	325	275	205
118-123	11.8	1.8	24.2	8.3	50.4	57.5	150	217	140
123-128	13.2	27.8	24.8	8.3	51.7	93.8	358	233	210
145-150	14.8	3.2	24.2	8.3	51.7	62.2	217	400	232
<i>Core 32</i>									
0-1	3.7	2.5	29.6	11.5	49.8	12.5	533	525	454
1-2	-	68.4	-	-	-	14.3	308	558	447
2-4	3.1	14.2	22.5	6.0	42.4	17.5	167	567	397
4-7	3.1	5.4	23.5	9.0	47.1	16.5	450	492	442
7-11	4.3	7.2	27.9	9.6	49.8	23.7	375	450	384
11-16	3.9	3.6	27.4	9.3	-	28.7	433	550	442
20-25	6.3	2.3	26.8	9.3	49.8	53.0	375	175	359
30-35	8.1	2.5	25.1	9.3	48.8	52.4	525	358	319
45-50	16.1	3.2	26.4	9.0	49.8	49.3	392	158	302
70-75	23.2	2.3	24.9	9.0	49.3	71.8	517	333	342
95-100	17.3	3.1	22.6	9.0	49.1	59.5	483	333	342
120-125	18.9	2.2	20.0	8.3	45.1	65.5	358	150	297
145-150	37.0	4.0	20.5	9.0	49.1	87.3	392	233	282
170-175	32.7	2.9	18.9	9.0	48.4	93.6	467	483	492
195-200	33.8	2.3	16.6	9.0	47.8	84.2	417	292	299

*1 Nonlith = HOAc + ER + H₂O₂ + MR.

*2 Total P was measured using the HF-HClO₄-HNO₃ digestion on a separate sediment sample.

*3 Molar ratio of organic C to organic P, using H₂O₂-P as organic P.

Solid phases in $\mu\text{mol/g}$ dry sediment

HOAc-K	HOAc-Mg	HOAc-Mn	ER-Mn	HOAc-Fe	HOAc-P	Nonlith-P**1	Lith-P	Total P**2	(C/P) _{org} **3
35.7	94	5.11	0.71	28.7	5.21	13.9	3.2	15.7	168
48.2	103	4.75	0.53	31.3	5.72	12.2	3.2	16.3	177
51.8	98	4.62	0.47	48.9	6.95	12.5	2.9	16.5	230
50.0	92	4.73	0.67	28.2	4.96	14.2	3.5	15.6	165
52.0	91	4.80	0.74	39.3	5.73	15.5	3.2	14.3	113
57.6	94	4.86	0.58	59.0	6.60	13.4	2.9	13.5	213
55.6	99	5.50	0.56	51.7	7.50	13.2	2.9	16.1	174
52.4	93	5.50	0.76	37.9	5.79	13.0	3.6	14.8	217
58.1	101	5.50	0.69	63.5	7.37	13.1	3.4	15.4	269
62.4	99	5.55	0.77	60.8	7.27	12.8	3.3	15.2	244
59.4	99	6.72	0.77	52.3	7.16	13.4	2.9	16.1	287
66.5	106	6.32	0.71	60.2	8.80	14.9	3.5	16.2	621
49.0	99	5.13	0.67	50.1	7.47	13.3	2.7	16.3	399
55.2	105	5.90	0.74	50.1	8.20	15.9	2.3	16.5	306
54.1	120	5.64	0.77	54.1	9.40	16.6	2.5	18.1	218
16.1	71	8.61	0.59	10.4	2.58	13.1	—**5	—	94
25.5	85	3.24	0.59	17.7	3.86	11.4	—	—	164
20.2	81	2.97	0.44	22.5	4.16	10.1	—	—	121
20.8	71	2.51	0.40	27.6	4.22	9.4	—	—	99
28.9	80	2.71	0.47	32.1	4.48	9.6	—	—	86
30.5	82	2.69	0.46	35.6	5.13	9.7	—	—	168
33.8	74	2.89	0.49	34.1	4.38	9.5	—	—	159
33.2	101	3.24	0.61	34.7	6.18	10.9	—	—	172
33.5	91	3.51	0.64	30.0	5.28	9.2	—	—	208
37.3	80	3.73	0.80	40.2	6.67	10.6	—	—	355
45.9	108	3.84	0.86	35.0	7.05	10.7	—	—	413
16.3	58	2.31	0.50	17.8	4.84	7.8	—	—	134
28.7	91	3.42	0.72	24.3	6.74	11.0	—	—	306
25.5	99	3.15	0.55	20.4	5.90	9.6	—	—	175
28.2	80	5.73	0.78	16.1	3.99	—	—	—	—
32.5	120	5.13	0.60	19.9	5.64	—	—	—	—
28.4	111	4.53	0.54	17.0	4.51	—	—	—	—
37.6	116	5.51	0.74	34.6	5.60	—	—	—	—
34.5	104	4.64	0.63	30.9	5.48	—	—	—	—
36.3	88	4.55	0.64	39.7	5.12	—	—	—	—
57.4	96	5.75	0.72	51.6	8.55	—	—	—	—
53.6	122	5.26	0.85	59.4	8.10	—	—	—	—
51.2	131	5.33	0.83	66.5	9.01	—	—	—	—
58.8	134	6.28	0.97	66.7	8.27	—	—	—	—
53.3	106	6.57	1.02	49.1	8.15	—	—	—	—
51.6	111	6.72	1.01	55.2	9.41	—	—	—	—
48.2	118	6.64	1.20	35.6	9.69	—	—	—	—
52.6	132	7.03	1.08	29.0	8.72	—	—	—	—
44.9	184	5.84	0.96	40.4	9.24	—	—	—	—

**Core 19: 118–123 cm — sand lens; and 123–128 cm — muddy.

**5 — = not measured.

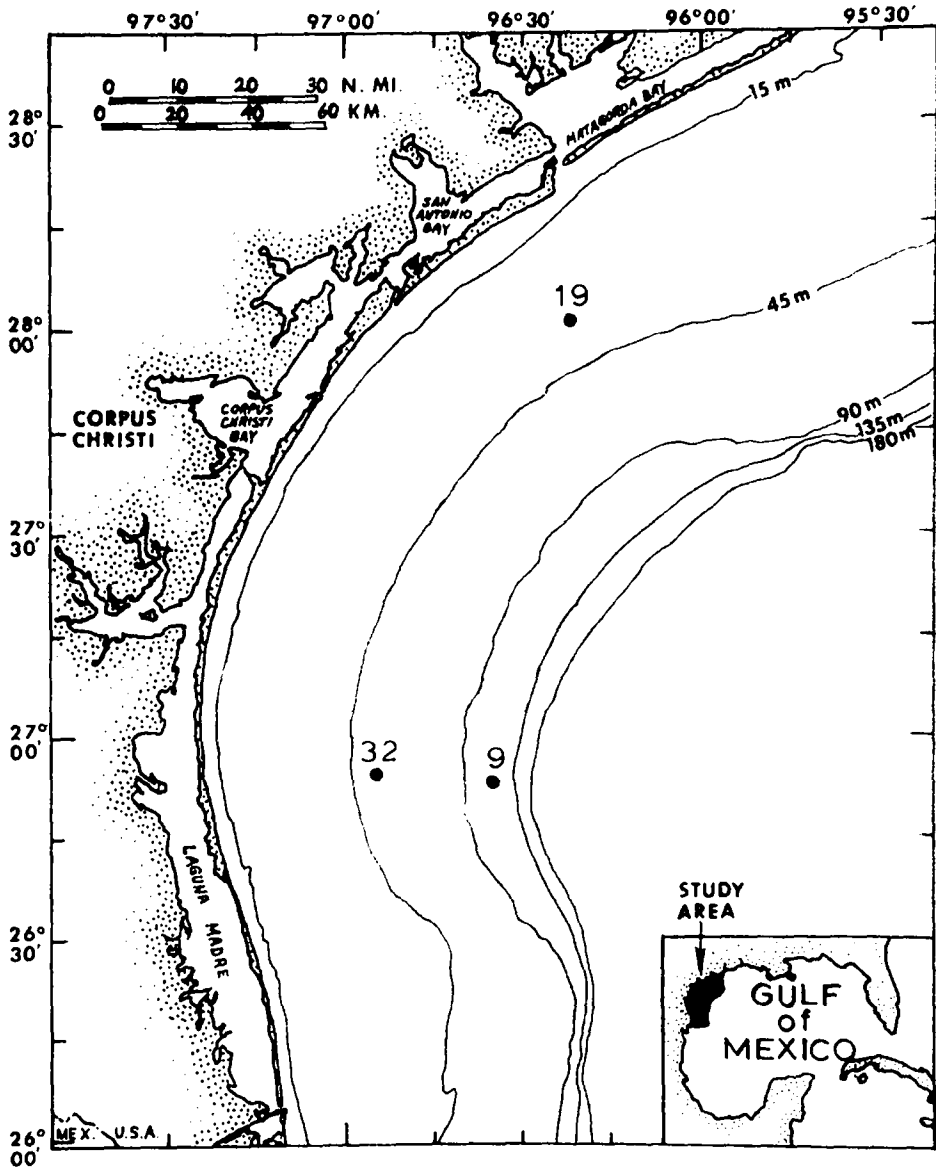


Fig. 1. The South Texas shelf of the Gulf of Mexico showing sampling locations.

Analytical methods

Within three weeks after collection, the sediment sections were subjected to a sequential extraction scheme (Fig. 2) designed to isolate heavy metals and associated P in the following geochemical fractions: (1) adsorbed species, carbonates, and acid-soluble Fe-sulfides; (2) easily reducible, including mainly

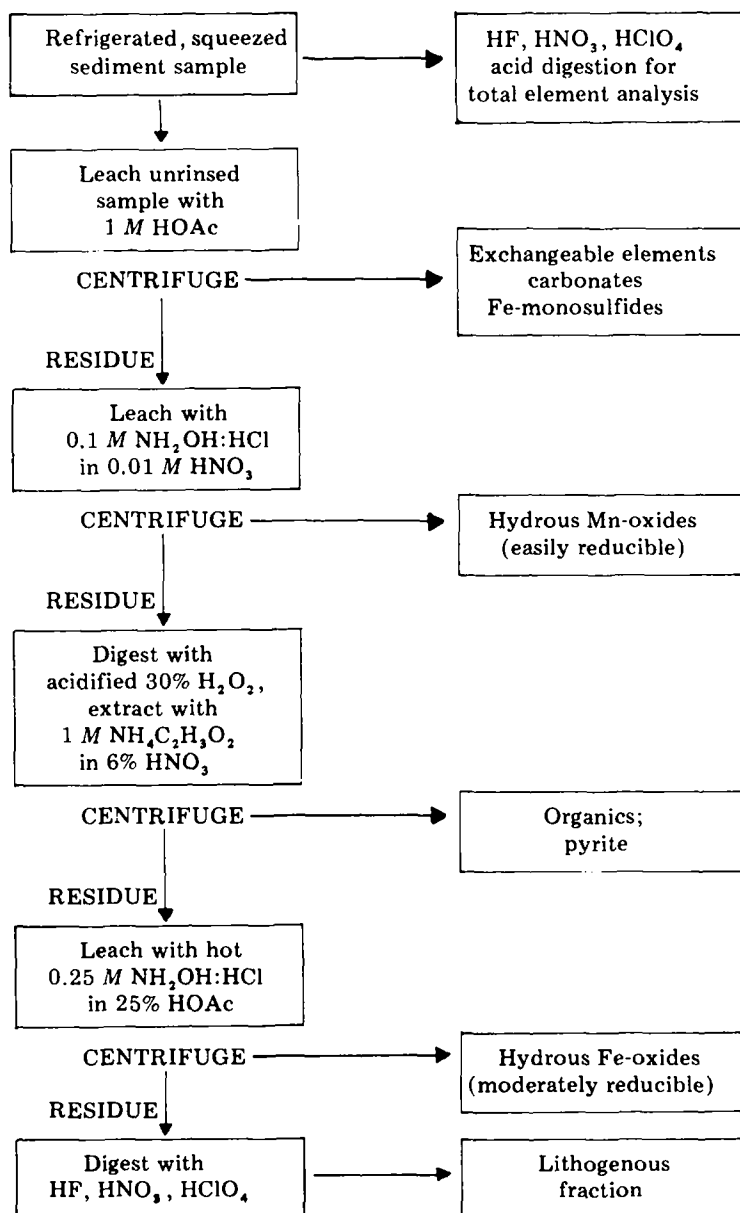


Fig. 2. Flow-chart of the sequential extraction scheme used in this study.

Mn-oxides (Chao, 1972); (3) oxidizable organics and pyrite (Nissenbaum, 1972; Presley et al., 1972); (4) moderately reducible, including mainly hydrous Fe-oxides (Chester and Hughes, 1967); and (5) the lithogenous fraction, consisting of residual crystalline minerals. Details of the extraction scheme have been published elsewhere (Gupta and Chen, 1975; Filipek and

Owen, 1978). The sediment sections were subsampled in a glove box under a N_2 atmosphere to keep the sediments from oxidizing before the initial HOAc extraction. Deaerated acetic acid (HOAc) was added to the samples in the glove box, and separate samples were taken to determine the moisture content of the squeezed sediment.

The reproducibility of replicate analyses varied somewhat with element and extraction, but was generally better than $\pm 25\%$. For P, reproducibility was $\sim \pm 10\%$. The sums of the measured P and Fe concentrations from the above five extractions were within $\pm 10\%$ of their value determined by a total sediment digestion on separate samples, which indicates no loss or matrix effects due to the solution used.

The Fe, Mn, Mg, Ca, Al and Si were determined by atomic absorption and K by flame emission spectrophotometry. Unrinsed sediment was used in the HOAc extraction to avoid shifts in the Donnan equilibrium caused by rinsing with distilled water (Sayles and Mangelsdorf, 1977). Therefore, HOAc-K and -Mg values were corrected to remove the contribution by diss (dissolved)-K and -Mg. This correction was unnecessary for the other elements because their concentrations in the pore water were insignificant compared with their HOAc-soluble values.

The method of Strickland and Parsons (1972) was used to determine P colorimetrically in dilutions (generally 1:20) of all extracts. Total C was determined on untreated samples, using a Hewlett-Packard[®] C,H,N analyzer. Organic C was measured using the C,H,N analyzer on sediments that had been previously treated with 1 N HCl overnight to remove carbonate C. Finally, carbonate C was determined by the difference between total and organic C. Solid-phase S (mainly pyrite) was determined gravimetrically by precipitation of $BaSO_4$ from rinsed sediment samples after oxidation of pyrite, using the method of Maxwell (1968). The resulting S was labeled "pyrite S" because the same analysis performed on HOAc-treated samples resulted in values of S generally within $\pm 10\%$ of untreated sediments, except for the upper 15 cm of core 9, in which $\sim 40\%$ of the S was acid-soluble. The Fe-labeled "org-Fe" (organic Fe) in the following discussion was calculated by subtracting one-half the molar concentration of S from the molar concentration of H_2O_2 -extractable Fe, based on the formula for pyrite (FeS_2). Errors in org-Fe due to inclusion of monosulfides are probably very small because acid-soluble Fe-sulfides are a significant fraction of the solid S only in near-surface sediments where total S is much less than H_2O_2 -Fe.

RESULTS

Core 9 has the most complete data set (Table I). Lith-P was not determined for core 19. For core 32, only the pore-water and the HOAc fraction were analyzed for P. However, partitioning results and inter-element correlations were generally similar among variables measured in all three cores. Therefore, data are presented for all three cores in Table I, but the emphasis

of the discussion is on cores 9 and 19, and a complete correlation matrix is given only for core 9 (Table II).

Approximately 20% of the P in core 9 was found in the lithogenous fraction (Table I), and is therefore probably occluded within the matrices of crystalline mineral components. This value is relatively constant with depth above 150 cm, but decreases to 13% below this depth, where changes in other sediment parameters (Table I) suggest a source change. Because both the total-P and the sum of the nonlith-P fractions (i.e. HOAc + ER + H₂O₂ + MR, in which ER and MR are the easily and moderately reducible fractions, respectively) are fairly constant throughout each of the cores where measured (Table I), these quantities provide little information on P diagenesis. Therefore, each of the nonlith-P fractions must be examined individually.

The outstanding feature of the P distribution in all three cores is the increase with depth of HOAc-P and diss-P, except near the subsurface oxidation maximum at ~ 10 cm (Table I). The decrease in HOAc-P and diss-P at the oxidation maximum is accompanied by an increase in H₂O₂-P, ER-P and MR-P (Fig. 3). Also noticeable is the similarity between the HOAc-Fe, -K, -Mg, and -P distributions in each core, and the insignificant or negative relationship of these elements with carbonate C and HOAc-Ca (Tables I and II).

Carbonate C shows a maximum concentration near the subsurface oxidation maximum of cores 9 and 19 (Table I). This maximum may be due to a

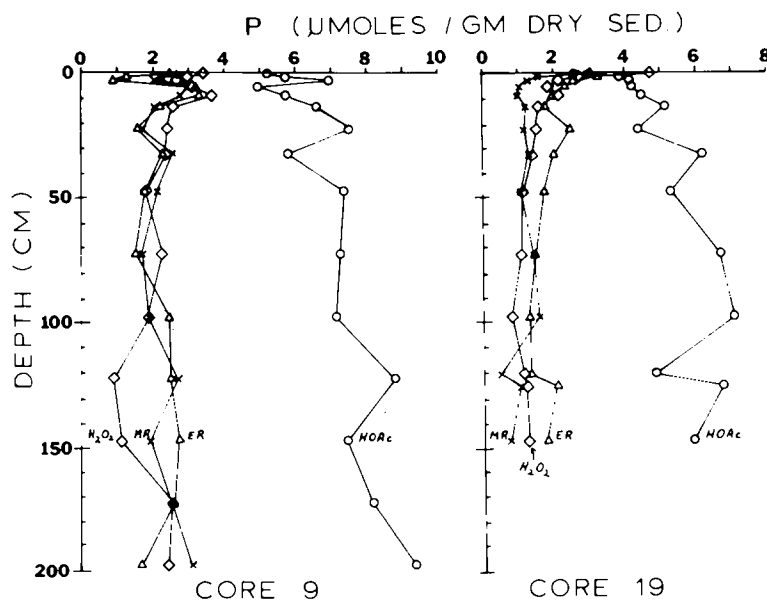


Fig. 3. Distribution of nonlithogenous P for cores 9 and 19 (HOAc = exchangeable elements, carbonates and Fe-monosulfides; ER = easily reducible species, mainly Mn-oxides; H₂O₂ = organics and pyrite; MR = moderately reducible species, mainly hydrous Fe-oxides).

TABLE II

Correlation matrix for core 9

	Diss-P	Sulfate	HOAc-P	HOAc-Fe	HOAc-Mn	HOAc-K	HOAc-Mg	HOAc-Ca	Carb-C	H ₂ O ₂ -P
Diss-P	1.00									
Sulfate	-0.39	1.00								
HOAc-P	0.83	-0.57	1.00							
HOAc-Fe	0.69	-0.06	0.78	1.00						
HOAc-Mn	0.75	-0.07	0.60	0.49	1.00					
HOAc-K	0.63	-0.01	0.61	0.80	0.57	1.00				
HOAc-Mg	0.62	-0.73	0.83	0.42	0.43	0.30	1.00			
HOAc-Ca	-0.58	0.40	-0.37	-0.37	0.02	-0.29	-0.28	1.00		
Carb-C	-0.59	0.24	-0.50	-0.45	-0.35	-0.31	-0.41	0.46	1.00	
H ₂ O ₂ -P	-0.71	0.26	-0.65	-0.67	-0.60	-0.60	-0.38	0.42	0.71	1.00
H ₂ O ₂ -Fe	-0.39	0.07	-0.31	-0.25	-0.45	-0.18	-0.10	0.24	0.50	0.70
Org-Fe	-0.78	0.36	-0.63	-0.48	-0.68	-0.39	-0.38	0.53	0.63	0.82
H ₂ O ₂ -Mn	-0.20	0.21	-0.18	-0.07	-0.22	-0.11	-0.01	-0.07	0.49	0.52
Org-C	-0.22	0.20	-0.06	-0.45	-0.06	0.04	-0.03	0.10	-0.33	-0.02
Pyrite S	0.90	-0.52	0.73	0.55	0.70	0.46	0.56	-0.63	-0.57	-0.72
ER-P	0.03	0.15	-0.26	-0.30	0.10	-0.12	-0.36	-0.26	0.20	0.08
ER-Fe	-0.55	0.22	-0.67	-0.81	-0.40	-0.61	-0.28	0.20	0.37	0.64
ER-Mn	0.56	-0.01	0.21	0.11	0.59	0.18	0.18	-0.53	-0.18	0.35
MR-P	-0.13	-0.25	-0.09	-0.47	-0.11	-0.32	0.21	-0.13	0.14	-0.09
MR-Fe	-0.24	-0.05	-0.40	-0.66	-0.19	-0.48	-0.26	-0.02	0.45	0.54
MR-Mn	-0.30	-0.06	-0.46	-0.74	-0.27	-0.53	-0.28	0.03	0.45	0.67

$P = 0.01$, $R \geq 0.64$; and $P = 0.05$, $R \geq 0.51$.

concentration of living shelled organisms at this depth. Another possibility is that some of this increase could be an artifact of the method of determining carbonate C, which may overestimate carbonate C and underestimate organic C by as much as 10% due to hydrolysis of organic C during the acid treatment (Froelich, 1980). The lack of concomitant increase in HOAc-Ca concentration at the oxidation maximum (Table I) suggests that easily hydrolyzable organics may be more prevalent there.

The redox conditions of the bulk sediment, even at the subsurface oxidation maximum, appear to be too low to support an extensive Mn-oxide phase. The Mn partitioning data (HOAc-Mn and ER-Mn are given in Table I) indicate that the majority (~ 65%) of the nonlith-Mn is in the HOAc fraction in all three cores. The HOAc extraction previously has been shown to remove only ~ 10% or less of the Mn from the Mn micronodules found in lacustrine sediments (Filipek and Owen, 1979) and from black Mn-oxide coatings of stream boulders (Filipek et al., 1981). The ER fraction, which should include the bulk of the hydrous Mn-oxides, has very low concentrations of Mn, averaging less than one-third of the ER-P concentrations (Table I; Fig. 3).

On the other hand, the generally high correlations among the ER- and MR-P, -Fe, and -Mn fractions (Table II) suggest that the ER-P and MR-P fractions are both associated with hydrous Fe-oxides (MR-Fe), which dominate the nonlith-Fe distribution throughout the core intervals (Fig. 4). Both MR-Fe and org-Fe (H₂O₂-Fe minus pyrite Fe) show maximum concentrations

$H_2O_2^-$ Fe	Org-Fe	$H_2O_2^-$ Mn	Org C	Pyrite S	ER-P	ER-Fe	ER-Mn	MR-P	MR-Fe	MR-Mn
1.00										
0.83	1.00									
0.67	0.54	1.00								
-0.06	0.17	-0.18	1.00							
-0.47	-0.89	-0.30	-0.28	1.00						
-0.44	-0.33	-0.01	-0.39	0.16	1.00					
0.34	0.56	0.42	-0.01	-0.60	0.23	1.00				
-0.20	-0.44	-0.29	-0.23	0.53	0.53	0.14	1.00			
-0.09	-0.09	0.17	-0.03	-0.16	0.46	0.60	0.35	1.00		
0.57	0.11	0.18	-0.40	-0.18	0.75	0.57	0.14	0.74	1.00	
0.17	0.24	0.15	-0.24	-0.24	0.60	0.60	0.29	0.67	0.94	1.00

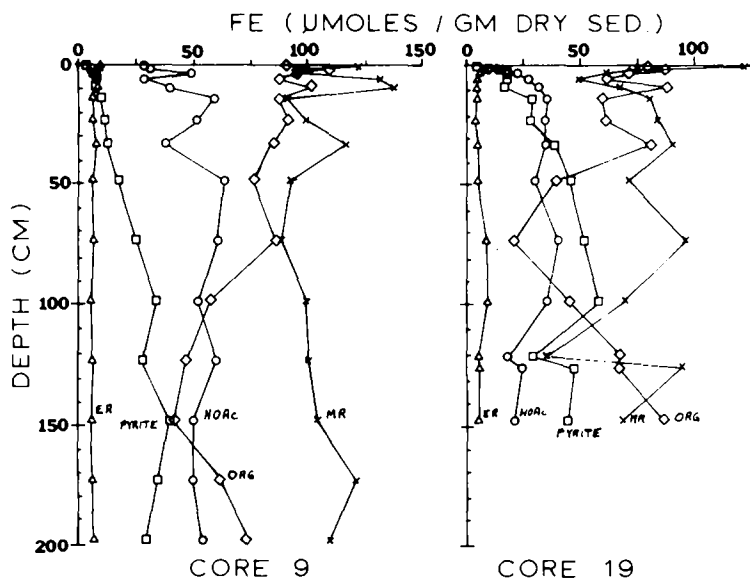


Fig. 4. Distribution of nonlithogenous Fe for cores 9 and 19 (HOAc = exchangeable elements, carbonates and Fe-monosulfides; ER = easily reducible species, mainly Mn-oxides; PYRITE = FeS_2 , determined using solid S concentrations; ORG = $H_2O_2^-$ -Fe minus pyrite Fe; MR = moderately reducible species, mainly hydrous Fe-oxides).

at the surface and subsurface oxidation maximum. However, pyrite Fe constitutes only a relatively small percentage of the nonlith-Fe, except in the lower half of core 19 (Fig. 4). Together with the very gentle sulfate gradients, these facts suggest that either sulfate reduction in these cores is minor, or a cyclic process occurs in which some of the diagenetic pyrite is reoxidized to Fe-oxides and sulfate in oxidizing micro-environments.

Interrelationship among P phases

Scatter plots (not shown) were made to determine more closely the interrelations of the extractable P phases and their changes with depth in the cores. HOAc-P showed the most consistent relation with diss-P throughout the depth range. Both phases appear to be produced during oxidation of organic matter by hydrous Fe-oxides (MR-Fe). This conclusion is based on the strong negative correlation of HOAc-P and diss-P with ER-P, H_2O_2 -P, MR-P, org-Fe and MR-Fe in the uppermost 50 cm of the cores, which is the depth range of the largest gradients in redox potential (Figs. 3 and 4).

Below ~ 50 cm, HOAc-P shows no correlation with ER- and H_2O_2 -P, whereas it becomes *positively* correlated with MR-P (Fig. 5). In both cores 9 and 19, the least-squares regression curve of HOAc-P vs. MR-P below 50 cm is strikingly similar:

$$\text{HOAc-P} = 4.2 + 1.6 \text{ MR-P} \quad (r = 0.97), \quad \text{for core 9}$$

and

$$\text{HOAc-P} = 4.3 + 1.7 \text{ MR-P} \quad (r = 0.79), \quad \text{for core 19}$$

In the deeper parts of the cores, HOAc-Fe continues to be highly correlated with HOAc-P, whereas in the MR phase, which has a much higher molar Fe/P ratio ($\sim 50:1$), Fe is not well correlated with P (Figs. 3 and 4).

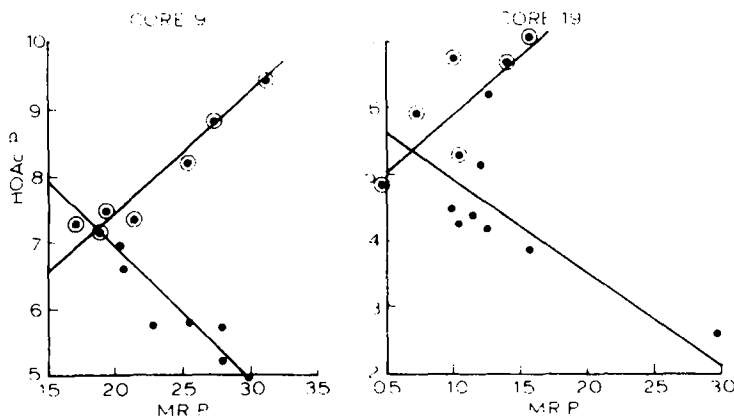


Fig. 5. Plots of MR-P vs. HOAc-P for cores 9 and 19, in $\mu\text{mol/g}$ dry sediment. Circled points represent values at depth ≥ 48 cm; uncircled points are from depth < 48 cm.

Interrelationships among HOAc-soluble elements

HOAc-P, -Fe, -Mg and -K are positively correlated in all three cores (Tables II and III), suggesting a common mode of occurrence or geochemistry. These elements are not likely to be in carbonate phases because they are all negatively or insignificantly correlated with HOAc-Ca and carbonate C. On the other hand, HOAc-Mn behaves differently in each core (Table I), perhaps due to the presence to two or more HOAc-soluble Mn phases, such as exchangeable Mn and Mn-carbonates.

The evidence suggests that HOAc-Mg and -K are present in exchange sites on clays. Both increase in concentration from core 19, which is a sandy-silt sediment, to core 9, which is muddy (Table I). Also, Drever (1971), Bischoff et al. (1975), and Sayles and Mangelsdorf (1977), using a variety of techniques to determine exchangeable cations on marine clays, have reported values of exchangeable -K and -Mg similar to the present concentrations of HOAc-K and -Mg.

The high concentrations of HOAc-Fe and -P (Figs. 3 and 4) and their apparent association with HOAc-K and -Mg warrant further discussion. First, the possibility must be considered that their high concentrations are an artifact of our sampling methods, because the sediments were exposed briefly to the atmosphere during the sectioning process aboard ship. Bray et al. (1973) showed that oxidation during the sampling can significantly decrease the inorganic phosphate concentrations in pore water which is rich in Fe(II), due to precipitation of the oxidized interstitial Fe with concomitant adsorption and/or precipitation of the P. However, the precipitation of interstitial P is not significant in our study for two reasons:

(1) The sediments that Bray et al. (1973) investigated were highly anoxic, and almost totally depleted of sulfate within the first 20 cm (Holdren et al., 1975; Matisoff et al., 1975). Our sediments show only minor sulfate reduction (Filipek and Owen, 1980; see also Table I). Also, oxidizing environments at depth in our core 19, which has the highest concentrations of pyrite, are evidenced by the abundance of live worms found at depths of at least 35 cm.

(2) Visual inspection of vertical variations in our Fe phases (Fig. 4 and Table I) reveals that maxima and minima of diss-Fe concentrations lie just beneath the same features in the MR-Fe (hydrrous ferric oxides) distribution, indicating that dissolved Fe reaches a maximum at depths where Fe is undergoing a change in oxidation state. On the other hand, diss-P does *not* show a similar distribution (Table I).

Based on the following estimate, even if some precipitation of diss-P and -Fe did occur during sampling, the HOAc-P and -Fe concentrations would not be significantly affected. In their extremely anoxic sediments, in which diss-P concentrations were 1–2 orders of magnitude greater than ours, Bray et al. (1973) reported a cumulative error of ~25% in interstitial phosphate concentrations under oxidizing sampling conditions, resulting in a precipitation of roughly 30 μmol P per liter pore water, based on inspection of their curves.

TABLE III

Molar ratios and correlation coefficients (r) of dissolved and HOAc-soluble elements

Depth (cm)	Core 9 (112 m ^{*1})						Core 19 (30 m ^{*1})					
	(Mg/K) _{diss}	(Mg/K) _{HOAc}	(K/Fe) _{HOAc}	(Mg/P) _{HOAc}	(N _g /Fe) _{HOAc}	(Al/P) _{HOAc}	(Mg/K) _{diss}	(Mg/K) _{HOAc}	(Al/P) _{HOAc}	(Mg/K) _{HOAc}	(K/Fe) _{HOAc}	
0-1	2.8	2.6	1.24	18.0	3.3	1.22	5.2	4.4	1.22	4.4	1.55	
1-2	6.3	2.1	1.54	18.0	3.3	1.21	6.0	3.3	1.21	3.3	1.44	
2-4	5.4	1.9	1.06	14.1	2.0	1.11	5.8	4.0	1.11	4.0	0.90	
4-7	4.8	1.8	1.77	18.5	3.2	1.25	6.1	3.4	1.25	3.4	0.75	
7-11	5.1	1.8	1.32	16.0	2.3	1.09	..	2.8	1.09	2.8	0.30	
11-16	5.1	1.6	0.98	14.2	1.6	1.28	5.7	2.7	1.28	2.7	0.86	
20-25	5.2	1.8	1.08	13.1	1.9	1.16	6.1	2.2	1.16	2.2	0.99	
30-35	4.9	1.8	1.38	16.1	2.5	—	6.1	3.0	—	3.0	0.96	
45-50	5.0	1.7	0.91	13.6	1.6	1.23	6.2	2.7	1.23	2.7	1.12	
70-75	5.1	1.6	1.03	13.6	1.6	1.25	6.1	2.9	1.25	2.9	0.94	
95-100	5.1	1.7	1.14	13.9	1.9	1.10	6.1	2.3	1.10	2.3	1.31	
120-125 ^{*2}	5.0	1.6	1.10	12.1	1.8	—	6.1 ^{*2}	3.6	—	3.6	0.92	
145-150 ^{*3}	4.9	2.0	0.98	13.3	2.0	—	6.2	3.2	—	3.2	1.18	
170-175	5.0	1.9	1.10	12.9	2.1	...	6.2	3.9	...	3.9	1.25	
195-200	5.2	2.2	1.00	12.7	2.2	...	6.2	3.9	...	3.9	1.25	
Average	5.0	1.9	1.2	14.7	2.2	1.2	6.0	3.2	1.2	3.2	1.1	
Standard deviation	0.7	0.3	0.2	2.1	0.6	0.1	0.3	0.6	0.1	0.6	0.2	
r	0.50	0.30	0.80	0.83	0.42	0.92	0.36	0.78	0.92	0.78	0.82	

TABLE III (continued)

Core 19 (30 m ^{*1}) (cont.)		Core 32 (61 m ^{*1})				
(Mg/P)HOAc	(Mg/Fe)HOAc	(Mg/K)HOAc	(Mg/K)HOAc	(K/Fe)HOAc	(Mg/P)HOAc	(Mg/Fe)HOAc
27.3	6.8	4.3	2.8	1.75	20.0	5.0
21.9	4.8	— ^{*4}	3.7	1.63	21.3	6.0
19.4	3.6	7.1	3.9	1.67	24.5	6.5
16.8	2.6	5.2	3.1	1.09	20.8	3.4
17.9	2.5	5.2	3.0	1.12	19.0	3.4
15.9	2.3	5.4	2.4	1.11	11.3	2.2
16.8	2.2	5.4	1.7	1.11	11.3	1.9
16.3	2.9	5.2	2.3	0.90	15.0	2.0
17.3	3.0	5.5	2.5	0.77	14.5	2.0
16.2	2.7	5.5	2.3	0.88	16.1	2.0
15.3	3.1	5.5	2.0	1.09	13.1	3.2
12.0	3.3	5.4	2.1	0.84	11.8	2.0
13.4	3.7					
16.7	4.8					
17.4	3.4	5.4	2.7	1.2	16.8	3.4
3.7	1.3	0.6	0.7	0.4	4.0	1.6
0.77	0.56	0.82	0.30	0.83	0.55	0.25

*¹ Water depth.*² Cores 9 and 32: sampling interval is 120–125 cm; core 19: 118–123 cm — sand lens and 123–128 cm — muddy.*³ Core 19: maximum sampling depth was 150 cm.*⁴ — = not measured.

Our concentrations of HOAc-P are ~ 6 mmol/l pore water, or 200 times this amount.

Although the high correlations among HOAc-P, -Fe, -Mg and -K suggest adsorption onto clays, the possibility that the P and/or Fe exist as other mineral phases must be considered. The increases in HOAc-Fe concentrations in more reduced parts of the cores (Fig. 4) suggest that the HOAc-Fe is at least partially in the Fe(II) state. Vivianite [$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$], siderite (FeCO_3), and acid-soluble Fe-sulfides are the Fe(II) minerals most likely to be formed under sedimentary conditions, based on thermodynamic equilibrium arguments (Stumm and Morgan, 1970). However, exact saturation calculations could not be made because certain necessary parameters, i.e. alkalinity, pH, dissolved sulfide and ammonia, were not measured. Therefore, estimates of the maximum saturation for each core were made by using the maximum concentrations of our measured species for each core and determining the saturation index ($\log \Omega$) by means of ratios with ($\log \Omega$)-values calculated by Murray et al. (1978) for anoxic sediments of Saanich Inlet. That is, we adjusted the ($\log \Omega$)-values of Murray et al. in proportion to the ratio of concentration of our *measured* species to their concentrations (raised to the appropriate exponent) and used their concentration values for species which we did not measure. Although this method gives only a rough estimate, the results indicate that even at the maximum concentrations of pore-water constituents measured in our cores, the interstitial waters of all three cores appear undersaturated with respect to vivianite and siderite. Moreover, as mentioned earlier, the low concentrations of S in the HOAc phase indicate that Fe-monosulfides are also not important. Finally, for any reasonable pH, pure $\text{Fe}(\text{OH})_2$ is undersaturated (Stumm and Morgan, 1970). Consequently, it is not likely that vivianite, siderite, Fe-monosulfides, or $\text{Fe}(\text{OH})_2$ occur in these cores.

The pore waters of all three cores may be saturated with respect to apatite minerals on the basis of the above calculations. However, it has been shown that CaCO_3 acts as a nucleating agent for the crystallization of apatite (Stumm and Leckie, 1970). In the absence of carbonates, high degrees of supersaturation can be maintained because precipitation of apatite is strongly hindered by the presence of Mg^{2+} from seawater (Martens and Harriss, 1970). All three cores contain only a few percent carbonate (Table I), mostly in the form of coarse shell debris with low specific surface area. Also, HOAc-P is negatively correlated with carbonates (Table II). Consequently, apatite is not likely to be an important phase in these sediments. Struvite [$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$] is another possible authigenic phosphate mineral. However, estimates based on ammonia concentrations in highly reducing sediments (e.g., Martens et al., 1978; Murray et al., 1978) suggest that the waters are undersaturated with respect to struvite by at least two orders of magnitude.

Another possibility is that the HOAc-P is associated with easily hydrolyzable organics, which might be soluble in the HOAc extraction. However, organics are unlikely to account for a significant fraction of the HOAc-P because the

concentration of hydrolyzable organics increases at the oxidation maximum, whereas the HOAc-P concentrations decrease.

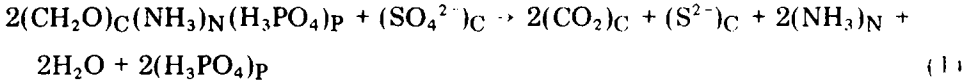
All of the evidence presented above suggests that HOAc-P, -Fe, -K and -Mg concentrations are related to the clay fraction of the sediment and possibly to each other. Moreover, the rapid increases in concentrations of these HOAc-soluble elements in reducing parts of the cores suggest that reduction of Fe-oxide coatings exposes reactive sites on the clays, as has been reported by Townsend and Reed (1971) and Sholkovitz (1973). In these mildly reducing sediments, it appears that Fe reduction, which is favored energetically over the sulfate reduction (Stumm and Morgan, 1970; Froelich et al., 1979), results in excess reduced Fe over that used in the formation of pyrite. This excess Fe may then remain associated with clays, perhaps as an amorphous (hydroxide?) phase containing also P, Mg and/or K.

Several observations suggest that the association of HOAc-P, -Fe, -Mg and -K is not a simple adsorption phenomenon. The (Mg:K:Fe:P)_{HOAc} ratio varies from ~ 17:5:5:1 for core 19 to ~ 15:7:7:1 for core 9 (Table III). For comparison, the interstitial-water ratio of these elements is ~ 5,000:1,000:0.5:1, indicating that P, Fe and K are being adsorbed preferentially to Mg. This preference seems to increase with depth. The decreasing (Mg/K)_{HOAc} ratios (Table III) could be indicative of increasing illite/chlorite ratios with increasing water depth due to differential settling of the smaller K-rich illite particles (Pinsak and Murray, 1960). Sayles and Mangelsdorf (1977) found that the ratio of exchangeable (K/Mg) was higher for illite than for any other type of clay that they studied. However, the 1:1 molar (K/Fe)_{HOAc} ratio in all three cores suggests the availability of nonpyrite reduced Fe may also be important in the selection of major cation (Mg or K) by clays. This process could be analogous to the formation of glauconite in the sulfide-poor reducing micro-environments of fecal pellets (Porrenga, 1966).

Concentrations of HOAc-soluble Al and Si were measured on selected samples from core 9 in order to determine whether Al or Si might also be significant in this fraction. The HOAc-Al was found to correlate very strongly with the other elements removed by HOAc, with an (Al/P)_{HOAc} ratio of just over 1:1 (Table III). The HOAc-Si concentrations were low (~ 5.5 $\mu\text{mol/g}$ dry sediment) and were not significantly correlated with the other elements. The 1:1 relationship between Al and P could indicate the presence of variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) or an amorphous Al-phosphate phase. On the other hand, the 6:1 average molar (Fe/P)_{HOAc} ratio in the shelf sediments is the same as that found in reduced lacustrine sediments by Williams et al. (1971), who postulated the association of P with a reduced-Fe gel of the form $\text{Fe}(\text{OH})_2$. In any case, the strong relationships among HOAc-P, -Al, -Fe, -Mg and -K suggest either a mixed phase or a few phases that vary together. Further studies involving scanning-electron or Auger microscopy or ESCA analysis would be necessary to determine whether AlPO_4 , Fe and Mg phases, for example, exist as physically distinct patches or whether there is some type of Mg-Fe-Al hydroxy framework that fixes K and phosphate.

Stoichiometry of phosphate regeneration

If we assume that $\text{H}_2\text{O}_2\text{-P}$ constitutes the majority of organic P in our sediments, we can calculate directly the ratio of C/P in the sediment organic matter, $(\text{C/P})_{\text{org}}$. This ratio is considered important in the understanding of the process of organic-matter decomposition and the resultant release of phosphate from sediments. Its relevance is based on stoichiometric reactions, such as the following:



In the classic Redfield—Ketchum—Richards reaction (Redfield et al., 1963), the molar C:N:P ratio is given as 106:16:1, based on the average ratio for marine plankton. However, the $(\text{C/P})_{\text{org}}$ ratio often has been found to be much greater than 106:1 in sediments (e.g., Sholkovitz, 1973; Hartmann et al., 1973; Martens et al., 1978), suggesting either that the biota supplying organic matter to these sediments were impoverished in P or that organic P was released preferentially to organic C during decomposition. The latter possibility could be due to the lower activation energy necessary to split C—O—P bonds as compared with C—C and C—H bonds (Toth and Lerman, 1977).

In our outer Texas shelf sediments, the $(\text{C/P})_{\text{org}}$ ratio, obtained using $\text{H}_2\text{O}_2\text{-P}$, is lowest at the surface and the subsurface oxidation maximum, and increases with depth (Table I). Some of this increase could be an artifact of the method of determining organic C using 1 M HCl to dissolve carbonates, as discussed above. However, the P associated with easily hydrolyzable organics dissolved in the HCl should also be removed by the HOAc extraction, which would tend to cancel this effect. Moreover, these results are similar to those of Hartmann et al. (1973) and Sholkovitz (1973), and corroborate the theory that the organic P is preferentially stripped during organic decomposition. [The anomalously high $(\text{C/P})_{\text{org}}$ ratio at 125 cm in core 9 coincides with anomalies in other sediment parameters and is probably caused by a source change or catastrophic event.] Both the surface $(\text{C/P})_{\text{org}}$ ratio and the average ratio throughout the core are lower at site 19, the shallower of the two locations in which $\text{H}_2\text{O}_2\text{-P}$ was measured. [The average molar $(\text{C/P})_{\text{org}}$ ratio for core 19 is 190, and for core 9, 253. Below the subsurface oxidation maximum, this average is 207 for core 19 and 259 for core 9, not including the anomalous value of 621 at 125 cm.] Increasing sediment $(\text{C/P})_{\text{org}}$ ratios with increasing water depth have been reported by other researchers (e.g., Martens et al., 1978) and have been interpreted as due to more rapid deposition shoreward, and thus less preferential stripping of organic P before burial in shallow environments.

We determined $(\text{C/P})_{\text{org}}$ ratios directly, using $\text{H}_2\text{O}_2\text{-P}$ concentrations. However, these ratios are usually determined *indirectly*, using the model of Berner

(1977), which is based on the ratio of the change in interstitial sulfate to the change in dissolved phosphate with depth in a sediment column. This model assumes that all increases in dissolved P are due to decomposition of organic matter by sulfate reduction, and that phosphate adsorption can be described in terms of a simple linear isotherm. However, the assumptions of this model are not always valid in marine environments. For example, Martens et al. (1978) showed that authigenic phosphate minerals may precipitate in anoxic sediments. Moreover, in organic-rich sediments, Murray et al. (1978) reported that sulfate may be consumed by methane diffusing up from the underlying sediments, as well as by particulate organic matter. These two processes tend to increase the apparent $(C/P)_{org}$ ratio if they are ignored by using Berner's (1977) model. On the other hand, phosphate may be released into the sediments by reduction of oxidized Fe compounds (Suess, 1976), which tends to *decrease* the apparent $(C/P)_{org}$ ratio.

In our outer Texas shelf sediments, Berner's (1977) model is not valid, because it appears that P is released not only by sulfate-induced decomposition of organic matter, but also during reduction of hydrous Fe-oxides, in which P is supplied by both the Fe-oxides and the organic matter. Moreover, we do not know whether the formation of the HOAc-P phase can be described by a linear isotherm. If not, then this also invalidates Berner's model.

Fluxes and accumulation rates of phosphorus

Knowledge of both the flux of dissolved reactive P from the sediments and of accumulation rates of solid P in sediments is vital to the understanding of the overall oceanic P budget. In core 9, both total nonlith- (or hydrogenous) P and lith-P (Table I) are fairly constant throughout the depth range of the core. This constancy is also true of nonlith-P in core 19 below the first few centimeters. (Lithogenous P was not measured for core 19.) We can, therefore, estimate the accumulation rate R of solid P in these cores, using the following expression:

$$R = (1 - \phi_{\infty}) \rho \omega P_s \approx (1 - \bar{\phi}) \rho \omega P_s \quad (2)$$

where P_s = the average concentration of solid P; ρ = density of the solid grains ($\sim 2.7 \text{ g/cm}^3$); $\bar{\phi}$ = average porosity; and ω = sedimentation rate. Substituting the values given in Table IV into eq. 2 gives an accumulation rate of nonlith-P in core 9 of $\sim 16 \mu\text{g P cm}^{-2} \text{ yr.}^{-1}$ (or $0.53 \mu\text{mol P cm}^{-2} \text{ yr.}^{-1}$). The total solid-P accumulation rate for core 9 is $20 \mu\text{g P cm}^{-2} \text{ yr.}^{-1}$ ($0.64 \mu\text{mol P cm}^{-2} \text{ yr.}^{-1}$). For core 19, the resulting accumulation rate of nonlith-P is $45\text{--}140 \mu\text{g P cm}^{-2} \text{ yr.}^{-1}$ (or $1.4\text{--}4.5 \mu\text{mol P cm}^{-2} \text{ yr.}^{-1}$). These accumulation rates are about an order of magnitude greater than rates along the East Pacific Rise crests ($\sim 4 \mu\text{g P cm}^{-2} \text{ yr.}^{-1}$) and 2–3 orders of magnitude greater than rates along the flanks of the rise (Froelich et al., 1977). If the rates found in this study are typical for continental shelves in general, which occupy $\sim 8.5\%$ of the surface area of the ocean floor (Menard and Smith, 1966; Manheim, 1976), then the shelves appear to be important sinks for P derived from continental erosion.

TABLE IV

Values of parameters used in the calculation of the accumulation rate of solid P and the flux of dissolved P for cores 9 and 19*:

	ϕ_0	$\bar{\phi}$	ω (mm yr. ⁻¹)	D_s (10^{-6} cm ² s ⁻¹)	D_p (10^{-6} cm ² s ⁻¹)	Nonlith-P ($\mu\text{mol g}^{-1}$)	Total P ($\mu\text{mol g}^{-1}$)	ΔP_d ($\mu\text{mol l}^{-1}$)
Core 9	0.8	0.74	0.54	2.2	1.5*2	14	17	0.8
Core 19*1	0.7	0.62	1.4-4.4	20-60	20-60	10	-	2.3

*1 Values of ϕ_0 , $\bar{\phi}$ and D_s taken from Filipek and Owen (1980); and values of ω taken from Holmes and Martin (1978), as discussed by Filipek and Owen (1980).

*2 Li and Gregory (1974) have reported that $D_p = 0.7 D_s$ (sulfate diffusion coefficient) in marine sediments when diffusion is due to molecular processes. Therefore, we will use $D_p = 0.7 D_s$ for core 9, where the D_s appears to be mainly to molecular processes, and $D_p = D_s$ for core 19 because this D_s appears due to bioturbation throughout the core (Filipek and Owen, 1980).

The sediments act not only as a sink for solid P, but also as a source of dissolved P to the overlying water. The flux J of dissolved reactive P out of the sediment can be estimated by two methods. The first is by determining the decrease in solid P with depth in the cores. The second is by using the Fickian diffusion equation:

$$J = -D_p \phi \left(\frac{\partial P_d}{\partial z} \right)_{z=0} \quad (3)$$

An approximate solution can be calculated if the gradient in the upper few centimeters is roughly linear, using the relation:

$$J = -D_p \phi_0 (\Delta P_d / \Delta z) \quad (4)$$

where Δz is a small depth interval of sediment starting at the sediment surface; ΔP_d is the change in dissolved reactive P within that interval, D_p is the pore-water diffusion coefficient for dissolved phosphate (taking into account sediment tortuosity and biogenic enhancement of flux due to bioturbation); and ϕ_0 is the porosity of the surficial sediment.

For core 19, the first method yields a flux of diss-P out of the sediment of between 18–55 $\mu\text{g P cm}^{-2} \text{yr}^{-1}$, depending on the value of ω used (i.e. $\sim 25\%$ of the P accumulation rate for core 19 based on the decrease of solid P in the first 5 cm). In core 9, the solid-P concentration is roughly constant with depth. Therefore, the flux of dissolved P must be less than 10% of the solid P, which is the amount of uncertainty in the solid-P measurements. The first method thus yields a flux of $< 2 \mu\text{g P cm}^{-2} \text{yr}^{-1}$. The second method, using eq. 4 with the values given in Table IV and $\Delta z = 5$ cm, yields a flux of 6–18 $\mu\text{g P cm}^{-2} \text{yr}^{-1}$ for core 19 and 0.2 $\mu\text{g P cm}^{-2} \text{yr}^{-1}$ for core 9. The values calculated by the second method should be considered minimum values for two reasons:

(1) The diffusion coefficients used had been calculated for the pore waters below ~ 10 cm (Filipek and Owen, 1980). The upper 10 cm is probably more highly bioturbated and therefore has a higher effective diffusion coefficient.

(2) Concentrations of dissolved P in the bottom waters were not measured. If they are much lower than the surficial pore-water concentrations, the gradient of dissolved P at the sediment surface would be higher, and the diffusive flux would therefore increase.

CONCLUSION

The results of this study show that total concentrations of P do not vary much in cores from mildly reducing, low-carbonate sediments of the outer Texas shelf of the Gulf of Mexico. Use of only these total values gives little information on P diagenesis because the nonlithogenous forms of P shift from one phase to another with only minor net diffusive flux out of the core.

Both inorganic P associated with oxidized forms of Fe and organic P decrease in more reduced parts of the cores, suggesting significant oxidation of organics via reduction of hydrous Fe-oxides in these regions. The P released

during these redox reactions then becomes associated with Mg, K, Al and reduced Fe in one or more highly reactive (HOAc-soluble) phases, adsorbed on clays. More research is required to determine the exact nature of the HOAc-P phase, which may prove to be common in other low-carbonate marine environments where sulfate reduction is not intense. The P released by Fe-oxides and organic-matter decomposition appears to be controlled by this HOAc phase, with pore-water concentrations never rising high enough to allow precipitation of other P phases such as struvite or vivianite. Although the pore waters appeared to be saturated with respect to apatite, the negative correlation between carbonates and HOAc-P suggests that apatite is not an important sink for P in these sediments, probably due to kinetic factors hindering apatite formation.

$(C/P)_{org}$ ratios, determined directly using H_2O_2 -P, increase both with depth in the sediment column and with distance from shore (i.e. water depth). This increase of ratios suggests preferential P removal during organic decomposition.

Accumulation rates of solid P calculated for these sediments were high compared with rates for mid-ocean rise and flank sediments. If these results are typical for continental shelves in general, then the shelves appear to be a major sink for P derived from continental erosion. Flux calculations of dissolved P reveal that the shallowest site, which has less refractory organic matter based in lower $(C/P)_{org}$ ratios, has both a higher flux rate of dissolved reactive P out of the sediment and a higher percentage loss of originally solid-phase P. Together, these results emphasize the importance of continental-shelf environments in the cycling of P in the oceans.

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