Phosphorus Cycle in the Ocean

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Abstract—The behavior of phosphorus is considered at major stages of the sedimentary cycle beginning with supply sources for its delivery into the ocean to precipitation and its sedimentation, localization and subsequent diagenetic redistribution in bottom sediments. River runoff represents the main phosphorus source in the ocean. It delivers annually about 1.5 Mt of dissolved phosphorus and more than 20 Mt of suspended phosphorus into the ocean. Up to 80% of the suspended phosphorus incorporated in the lithogenic material precipitates within submarine continental margins. Phosphorus dissolved in seawater repeatedly participates in biogeochemical processes owing to its assimilation by phytoplankton that annually consumes from 1.5 to 2.5 Gt of phosphorus. Dissolved phosphorus is incorporated in organic remains and precipitates from seawater by a biogenic mechanism, too. Only a part of phosphorus settled onto the bottom is buried in sediments. Due to reducing diagenetic processes, up to 30–40% of the primarily precipitated phosphorus diffuses from the upper layer of sediments into bottom water. Diffusion flux into the ocean significantly exceeds the supply of dissolved phosphorus from river runoff. The absolute mass phosphorus dispersed in sediments is several orders of magnitude greater than the mass concentrated in phosphorus accumulation in marine sediments in conditions of humid climate, intense chemical weathering of rocks on continents, and considerable expansion of the oceanic shelf area.

Geochemical cycle of elements in the oceanic lithogenesis includes several stages beginning with their migration to final drainage basins and ending with fixation in bottom sediments and diagenesis (Strakhov, 1963). Phosphorus, a major biogenic element, passes through these stages together with other biogenic elements (carbon, oxygen, and nitrogen).

The behavior of phosphorus in this cycle is interesting for lithology (origin of phosphorites), paleogeography (role of biogenic elements in climatic changes), and ecology (influence of phosphorus on eutrophication of marine basins).

Various aspects of phosphorus geochemistry in natural environments are actively discussed in scientific literature. However, general patterns of its behavior in the oceanic sedimentary cycle are still insufficiently elucidated. This work is an attempt to schematically present these patterns based on materials published in Russian and foreign literature mainly during the last few years.

The following problems are discussed in the present work: (1) sources and amounts of phosphorus delivery into the World Ocean; (2) species and absolute masses of phosphorus in the oceanic water, suspended matter, and bottom sediments; (3) fluxes of total and reactive phosphorus from seawater into sediments and from sediments into bottom water; (4) role of phosphorus in climatic changes; and (5) anthropogenic influence on the global phosphorus cycle.

PHOSPHORUS DELIVERY INTO THE WORLD OCEAN

A major share of phosphorus is supplied into the ocean from continents mainly with river runoff. Estimates of the global river runoff into the ocean given in literature considerably differ, but they generally vary within the following limits: $(35-44) \cdot 10^3$ km³ of water, 13–22 Gt of suspended matter, and 3.3–4.8 Gt of dissolved components (Compton *et al.*, 2000; Gordeev, 1983; Martin and Meybeck, 1979; Milliman and Meade, 1983; Savenko, 2001; Savenko and Zakharova, 1997; and other).

The river runoff intensity depends on climate, topography, rock and soil composition of drainage areas (Strakhov, 1963).

Phosphorus occurs in the river runoff as solution and suspended matter in both mineral and organic forms. Median concentration values of dissolved mineral and total phosphorus are 31 and 95 μ g/l, respectively, in waters of middle and large rivers, and 38 and 108 μ g/l, respectively, in waters of small rivers (Savenko and Zakharova, 1997).

Average phosphorus content in the riverine suspended matter ranges from 0.07 to 0.11% according to different estimates (Baturin, 1978; Gordeev, 1983). The portion of suspended phosphorus incorporated in minerals is geochemically inert, whereas its another portion associated with organic matter and iron hydroxides is geochemically reactive. Relationship between two forms varies within wide limits in different rivers. In suspended matter of the Mackenzie River, 25% of

Source	Supply, Mt/yr
River runoff	24.2
Glacier discharge and glacier erosion	1.4
Groundwater discharge	0.1
Coastal abrasion	0.4
Atmospheric precipitation	1.7
Volcanism of active continental margins	3.3
Total	31.1

Table 1. Total present-day phosphorus supply into the WorldOcean (Savenko, 2001)

phosphorus associate with organic matter (Ruttenberg and Goni, 1997). The share of reactive phosphorus in suspended matter and sediments of the Laguntas Creek River (California) is 45–55% (Vink *et al.*, 1977), and the value is as high as 75–80% in suspended matter and sediments from the Amazon River (Berner and Rao, 1994). It is assumed that the share of reactive phosphorus may generally reach a half or more of total phosphorus content in the riverine suspended matter (Colman and Holland, 2000; Ruttenberg and Goni, 1997). However, other estimates show that the share hardly exceeds 30% (Compton *et al.*, 2000).

The present-day total phosphorus supply into the ocean from continents is estimated at 18.7–31.4 Mt/yr. It includes the river runoff and other sources, such as glacier and subterranean water discharge, coastal abrasion, atmospheric precipitation, and volcanism of active continental margins (Tables 1, 2). According to earlier calculations, the amount of phosphorus in river runoff is 1.5 times lower (Meybeck, 1982).

Volcanic-hydrothermal source is traditionally suggested to play a significant role in phosphorus delivery into the ocean (Shatsky, 1955; Kurnosov, 1986; Sokolov, 1999). However, detailed studies of both hightemperature and low-temperature hydrothermal solutions from different parts of the ocean shows that their phosphorus content is similar or lower than that in seawater (Gordeev, 1992; Tunnicliff *et al.*, 1986; Wheat *et al.*, 1996). Increased phosphorus content in some postvolcanic springs on islands and continents is likely related to a drainage of friable volcaniclastic rocks by vadose waters (Baturin, 1978).

Phosphorus content in present-day rivers exceeds the natural (preanthropogenic) background value by 1.5–2 times. The natural background value is disturbed by cutting out of forests, soil erosion in drainage areas, wide application of phosphatic fertilizers, and discharge of industrial and domestic waste waters. Annual phosphorite mining reached 140–165 Mt (or 20–25 Mt of phosphorus) at the end of the last century. A major portion of the mined phosphorus was introduced into soil as fertilizer that was partially transferred to river systems (Baturin, 1997). The average total phosphorus content is 28 μ g/l in rivers draining forest landscapes, 250 μ g/l in rivers within agriculture regions, and as high as 1500 μ g/l in rivers flowing through urban areas (Edel'shtein, 1998; Savenko, 2001).

PHOSPHORUS IN OCEANIC WATER, SUSPENDED MATTER, AND BIOTA

Phosphorus content in the World Ocean varies from less than 1 μ g/l in surface waters during active phytoplankton bloom to 300 μ g/l in waters of stagnant basins of the Black and Baltic seas. Average phosphorus content in waters of the World Ocean is 70–72 μ g/l. The dissolved mineral phosphorus and organic phosphorus account for ~90 and 10%, respectively. Phosphorus is unevenly distributed in the water column showing minimum concentration values in surface waters and maximum content within the intermediate layer. The intermediate layer occurs at a depth of 1800–2000 m in the southern subtropical zone of the Pacific and 400–800 m in northern and southern marginal parts of this ocean (Bruland, 1983; *Khimiya okeana*, 1966).

Phosphorus sources and species	Preanthropogenic supply	Present-day supply
1. River runoff		
Dissolved P:		
inorganic	0.3–0.5	0.8–1.4
organic	0.2 (maximum)	0.2 (average)
Suspended P:		
organic	0.9 (maximum)	0.9 (average)
inorganic	1.5–3.0	1.3–7.4
detrital	6.9–12.2	14.5–20.5
2. Eolian	1.0 (including 20% of reactive P)	1.05 (including 20% of reactive P)
Total	10.8–17.8	18.7–31.4
Reactive	3.1–4.8	3.4–10.1

Table 2. Forms of present-day and preanthropogenic phosphorus supply into the World Ocean, Mt/yr (Compton et al., 2000)

The total amount of phosphorus dissolved in oceanic waters ($\sim 14 \cdot 10^8$ km³) is approximately 100 Gt. A major share of dissolved mineral phosphorus occurs in oceanic water as HPO₄^{2–} (87%) and PO₄^{3–} (12%) ions, which form monocharge complexes with Ca and Mg (Kester and Pytkovicz, 1967). Content of dissolved organic phosphorus in oceanic surface waters varies from 1 to 40 µg/l and commonly decreases to analytical zero in deep waters (*Khimiya okeana*, 1966).

Phosphorus content in the oceanic suspended matter ranges within 0.1–0.8% or $< 1-8 \mu g/l$ taking into account the suspended matter concentration in oceanic water. Generally, the suspended phosphorus (mainly represented by organic phosphorus) makes up 3–5% of its total concentration in oceanic waters (Bogdanov *et al.*, 1971).

Living matter constantly contains phosphorus as a major biogenic element, but its distribution is variable in different types of organisms. Phosphorus content ranges within the following limits (% of dry weight): 0.3-2% in marine and oceanic phytoplankton, 0.04-3% in different benthic algae, 0.05-1.6% in zooplankton, and <0.1-2.55% in zoobenthos. Certain parts of organisms contain much more phosphorus. For example, the phosphorous content reaches 6% in ashes of crustacean carapaces, 15-18% in phosphate brachiopoda (e.g., lingula) shells, 8% in bones, and 16% in fish scales (Baturin *et al.*, 1978).

The total wet mass of phytoplankton and zooplankton, which dominate in the bulk biomass of the ocean, is estimated at 10×10^9 and 15×10^9 t, respectively (Vinogradov, 1967). Corresponding amounts of phosphorus are about 25×10^6 and 37×10^6 t. However, primary production is mainly related to the vital activity of phytoplankton producing annually produces 60–100 Gt of organic carbon (Romankevich et al., 1999; Vinogradov, 1967; Vinogradov et al., 1996) and consumes 1.5-2.5 Gt of phosphorus. Consequently, phytoplankton annually uses almost two orders of magnitude more phosphorus during its vegetation cycles, relative to the total phosphorus amount in phytoplankton at any certain moment. The repeated recycling mainly involves phosphorus from the most intensely mixed upper euphotic layer of the ocean. Phosphorus of deep waters is less intensely involved in the general biogeochemical recycling, because the complete mixing of oceanic waters takes place during ~1000 yr. However, the biogeochemical phosphorus cycle may be accomplished much faster during a day or even several hours) in some local ecosystems, e.g., in coral reefs (Sorokin, 1990).

PHOSPHORUS PRECIPITATION FROM OCEANIC WATERS

The above data on active participation of phosphorus in biogeochemical cycles testify to the transfer of dissolved phosphorus from seawater to sediments mainly with biogenic components, i.e., remains of phytoplankton, zooplankton, and other organisms. Phosphorus of suspended matter delivered to the ocean with river runoff largely accumulates within continental margins, whereas dissolved phosphorus is immediately involved in the biogenic cycle near river mouths.

Detailed studies of the vertical migration of phosphorus and other biogenic elements from surface waters of the open ocean onto the bottom were carried out using sediment traps, which collect settling particles at different water column levels. In particular, data obtained by a series of sediment traps from pelagic regions of the Pacific and Atlantic oceans showed that relatively fresh material from upper water column levels is richest in phosphorus, nitrogen, and organic carbon (Honjo et al., 1982; Tsunogai et al., 1982). The material from depths less than 1000 m contains 0.41% P, 4.8% N, and 34.7% Corg. Composition of the material changes at deeper levels owing to the dissolution of carbonates and biogenic opal and organic matter destruction. This is accompanied by a decrease in phosphorus content (Table 3). The C : N : P atomic ratio mainly changes toward increase in the relative proportion of carbon due to higher dissolution rates of phosphorus and nitrogen. Such transformation takes place mainly within the mesopelagic zone (intermediate depths) and becomes slower within the bathypelagic zone (deep levels). However, distinct regularities in variations of C : P and C : N atomic ratios with depth in the material from traps are absent. According to Honjo et al. (1982), the C: P value ranges within 78–318 at depths less than 1000 m and 104-303 at deeper levels. Corresponding values for the C : N ratio are 5.2–9.0 and 10.1–11.2.

A series of traps in the Drake Strait revealed similar patterns, but here the material was also analysed for phosphorus species (Wefer et al., 1982). The total phosphorus content in dry material from the surface water is 0.6231%. Corresponding values for depths of 965 and 2540 m are 0.0650 and 0.0961%, respectively (Table 3). The share of water-soluble phosphorus is 87.5% in surface samples and 38-58% in from deep-water samples. Meanwhile, the share of acid-soluble phosphorus increases from 2.5% in surface samples to 9.5-10% in deep-water samples, and the share of insoluble phosphorus increases correspondingly from 10 to 32–52%. Calculations based on these data show that vertical fluxes of water-soluble and insoluble phosphorus in surface waters are 2.57 and 0.29 $g/m^2/yr$ respectively. They decrease to 0.041-0.079 and 0.046-0.057 g/m²/yr, respectively, in deep-water samples.

Thus, results of the study of trap samples show that the bulk phosphorus flux decreases during the settling of particulate material from the ocean surface to the bottom mainly owing to the removal of its most labile water-soluble fraction.

Based on the study of primary production of the ocean as a whole and its separate physiogeographic zones (Gusarova and Bordovskii, 1993; Koblents-Mishke *et al.*, 1968; Ryther, 1970; Vedernikov and Starodubtsev, 1971; Vinogradov *et al.*, 1996), as well as verti-

BATURIN

	C _{org} flux		P f		
Deptn, m	mg/m²/day	g/m²/yr	mg/m²/day	mg/m²/yr	C/P ratio
1.	California region (36	°42′ N, 122°01′ W),	shallow-water zone	during upwelling per	iod
50	342	158	5.9	2150	73
250	252	92	40	1460	63
700	115	41	1.6	600	68
	2. California 1	egion, shallow-wate	r zone during nonup	welling period	
50	91.2	33.3	0.90	330	101
250	14.4	18.8	0.40	146	129
700	12	17.9	0.34	124	144
	3. Califor	nia region (32°47' N	, 144°26' W), deep-v	vater zone	
75	68.4	25	0.43	158	158
575	14.4	5.25	0.08	29	181
1050	12	4.38	0.034	12.4	353
		4. Pacific Ocean (13	^{3°} 21′ N, 151°21′ W)		
378	3.56	1.30	_	_	_
978	0.55	0.20	_	_	_
2778	1.09	0.40	_	_	_
4280	0.88	0.32	0.009	3.28	97
5582	0.66	0.24	0.009	3.28	73
		5. Pacific Ocean (5	5°21' N, 81°53' W)		
667	12.57	4.59	0.102	37.2	123
1268	8.95	3.27	0.102	37.2	88
2265	9.06	3.31	0.112	40.9	81
2869	10.86	3.96	-	-	-
3769	11.38	4.15	112	40.9	101
3791	10.50	3.83	127	46.3	83
		6. Atlantic Ocean (3	31°32′ N, 55°35′ W)		
976	2.436	0.89	0.081	29.4	30
3694	0.876	0.32	0.022	6.7	48
5206	0.072	0.026	_	-	—
		7. Atlantic Ocean (1	3°30' N, 54°00' W)		
389	6.75	2.46	0.096	35.4	69
988	3.95	1.44	0.037	13.6	106
3755	1.73	0.63	0.025	9.05	70
5068	1.70	0.62	0.022	8.03	77
	8	8. Atlantic Ocean (2°	246.4' N, 12°33.6' W)	
240	5.57	2.03	0.33	120.4	17
940	8.17	2.98	0.11	40.1	74
2980	8.40	3.07	0.07	25.5	120
4040	8.53	3.11	0.07	25.5	122

Table 3. Vertical phosphorus and organic carbon fluxes in waters of the open ocean

Note: Regions and sources: (1-3) Knauer et al. (1979), (4-7) Honjo et al. (1982), and (8) Lukashin et al. (2002); (-) no data.

PHOSPHORUS CYCLE

Sea	Sand	Coarse aleurite	Fine aleurite	Aleuritic–pelitic mud	Pelitic mud
Barents Sea	_	(0.053-0.160)	(0.067–0.240)	(0.070-0.250)	_
Kara Sea	_	(0.075–0.160)	(0.058–0.117)	(0.077–0.115)	(0.1300.220)
Kara Sea	0.035	0.058	0.121	0.118	0.156
		(0.050-0.068)	(0.036–0.84)	(0.032–0.90)	(0.094–0.217)
Baltic Sea	0.045	0.66	0.07	0.07	0.08
	(0.01–0.07)	(0.02–0.14)	(0.03–0.08)	(0.01–0.16)	(0.03–0.18)
Baltic Sea (southern part)	0.037	0.050	0.068	_	0.080
White Sea	0.03	0.03	0.05	0.12	0.20
Norwegian-	0.09	_	_	_	_
Greenland basin	$(0.014 - 0.25^{1})$				
Norwegian fjords	_	_	_	_	0.11 (0.06–0.16)
Sea of Okhotsk	0.075	0.073	0.090	0.068	0.057
	(0.017–0.135)	(0.043-0.109)	(0.065–0.117)	(0.035–0.148)	(0.039–0.130)
Bering Sea	0.05	0.07	0.09	0.07	0.06
	(0.01–0.09)	(0.04–0.12)	(0.05–0.15)	(0.03–0.16)	(0.02–0.08)
Aral Sea	0.063	0.1	0	0.	16
Caspian Sea	0.032	0.048	0.063	0.072	0.078
Black Sea	0.043	0.0	52	0.049–	0.059^2
Sea of Azov	0.05	0.0)45	0.	05
	(0.03–0.06)	(0.036	-0.07)	(0.03-	-0.07)
Mediterranean Sea	_	0.04	(0.05 - 0.065)	(0.035–0.065)	(0.04–0.06)
Arabian Sea	0.10	0.1	0	0.10	0.12
	(0.06–0.15)	(0.05-	-0.15)	(0.07–0.13)	(0.08–0.16)
Average	0.05	0.06	0.075	0.08	0.10

 Table 4. Phosphorus content (%) in the upper layer of marine sediments (Baturin, 1978)

Note: Numbers in parentheses are range limits; ¹bulk sediment; ²calcareous clay; (–) no data.

cal fluxes and composition of suspended matter (Honjo *et al.*, 1982; Knauer and Martin, 1979; Tsunogai *et al.*, 1982; Wefer *et al.*, 1982; and others), we can approximately estimate the bulk phosphorus flux that reaches the bottom. It ranges from ~1 g/m²/yr in shallow-water (high-productivity) coastal upwelling zones to 0.1 g/m²/yr in other shelf zones and continental slopes and 0.01 g/m²/yr within pelagic zones of the ocean. The zones listed occupy an area of $1 \cdot 10^6$, $26 \cdot 10^6$, $63 \cdot 10^6$, and $270 \cdot 10^6$ km², respectively. Therefore, the total annual phosphorus flux from water to ocean bottom may reach about 10–12 Mt, or less than 1% of the phosphorus mass involved in biological cycle.

PHOSPHORUS IN MARINE AND OCEANIC SEDIMENTS

Phosphorus content in the studied sediments from the Arctic seas (Barents, Kara, and Norwegian), intracontinental seas (Baltic, White, Aral, Caspian, Black, Azov, and Mediterranean), and marginal seas of the Pacific and Indian oceans (Bering, Sea of Okhotsk, and Arabian) ranges from 0.1 to 0.9%. Commonly, the P content has a positive correlation with the organic-rich pelite fraction. The average phosphorus content in main granulometric types of sediments from these seas is as follows (%): 0.5 in sand, 0.6 in coarse aleurite, 0.075 in fine aleurite, 0.8 in aleuritic pelite, and 0.1 in pelite (Table 4). The average phosphorus content in marine sediments is 0.07% (Baturin, 1978). This corresponds to its average content in sedimentary rocks from continents (Turekian and Wedepohl, 1961; Vinogradov, 1962).

In closed and semiclosed marine basins, phosphorus concentrates in sediments of deep depressions, whereas higher phosphorus concentrations in open seas occur near continental coasts. Phosphorus distribution patterns are commonly similar to those of organic carbon (Black and Baltic seas), but in some cases (e.g., the Kara Sea and some zones of the Caspian Sea), phos-

	Ocean						
Sediment type	Atlant	ic	Paci	fic	India	for all	
	range limits	average	range limits	average	range limits	average	seaments
Terrigenous sediments, including hemipelagic mud	0.01–0.46	0.07	0.05-0.22	0.085	0.031-0.118	0.06	0.073
Calcareous ooze (>50% CaCO ₃)	$< 0.01 - 0.22^2$	0.05	0.02–0.43	0.095	0.017-0.032	0.025^4	
					0.035–0.061	0.049^{5}	0.062
Slightly siliceous and siliceous ooze	$< 0.01 - 0.04^3$	0.02	0.04–0.29	0.11	0.038–0.118	0.073	0.073
Red clay	0.05–0.11	0.08	0.02–0.61	0.16	0.085-0.235	0.145	0.145
Volcanogenic mud and aleurite	0.06–0.18	0.11	0.04–0.31	0.12	_	_	0.133
Metalliferous sediments	_	_	0.03–0.90	0.19	_	_	0.19

Table 5. Phosphorus content (%) in the upper layer of oceanic sediments¹

Note: ¹Data from (Baturin, 1988; Baturin and Sevast'yanova, 1986; Emel'yanov and Romankevich, 1979); ²excluding phosphatic sediments from the Namibian shelf; ³deep-water diatom ooze from the Antarctic region; ⁴foraminiferal ooze; ⁵nannoforaminiferal ooze; (–) no data.

phorus concentrates in sediments enriched in iron hydroxides (Baturin, 1978).

Phosphorus content in oceanic sediments ranges from 0.01% to 10-12%. Sediments in the latter can be qualified as phosphorites, because they contain about 50% of phosphates.

Among oceanic pelagic sediments, the lowest phosphorus content is noted in some calcareous and diatomaceous oozes (less than 0.01%), whereas highest values (up to 0.2–0.6%) occur in pelagic red clay and especially in zeolitic clay (Table 5). Phosphatic rocks and sediments from some continental margins and seamounts represent a special type of oceanic deposit (Baturin, 1978; *Gaioty...*, 1998; Hein *et al.*, 1993).

The lateral phosphorus distribution in surface sediments of the Atlantic and Indian oceans is characterized by a decrease from shelf areas to pelagic ones (Fig. 1). This pattern generally corresponds to that of the primary phytoplankton production shown in (Vinogradov *et al.*, 1996). However, increased phosphorus concentrations are also associated with domains of pelagic red clay and Fe-rich metalliferous sediments in central and southeastern parts of the Pacific Ocean (Fig. 1). The increased phosphorus content is a result of its accumulation on iron hydroxides, as well as the presence of fine-grained fish bone debris and authigenic zeolites in these sediments characterized by extremely low sedimentation rates.

The vertical phosphorus distribution in sediments depends not only on their lithology, but also on the intensity of diagenetic redistribution of elements. As it is noted in many publications, the upper layer of uniform near-continental and hemipelagic sediments is enriched in phosphorus relative to underlying layers. This is an evidence of the postsedimentary phosphorus migration to the sediment/water interface and its partial return into water column (Mach *et al.*, 1987; Reimers *et al.*, 1996; Volkov and Yagodinskaya, 1979; Volkov *et al.*, 1974).

Phosphorus species in sediments, especially in nearshore ones, were studied by many researchers. For example, four phosphorus species were determined in sediments from the Gulf of Mexico: (1) phosphorus soluble in acetic acid, which extracts exchange complex and dissolves carbonates and iron monosulfide; (2) organic phosphorus extracted by the treatment of samples with hydrogen peroxide; (3) species bound with iron oxides; and (4) species bound with manganese oxides (Filipek and Owen, 1981).

A refined sequental extraction method is recently applied for the determination of five (organic, absorbed, iron hydroxide-associated, detrital, and authigenic) phosphorus species in sediments. The latter species extracted by acetate reagent comprises authigenic apatite, biogenic apatite (mainly fish bones), and carbonatehosted phosphorus (Ruttenberg, 1992). Results of the study of sediments from the Mississippi delta, Amazon delta, Long Island Sound, equatorial Atlantic, and Black Sea by the sequential method are given in Table 6.

The average phosphorus content in these sediments is rather uniform and ranges from 0.054% in the Amazon delta to 0.078% in the equatorial Atlantic. The relative share of organic phosphorus in four former zones varies within 20–29% and increases to 43% in organicrich sediments of the Black Sea, although the total phosphorus content is low.

The contribution of Fe-associated phosphorus is up to 46% in sediments from the Amazon delta and falls to zero in sediments from the Long Island Sound. It varies from 19 to 23% in other samples. The contribution of phosphorus incorporated in detrital material also demonstrates wide variations from 1% in sediments from the equatorial Atlantic to 47% in sediments from the Long Island Sound and 6–11% in other samples. The contribution of absorbed phosphorus is negligible elsewhere (2-7%).



Fig. 1. Phosphorus distribution (%) in the upper sediment layer of the World Ocean, based on data from (Baturin, 1988; Baturin and Sevast'yanova, 1986; Baturin *et al.*, 1995; Emel'yanov and Romankevich, 1979). (1) <0.05%; (2) 0.05–0.1%; (3) 0.1–0.2%; (4) 0.2–0.3%; (5) >0.3% (for the Indian ocean: (2) 0.05–0.08%; (3) >0.08%).

80°

40°

107

Species	Region						
Species	Mississippi delta Amazon delta Long Island Sound Equatorial Atlant				Black Sea		
Organic P	29	26	20	27	43		
P bound with iron hydroxides	23	46*	0	20	19		
P bound with carbonates	28	22	29	49	20		
Detrital P	15	6	47	1	11		
Absorbed P	5	_	4	2	7		
Total P, %	0.067	0.054	0.059	0.078	0.061		
Number of samples	18	12	6	6	13		

 Table 6. Phosphorus species in sediments, % of total P content (Berner et al., 1993)

Composition of the so-called authigenic phosphorus, which comprises 20–49% of the total P, is the most interesting problem. In sediments with low contents of carbonate and biogenic phosphate (bone debris), this fraction is supposed to be composed of authigenic apatite, whose microscopic inclusions may be formed practically everywhere in sediments of continental margins (Berner *et al.*, 1993; Kim *et al.*, 1999; Reimers *et al.*, 1996; Ruttenberg, 1992; Ruttenberg and Berner, 1993).

Judging from the available few data, distribution patterns of phosphorus species in pelagic sediments differ from those described above. For example, 20 to 60% of total phosphorus content in pelagic red clay from the Pacific associates with iron hydroxides and ferromanganese micronodules; 20–45%, with clay minerals; 5–30%, with aleurite-size clastic minerals; 1–20%, with bone debris; and 1–5.5%, with zeolites (mainly phillipsite) (Sevast'yanova, 1983).

Distribution patterns of absolute phosphorus mass on the ocean bottom are generally similar to those of sediment mass as a result of the impact of circum-continental zonality. About 80% of bulk phosphorus accumulates within continental margins and in hemipelagic sediments; about 19%, in biogenic calcareous and siliceous oozes; and less than 1%, in pelagic red clay, volcanic mud, and metalliferous sediments (Table 7).

The total contribution of reactive phosphorus associated with organic matter, biogenic carbonates and phosphates, and hydrothermal and terrigenous iron hydroxides, to oceanic sediments is calculated in many previous publications based on general information about the composition of these materials (Baturin, 1978, 1988; Baturin and Savenko, 1997; Froelich *et al.*, 1982). According to one of the estimates, it reaches 1.8–3.5 Mt/yr (Table 8) and includes phosphorus left in sediments after the alteration of fresh suspended matter. Judging from another estimate, the average share of geochemically mobile phosphorus in sediments from the North Pacific is 20–25% (Baturin, 1988; Sevast'yanova, 1982; Volkov and Yagodinskaya, 1979). Extrapolating this value to all sediments, we obtain the reactive phosphorus accumulation rate of 2.5–4.5 Mt/yr (Table 7).

Finally, using numerous data on the accumulation rate of total phosphorus in sediments from different parts of the World Ocean (Baturin, 1988; Filipek and Owen, 1981; Filippelli and Delaney, 1994; Föllmi and von Breymann, 1992; Froelich *et al.*, 1977; Glenn and Arthur, 1985; Heggie *et al.*, 1990; Ingall and Jahnke, 1994; Moody *et al.*, 1988; Ruttenberg and Berner, 1993), the rate of nonterrigenous phosphorus burial in sediments is estimated at 2.1 Mt/yr (Schuffert *et al.*, 1998). This value generally corresponds to the previous calculations.

Since a considerable (or major) portion of phosphorus precipitates from the oceanic water in the form of organic-rich biogenic particles, it is interesting to compare the C : P ratio in living organisms, suspended matter, and sediments. The average value of this parameter (in terms of weight ratio) in planktons is 40:1 (the atomic Redfield ratio C : N : P = 106 : 16 : 1). It increases to 100-200 or more in suspended matter (especially deep-water material) (Table 3) owing to phosphorus release from organic matter, but considerably decreases in sediments (Table 7). This is likely related to organic matter decay and transition of the released organic phosphorus into mineral form with its partial fixation in sediments. The total amount of organic carbon accumulated in sediments, which is equal to 140 Mt/yr according to data by Romankevich (1977), versus phosphorus (~13 Mt/yr, Table 7) ratio is 11. The organic carbon accumulation rate versus mobile phosphorus (~3.5 Mt/yr) ratio is 40, i.e., the same as for phytoplankton.

PHOSPHORUS IN PORE WATER

Study of phosphorus behavior in the pore water of marine and oceanic sediments was started by S.V. Bruevich with his collaborators about 50 years ago (Bruevich and Vinogradov, 1947) and continued by many investigators from different countries.

Currently, it has been ascertained that phosphorus content in the pore water of oceanic sediments ranges from <0.01 to 40 mg/l. Minimal values characterize the

PHOSPHORUS CYCLE

		Sedin	Sedimentation rate			Content, %					
Sediment type	Distribution area, 10^6 km^2 (%)	$ma/am^2/V_0$		Mt/m		P _{tot}			P _{reac}		
		mg/cm /	'Na	WIU YI		I	Π	I		Π	C _{org}
Shelf and slope	27.2 (7.5)	15		13575	0.	06	0.08	0.01	1 ().02	0.52
sediments	63.3 (17.5)										1.02
Terrigenous hemi- pelagic sediments	20.6 (5.7)	6		1236	0.	06	0.07	0.01		0.02	0.57
Calcareous ooze	114.5 (31.7)	3		3435	0.	05	0.06	0.02	2 0	0.03	0.38
Siliceous ooze	43.3 (12.0)	0.5		217	0.	05	0.07	0.02	2 0	0.03	0.30
Red clay	82.8 (23.0)	0.4		331	0.	4	0.16	0.07	7 (0.08	0.27
Volcanogenic sediments	9.5 (2.6)	0.5		48	0.	11	0.12	0.01).02	0.32
Metalliferous sediments	(7.5–10)*	0.1–0.2		1–2	0.	1	0.2	0.1).2	-
Total	361.2 (100)		18843								
		Ν	lass acc	umulatio	n rate	, Mt/yr		•	(C/P	
Sediment type	Distribution area, 10^6 km^2 (%)	P _{tot}		ot P _{reac}			C	/P	C	P _{reac}	
		Ι	II	Ι		II	- C _{org}	Ι	II	Ι	II
Shelf and slope	27.2 (7.5)	8.145	10.860) 1.36		2.72	118	11	14.5	44	87
sediments	63.3 (17.5)										
Terrigenous hemi- pelagic sediments	20.6 (5.7)	0.741	0.865	5 0.12		0.24	7.0	8	9.5	29	58
Calcareous ooze	114.5 (31.7)	1.617	2.06	0.67		1.03	13.1	6	9.5	13	19
Siliceous ooze	43.3 (12.0)	0.108	0.152	2 0.04		0.06	0.7	4	6	10	15
Red clay	82.8 (23.0)	0.463	0.530	0.23		0.26	0.9	1.7	1.9	3.4	3.8
Volcanogenic sediments	9.5 (2.6)	0.05	0.06	0.00	5	0.01	0.2	2.7	2.9	16	32
Metalliferous sediments	(7.5–10)*	0.1	0.2	0.1		0.2					
Total	361.2 (100)	11.224	14.728	3 2.52		4.52	140				

Table 7. Phosphorus mass accumulation rates in the Upper Quaternary oceanic sediments (Baturin and Savenko, 1997)

Note: (I) Minimum estimate; (II) maximum estimate; (*) distribution area of metalliferous sediments is superimposed on those of other sediments, especially of carbonate ooze.

pore water from oxidized pelagic sediments, whereas maximal phosphorus contents are noted in the pore water from reduced sediments of near-shore productive zones of the ocean, such as the Namibian shelf, Chesapeake Bay, Long Island Sound, and Saanich Fjord (Baturin, 1972; Bray *et al.*, 1973; Martens *et al.*, 1978; Nissenbaum *et al.*, 1972).

Overview of a large data set on pore water composition in various sediment types from many zones of the World Ocean showed that the dissolved phosphorus content generally does not correlate with pH values, Ca content in solution, and organic matter content in the solid phase of sediments. Meanwhile, the direct correlation established between dissolved phosphorus and alkalinity depends on many factors, including the intensity of diagenetic organic matter alteration. The correlation is allegedly related to the formation of $Ca_2HPO_4CO_3$ - and $Ca_2PO_4CO_3$ -type phosphate–carbonate complexes of Ca in the solution (Savenko, 1979, 1990).

Generally, phosphorus content in the pore water of sediments from submarine continental margins sharply increases relative to that in bottom water with a spike at a depth of <10-30 cm. Below this level, the dissolved phosphorus content may increase, decrease, or remain the same (Fig. 2). The distribution of dissolved phosphorus in hemipelagic sediments may be more complicated and demonstrate a decrease in sediments covered with the oxidized layer. Pore water of totally oxidized pelagic sediments, such as red clay, contains minimum

Precipitating P-bearing material	Mass of P-bearing material, t/yr	Phosphorus content in P-bearing material, %	Mass of P, Mt/yr
Organic matter (C _{org})	$140 \cdot 10^{6}$	1:100-1:200	0.7–1.4
Carbonates	$6.85 \cdot 10^{9}$	0.01-0.02%	0.7 - 1.4
Iron hydroxides:			
hydrothermal	$1.6 \cdot 10^{6}$	$0.15 \pm 0.05\%$	0.16-0.32
terrigenous	$1.6 \cdot 10^{6}$	$0.15\pm0.05\%$	0.16-0.32
Fish bones	$(0.4-0.8) \cdot 10^{6}$	12–13%	0.05-0.1
Total			1.77–3.54

Table 8. Phosphorus precipitation from the oceanic water

phosphorus and often decreases to analytical zero (Bruevich and Zaitseva, 1964; Sevast'yanova, 1983).

Another specific feature is observed in the H_2S -contaminated zone of the Black Sea. The dissolved phosphorus content here is lower in pore water (0.03– 0.51 mg/l, average 0.15 mg/l) than in bottom water, which contains up to 1 mg/l P (Sevast'yanova, 1983; Zaitseva, 1959). This phenomenon may be attributed to the following process: iron hydroxides in suspended matter are reduced within the water column, and the phosphorus therein is released before the suspension reaches the bottom.

The problem of authigenic apatite formation by its precipitation from pore water, first registered in recent



Fig. 2. Distribution of dissolved phosphorus and fluorine (μ M) in pore waters of sediments from several continental margins. (a) Upper part of the continental slope of the California Peninsula, Mexico, depth 200–388 m (Jahnke *et al.*, 1983); (b) Central part of the Santa Barbara basin, depth ~550 m (Reimers *et al.*, 1996); (c) Continental slope of California, United States, depth 300–1300 m (Kim *et al.*, 1999).

Region	P flux, mg/m ² /yr	Literature source
Peruvian shelf	65	Shishkina, 1971
The same	12–690	Bordovskii et al., 1980
Gulf of Mexico	60–180	Filipek, Owen, 1981
Baja California	3500	Klump, Martens, 1981
Archus Bay	220	Jensen et al., 1995
Bazzard Bay, Massachusetts	680	Mc Nichol et al., 1988
Long Island Sound	125–238	Krom, Berger, 1981
The same	680	Aller, 1977
The same, northeastern zone	910	"
The same, deep-water zone	130	"

Table 9. Phosphorus diffusion fluxes from sediments calculated using concentration gradients in pore water

diatom oozes from the Namibian shelf (Baturin, 1969), deserves a special attention.

The detailed study of pore water and solid phase in sediments from the Santa Barbara basin and Californian continental slope showed that fluorcarbonate-apatite precipitates due to phosphorus diffusion to the water–bottom interface from below and an opposite fluorine diffusion from bottom water to the sediment (Fig. 2).

Based on *in situ* pH measurements and determination of corresponding elements in liquid and solid phases, it was ascertained that pore water of sediments from the Santa Barbara basin is saturated relative to fluorcarbonate-apatite and calcite already at a depth of 0.25 mm below the bottom surface and oversaturated relative to these compounds at a depth of 2 cm. However, the formation of apatite, which is registered by the precipitation of phosphorus and fluorine from pore water, occurs only at a depth of 5 cm below the waterbottom interface at the junction of the two fluxes. Judging from dissolved Ca profiles, the fine-dispersed calcium carbonate precipitates within the entire sediment core (Reimers *et al.*, 1996).

Another series of investigations on the continental slope of California revealed that rates of phosphorus and fluorine precipitation from the pore water are equal to 0.186–2.79 and 0.078–0.76 μ g/cm²/yr, respectively. A direct correlation exists between these values, and the molar ratio P/F averages at 2.4 corresponding to that for francolite (Kim *et al.*, 1999).

PHOSPHORUS FLUX FROM SEDIMENTS INTO BOTTOM WATER

Increased phosphorus content in the liquid phase of near-continental and hemipelagic sediments relative to the content in seawater suggests a possible phosphorus diffusion from sediments into the bottom water. Intensity of such diffusion flux was repeatedly evaluated using calculations based on diffusion coefficient, porosity, and water content of sediments, as it was first shown by Shishkina (1971). According to results of these calculations for nearshore sediments, the phosphorus diffusion flux ranges from 12 to 3500 mg/m²/yr (Table 9). Intensity of the flux shows seasonal variations. In bays and sounds (Table 9), the average summer flux accounts for 50% of the total. Respective values for the spring, autumn, and winter fluxes are 26, 17, and 7%, respectively. This corresponds to seasonal oscillations of the bioproductivity (Colman and Holland, 2000).

Using these data, the authors divided the entire ocean into two zones and calculated phosphorus diffusion flux therein: (1) shelf and continental slope (total area 8×10^6 km²) and (2) deep-water regions including continental slope base (306×10^6 km²). The accepted average sedimentation rate is 5.7 mm/yr for the first zone and 0.043 mm/yr for the second zone. Corresponding values for the diagenetic phosphorus flux are 1500 and 17 mg/m²/yr. The total diagenetic phosphorus flux is equal to 17.3 Mt/yr for the recent period and 12.5 Mt/yr for the preindustrial period (taking into account a lower accumulation rate).

However, such estimates seem to be too high, because they approach values of the total phosphorus flux and exceed the flux of reactive phosphorus (including both dissolved and suspended forms) into the ocean from continents. Moreover, average fluxes from nearcontinental zones were based on high values obtained for bays where fluxes are much higher than on shelves and continental slopes of the open ocean.

When evaluating the global phosphorus flux from the ocean bottom, we should keep in mind that the oxidized pelagic sediments, which are characterized by low phosphorus contents in the pore water and high ferromanganese hydroxide contents in the solid phase, extract rather than supply phosphorus from the bottom water. This statement is supported by the capture of dissolved phosphorus from oceanic water by iron hydroxides precipitated from hydrothermal plumes (Feely *et al.*, 1990; Wheate *et al.*, 1996) and the overall phosphorus enrichment of Fe-rich marine and oceanic sedi-

Zone	Area, $10^6 \mathrm{km}^2$	Reaches the bottom in suspended matter		Mineralizes at the	Diffuses fro	Remains in		
	IU KIII	t/km ²	Mt	bottom surface, wit	t/km ²	Mt	scument, wit	
High-productivity shelf	1	1	1	0.2	0.5	0.5	0.3	
Shelf	26	0.15	2.6	0.4	0.05	1.3	0.9	
Continental slope	63	0.1	6.3	2.1	0.05	3.0	1.2	
Pelagic area	270	0.01	1.7	0.3	0.001	0.2	1.2	
Total	360	_	11.6	3.0	_	5.0	3.6	

Table 10. Scheme of reactive phosphorus cycle in the ocean

ments (Baturin, 1978). Such sediments (pelagic red clays) occupy about a quarter of the Pacific floor area.

Moderately reduced terrigenous hemipelagic muds and deep-water biogenic sediments with P-rich pore water are commonly covered with an oxidized surface layer that increases in thickness from continents toward pelagic zones. The oxidized layer retards the phosphorus migration from sediments to bottom water, because dissolved phosphorus partially again precipitates on iron hydroxides.

Such an obstacle on the way of phosphorus to bottom water is absent in completely reduced sediments of continental margins, but a considerable portion of potentially mobile phosphorus is left in the solid phase that includes organic phosphorus, iron-phosphate complexes, and authigenic apatite (Table 6). Therefore, a part of reactive phosphorus is redistributed in these sediments and participates in fluorcarbonate-apatite formation. The second part is preserved in the primary form, whereas the third part diffuses into the bottom water.

Thus, the real phosphorus flux from sediments is considerably lower than the value based on its potential diffusion. Discrepant data on ascending and descending material fluxes in sediments from the Baja California area near the Mexican coast may support this suggestion, because the calculated phosphorus diffusion rate from sediments here appeared to be three times higher than the burial rate (Schuffert *et al.*, 1994, 1998).

Another way to estimate the phosphorus flux is based on the above-mentioned fact that the majority of homogeneous hemipelagic terrigenous and biogenic sediments of the Pacific and Indian oceans are characterized by enrichment of the surface layer and depletion of the subsurface layer in phosphorus. This phenomenon is interpreted as follows. The upper layer represents a relatively fresh unaltered sediment with the primary phosphorus content, whereas the underlying layer underwent diagenetic alteration and lost a part of phosphorus that diffused into bottom water. The share of this phosphorus was initially estimated at 25% for sediments from the northwestern part of the Pacific (Volkov *et al.*, 1974; Volkov and Yagodinskaya, 1979). Analogous calculations carried out later for sediments from the eastern part of the same Transpacific profile and for sediments from the northeastern and eastern parts of the Indian Ocean yielded a similar average value of 23.3% with variations from 7 to 59%. In one case, the upper layer contained less phosphorus than the underlying sediment (Table 10).

Judging from the distribution pattern of sediment accumulation rate in the World Ocean (Lisitsyn, 1974, 1978), the sedimentation rate ranges from 30 to 120 mm/ka in the regions named above. Phosphorus fluxes calculated from these data range from 2 to $62 \text{ mg/m}^2/\text{yr}$ average 15 mg/m²/yr).

Thus, we can suppose that the phosphorus flux from oceanic sediments varies from ~500 mg/m²/yr in near-shore zones with the highest bioproductivity to ~50 mg/m²/yr within other shelf zones and continental slopes, ~10 mg/m²/yr in zones of pelagic biogenic sediments, and close to zero in zones of red clay and metalliferous sediments. The total sum is ~5 Mt/yr.

PHOSPHORUS RESIDENCE TIME IN OCEANIC WATERS AND ITS BUDGET

Residence time of an element in the ocean is an aspect of its marine geochemistry that characterizes activity of the element in biogeochemical cycles. The resdence time is commonly defined as quotient of the division of total dissolved element reserves in the oceanic water either to annual delivery of its dissolved forms from external sources or to its total loss during sedimentation.

First estimates of dissolved phosphorus residence time in the oceanic water varied from 160000 (Ronov and Korzina, 1960) to 270000 yr (Vinogradov, 1967). They were based on underestimated values of dissolved phosphorus supply by river runoff (~0.5 Mt/yr) as the main phosphorus source in the ocean. Taking into account the dissolved organic phosphorus content in river runoff the residence time was latter reduced by three times, i.e., to 55000–90000 yr (Baturin, 1978, 1982). A close estimate (80000 yr) is given in (Froelich *et al.*, 1982).

However, based on a series of detailed investigations of phosphorus species in oceanic sediments (Table 6), these results were once again revised proceeding from the suggestion that it is more expedient to determine residence time of this element in the ocean using the amount of arbitrarily mobile (or reactive) phosphorus in sediments rather than river runoff. Taking into account the annual input of such phosphorus into oceanic sediments (2.5–5.7 Mt), Ruttenberg (1993) estimated the residence time of phosporus in the ocean at 16000–38000 yr.

The revision was continued in other works by adding estimates of the global phosphorus diffusion flux from oceanic sediments (12.5–17.3 Mt/yr, according to data given in the foregoing chapter), and the phosphorus residence time was reduced to about 10000 yr (Colman and Holland, 2000).

As shown above, our estimate of the global phosphorus diffusion flux is 5 Mt/yr. The corresponding phosphorus residence time in the ocean (20000 yr) is consistent with the result given in (Ruttenberg, 1993).

Thus, estimates of the phosphorus residence time in ocean differ by almost 30 times owing to different estimates of phosphorus input and output.

In the ideal case of a stationary sedimentation, including the accumulation of participating elements, a correspondence should exist between material supply into the basin and its accumulation on the bottom. However, the correct determination of fluxes is complicated by a wide variability in migration modes of elements, as well as their redistribution during diagenesis and exchange through the water–bottom interface, as shown above for phosphorus. When calculating the budget of an element, we have to take into account quantitative relationships between all of its components in order to improve the reliability of such calculations.

The above calculation results of phosphorus flux allow us to present the following idealized scheme of its budget in the ocean without considering effects of the anthropogenic factor.

About 14 Mt of total phosphorus, including 3.5 Mt of reactive one (Table 2), is annually delivered into the ocean from continents, which serve as the main phosphorus source. The major part (~80%) of the total and reactive phosphorus accumulates within submarine continental margins (~90 × 10⁶ km²) approximately in the same proportion. Another part is dispersed in deepwater sediments over an area of 270×10^6 km² (see Table 7).

The biogeochemical circulation of dissolved phosphorus takes place within the oceanic water—biota suspended matter—sediments—pore water—oceanic water system under the above-described conditions of phosphorus distribution. Phytoplankton consumes up to 2.5 Gt/yr of dissolved phosphorus mainly circulating within upper layers of the water column. Approximate estimates show that suspended matter mainly consisting of organic detritus and pellets annually carries ~11.6 Mt P of phosphorus onto the bottom. A part of this amount is released during organic matter decay at the bottom surface (~3 Mt). Another part (3.6 Mt) is buried in sediments, whereas the third part (~5 Mt) diffuses into the bottom water (Table 10). All values in this table are based on the data given above, except for the share of phosphorus dissolved at the bottom surface (it is is determined from the difference).

Variations in any part of the system obviously lead to changes in the system as a whole. Therefore, additional input of phosphorus into the ocean, particularly owing to anthropogenic effects, as it takes place today, leads to an intensification of all interrelated fluxes beginning with the increase in bioproductivity to the burial of phosphorus in sediments, its recycling, and the consequent reduction of phosphorus residence time in oceanic waters.

Since the character of continental weathering and the amount of phosphorus supply to the ocean considerably changed during the Earth's history and sometimes decreased by several times relatived to the present level (Cook abd McElhinny, 1979; Ronov, 1960, 1993; Sokolov, 1995), its residence time also periodically varied from a few thousand years to values of about 100000 yr.

PHOSPHORUS CYCLE, CLIMATE, AND PHOSPHORITES

The above data allow us to suggest that a certain interrelation exists between phosphorus cycle, climate, and marine phosphorite formation.

Let us recall in this context that according to many climatologists, the carbon dioxide content in atmosphere has a dominating influence on the Earth's climate. Increase in the carbon dioxide concentration leads to greenhouse effect that results in climate warming and humidization, melting of glaciers, and rise of the World Ocean level. This possibly takes place today as a result of anthropogenic CO_2 delivery to the atmosphere.

However, an opposite opinion is also discussed. It suggests that a surplus carbon dioxide delivery to the atmosphere, relative to the pre-anthropogenic level, is compensated by the ocean that assimilates CO_2 by both abiogenic (physicochemical equilibrium trend) and biogenic (reaction of oceanic biota) mechanisms. Today, the amount of such assimilation reaches a value comparable to the input of carbon dioxide into the atmosphere owing to fossil fuel combustion (Gorshkov and Makar'eva, 2002).

These mechanisms are only based on dynamics of changes in the atmospheric condition and gas exchange within the ocean–atmosphere system without considering the possible role of phosphorus and geological factors in climatic changes.

According to the opinion of other authors, the relationship between marine geochemistry of phosphorus and climate is primarily expressed due to linkages of the phosphorus cycle with the organic and inorganic carbon cycle, on the one hand, and the oxygen cycle, on the other hand. In this connection, phosphorus plays the role of an indirect regulator of the Earth's climate. For example, it serves as the main driving force in the fixation and burial of carbon in sediments (Broecker, 1982; Föllmi, 1996; Föllmi *et al.*, 1993; Holland, 1984).

Intensity of bioproductivity of the ocean is controlled to a considerable extent by phosphorus accessibility. During photosynthesis, marine plants consume inorganic carbon dissolved in seawater mainly as HCO_3^- ions, generate organic matter, and release free oxygen. The consequent pH value increase in seawater proceeded according to the following schematic reaction: $HCO_3 + H_2O = CH_2O + O_2 + OH^-$.

The role of phosphorus in this process consists in the following. Increased concentration of carbon dioxide in the atmosphere along with the greenhouse effect and high sealevel stand promote the chemical weathering and intensification of dissolved phosphorus supply from continents to the ocean. These processes increase bioproductivity, decrease carbon dioxide concentration in water, and induce a compensation flux of CO_2 into the ocean from the atmosphere. Enrichment of the atmosphere with carbon dioxide owing to its endogenous supply from volcanic or tectonic sources may be leveled just by such a way. Decrease of CO₂ reserves in the atmosphere results in weakening of the greenhouse effect up to the point of its replacement by the icehouse effect that leads to climate cooling and aridization. As a result, chemical weathering of continental rocks weakens, phosphorus flux into the ocean decreases, and the process starts to develop in the opposite direction (Föllmi, 1996).

However, calculation of carbonate accumulation budget in sediments of the World Ocean (Savenko, 1995, 2001) showed that at the stationary state of carbonate system during the preindustrial period, the ocean emanated rather than assimilated carbon dioxide into the atmosphere as a result of biogenic carbonate formation according to the reaction: $Ca^2 + 2HCO_3 =$ $CaCO_3 + H_2O + CO_2$. Carbon dioxide accomplished a closed cycle in this process: its amount used for the dissolution of carbonate rocks on continents (according to reaction $CaCO_3 + H_2O + CO_2 = Ca^2 + 2HCO_3$) was regenerated and returned from the ocean to the armosphere. However, phosphorus flux into the ocean increased more than twice during the industrial period (Savenko, 2001). This is accompanied by a corresponding bioproductivity rise, especially within some nearshore zones where the productivity increased by two to ten times according to different estimates (Gorshkov, 1991; Rabuille et al., 2001). Therefore, this process was inversed, and the ocean actually began to extract carbon dioxide from the atmosphere, although ability of the ocean to assimilate all surplus anthropogenic CO_2 is restricted (Mackenzie et al., 1993; Savenko, 2001).

Data given in other publications show that partial pressure of CO_2 in the atmosphere depends on the $CaCO_3$ - C_{org} production relationship in the ocean. For example, the atmosphere was depleted in carbon diox-

ide during the last glaciation characterized by a relatively low production of biogenic calcium carbonate (Archer *et al.*, 1994). Similar conclusions were inferred from data on carbon isotopes and Ca/Cd ratio in benthic foraminiferal tests, where these parameters are related to the P/Cd ratio in oceanic water. Judging from these data, the oceanic water was somewhat enriched in phosphorus (approximately by 17% relative to the present-day level), whereas partial pressure of carbon dioxide in the atmosphere was lower (Boyle, 1986) probably owing to a relative reduction of carbonate accumulation. Therefore, certain interrelations are traced between organic and inorganic carbon productions in the ocean, phosphorus cycle, and global climatic changes.

We can suggest in this connection that an increase of carbon dioxide reserves in the atmosphere, irrespective of its source, leads to climate warming and humidization, sealevel rise, intensification of chemical weathering and phosphorus input into the ocean from continents, increase in bioproductivity of the ocean, and accelerated rates of the sedimentation of organic matter, biogenic carbonates, and phosphorus that are accumulated mainly within shallow-water zones of submarine continental margins.

Interaction of phosphorus and organic matter cycles represents a special aspect of the problem. These cycles are linked during organic matter generation annually involving up to 2.5 Gt of phosphorus into recycling. After the death of organisms and settling of organic detritus onto the bottom, the cycles diverge owing to a faster mineralization of organic phosphorus and its return to the bottom water. The average atomic ratio Corg/Porg is 106 in living organisms and increases to 200–600 in sediments (Van Capellen and Ingall, 1994). Additionally, reductive processes during organic matter decomposition may lead to the reduction of iron hydroxides and release of absorbed phosphorus, which partially diffuses into oceanic water and supplements its dissolved mineral phosphorus reserves. The phosphorus partially precipitates as authigenic apatite and remains in sediments.

The issue of the probable climate-governing role of linkages between phosphorus and oxygen cycles is also considered in publications. For example, correlation between redox conditions in sediments and intensity of diagenetic phosphorus flux from the sediments is interpreted as an evidence of the role of phosphorus in stabilizing the partial pressure of oxygen in the atmosphere at a relatively uniform level over the last 350 Ma. Residence time of oxygen in the atmosphere is about 4 Ma, i.e., two orders of magnitude higher than the residence time of phosphorus in the ocean. This likely supports the steady state of such linkage (Colman and Holland, 2000).

Review of data on the relationship between phosphorus cycle and climate leads us to the issue of their influence on phosphorite-forming processes. This problem is repeatedly discussed in different aspects.

Many authors suggest that phosphorite formation is related to chemical weathering on continents and transport of phosphorus or phosphatic weathering products by rivers into the near-shore zone of their discharge basins (Bushinskii, 1966; Kholodov, 1970). However, Strakhov (1960) noted that phosphorite zones may be formed in both humid and arid climates. Recent data show that the humid climate promotes the accumulation of total phosphorus reserves in the ocean, whereas examples from Namibian and Chilean shelves show that phosphorites may be formed in arid zones (Baturin, 1978). It is well known that the idea about a spatial divergence of phosphorus delivery and concentration zones in the ocean was first suggested by Shatsky (1955) who distinguished remote phosphorite-bearing volcanogenic formations. Although such formations have not been found, the existence of remote sources appeared to be realistic.

Ronov and Korzina (1960) first noted a linkage between dispersed and concentrated phosphorus. It appeared that a relationship exists between phosphorite resources within the Russian Platform and phosphorus content in the coeval Ordovician, Upper Jurassic, Lower Cretaceous, and Upper Cretaceous sedimentary rocks.

Study of the global-scale linkage between Phanerozoic phosphorite deposits of the world based on data from (Cook and McElhinny, 1979; Ronov, 1993; Ronov *et al.*, 1990; and others) revealed that peaks of both maximal dispersed phosphorus accumulation (up to $5-8 \times 10^{12}$ t/Ma P₂O₅) and maximal phosphorite masses are actually typical of the Upper Cretaceous, Eocene, Miocene, and Pliocene. These peaks generally correspond to periods of the intense chemical weathering of rocks on continents (Baturin, 2001; Baturin *et al.*, 1995; Kholodov, 1997; Sokolov, 1995; Zanin, 2001).

Moreover, as shown in (Föllmi, 1996; Zanin, 1981, 2001), epochs of phosphorite formation correspond to the periods of high sealevel stand and expansion of seafloor mainly due to the flooding of coastal lowlands. Datings of Late Quaternary phosphorites from the Peruvian–Chilean shelf by absolute geochronology (Burnett, 1974, 1977) are very significant in this context. They show that all of the studied phosphorites were formed here under conditions of high sealevel stand, and they were only reworked during regressions (Fig. 3).

Based on the heavy carbon isotopic composition in oceanic carbonates, Föllmi (1996) showed that epochs of phosphorite formation during the last 160 Ma correspond to times of high bioproductivity in the ocean. He also noted that not all epochs of intense weathering and dispersed phosphorus accumulation in oceanic sediments (e.g., the Middle Devonian) were accompanied by phosphorite formation. For example, the largest Phosphoria deposit in the United States was formed in the Late Permian, whereas maximal masses of dispersed phosphorus were accumulated during the Early Permian (Zanin, 2001).



Fig. 3. Sealevel oscillations during the Late Quaternary and absolute age of phosphorites (shown by arrows) from Chilean and Peruvian shelves (Burnett, 1977).

Several additional conditions besides climatic ones are apparently necessary for the transition from high phosphorus contents to ore-grade concentrations. As shown by examples of recent and Late Ouaternary phosphorite formation (Baturin, 1978), the most important conditions are as follows: (1) geomorphological environment (wide gentle shelf); (2) hydrological environment (a stable alongshore current accompanied by coastal upwelling); (3) biological environment (high bioproductivity); (4) lithological environment (domination of biogenic sedimentation and accumulation of phosphorus- and organic-rich siliceous-calcareous oozes); and (5) tectonic environment (stable tectonic regime with weak fluctuations promoting a moderate reworking of sediments and concentration of ore components).

CONCLUSIONS

The complete cycle of phosphorus described above comprises its mobilization from continental rocks, delivery into the World Ocean, involvement in the oceanic biogeochemical cycle, precipitation onto the bottom, diagenetic redistibution in sediments, formation of authigenic phases, and a partial diffusion from sediments into the bottom water. During these processes, the phosphorus cycle is partially linked to cycles of organic and inorganic carbon, oxygen, and iron. The most important results obtained in this field during the recent years are as follows:

(1) Determination of phosphorus species in oceanic suspended matter and sediments, especially identification of authigenic apatite phase in nonupwelling continental margin sediments. This is an evidence of universal character of the embryonal phosphorite formation phase, which is completely realized only under favorable conditions provided by the upwelling regime.

(2) Quantitative evaluation of phosphorus diffusion from sediments. This allowed us to estimate its recycling rate and residence time in oceanic waters, which is about 20000 yr according to the latest data. (3) Determination of the climatic role of phosphorus that controls to a certain extent cycles of organic carbon, inorganic carbon, and oxygen and their exchange in the ocean–atmosphere–lithosphere system via bioproductivity.

(4) Consideration of the increasing influence of anthropogenic factor on the global phosphorus cycle that, in turn, affects the oceanic ecosystem, bioproductivity, CO_2 exchange in the ocean–atmosphere system, and climate.

(5) Establishment of linkage between phosphorus cycle and phosphorite-forming processes expressed by a partial temporal coincidence of accumulation masses of phosphorus dispersed in sedimentary rocks and concentrated in phosphorite deposits.

Summarizing the data otained, we can represent the following general scheme of interrelations between phosphorus cycle, climate, and phosphorite formation.

Processes of chemical weathering with the active participation of atmospheric carbon dioxide and oxygen lead to phosphorus release from continental rocks and its delivery to the ocean. This provides the bioproductivity of waters and accumulation of P-rich biogenic sediments, which represent a basis for phosphorite formation. These processes are most intense in warm humid climate that promote the chemical weathering of rocks on continents, acceleration of sedimentation as a whole, and accumulation of P-rich sediments within coastal upwelling zones.

The latter seems to be especially important, because about 90% of the total sedimentary material and a major portion of geochemically reactive components are delivered to submarine continental margins (Lisitsyn, 1978). However, a significant part of the sediment mass accumulates today on continental slopes. Sealevel rise leads to an expansion of the shelf area owing to the flooding of coastal lowlands, and the role of shelf as zone of sedimentation and sedimentary ore formation dramatically increases, as shown by the example of phosphorites.

However, when considering paleoceanological conditions of phosphorite formation, we should also take into account some geological factors. Thus, a considerable sealevel rise in the Late Cretaceous is thought to be related to acceleration of ocean floor spreading induced by an increase in solar activity. In turn, this led to a rise of the erosion base level with the corresponding decrease in suspended and dissolved material supply from continents, on the one hand, and a strong domination of biogenic sedimentation with centers shifted to shallow epicontinental seas, on the other hand (Lisitsyn, 1980; Sorokhtin and Ushakov, 1991; Ushakov and Yasamanov, 1984). A special study is necessary to answer the question, how the concept of phosphorus cycle would change if we accept that the greenhouse effect is a fiction and CO_2 exchange in the ocean-atmosphere system is only controlled by temperature depending on solar energy (Sorokhtin and Ushakov, 1991).

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REFERENCES

Aller, R.C., The Influence of Macrobenthos on Chemical Diagenesis of Marine Sediments, *Ph.D. Dissertation*, New Haven: Yale Univ., 1977.

Archer, D. and Maier-Reimer, E., Effect of Deep-Sea Sedimentary Calcite Preservation on Atmospheric CO₂ Concentration, *Nature* (London), 1994, vol. 367, no. 6420, pp. 260–263.

Baturin, G.N., Authigenic Phosphorite Nodules in Recent Sediments of the Southeastern African Shelf, *Dokl. Akad. Nauk SSSR*, 1969, vol. 183, no. 6, pp. 1359–1362.

Baturin, G.N., Phosphorus in Mud Waters of the Southeastern Atlantic, *Okeanologiya*, 1972, vol. 12, no. 6, pp. 1020–1027.

Baturin, G.N., *Fosfority na dne okeanov* (Phosphorites on the Ocean Floor), Moscow: Nauka, 1978.

Baturin, G.N., *Phosphorites on the Sea Floor: Origin, Composition, and Distribution*, Amsterdam: Elsevier, 1982.

Baturin, G.N., Disseminated Phosphorus in Oceanic Sediments—A Review, *Mar. Geol.*, 1988, vol. 84, no. 1, pp. 95–104. Baturin, G.N., Problem of Intensification of the Supply of Sedimentary Material and Some Chemical Elements in the Ocean, *Okeanologiya*, 1997, vol. 37, no. 2, pp. 270–284.

Baturin, G.N., Phosphorus in the Ocean and the Earths Climate, *Okeanologiya*, 2001, vol. 41, no. 1, pp. 138–146.

Baturin, G.N. and Savenko, V.S., Phosphorus in the Oceanic Sedimentogenesis, *Okeanologiya*, 1997, vol. 37, no. 1, pp. 115–122.

Baturin, G.N. and Sevast'yanova, E.S., Phosphorus in Sediments of the Indian Ocean, *Geokhimiya*, 1986, no. 5, pp. 636–644.

Baturin, G.N., Lucas, J., and Lucas-Prevot, L., Phosphorus Behaviour in Marine Sedimentation. Continuous P-Behaviour versus Discontinuous Phosphogenesis, *C. R. Acad. Sci.*, 1995, Ser. IIa, vol. 321, pp. 263–278.

Berner, R.A. and Rao, J.L., Phosphorus in Sediments of the Amazon River and Estuary: Implications for the Global Flux of Phosphorus to the Sea, *Geochim. Cosmochim. Acta*, 1994, vol. 58, pp. 2333–2339.

Berner, R.A., Ruttenberg, K., Ingall, E.D., and Rao, J.L., The Nature of Phosphorus Burial in Modern Marine Sediments, *Interaction of C, N, P, and S Biogeochemical Cysles and Global Change*, Wollast, R. and Mackenzie, F.T., Eds., London: Springer, 1993, pp. 365–378.

Bogdanov, Yu.A., Lisitsyn, A.P., and Romankevich, E.A., Organic Material in Suspension and Bottom Sediments of the World Ocean, *Organicheskoe veshchestvo sovremennykh i iskopaemykh osadkov* (Organic Material in Recent and Fossil Sediments), Moscow: Nauka, 1971, pp. 35–103.

Bordovskii, O.K., Domanov, M.M., and Fedikov, N.F., Exchange between Biogenic Elements at the Water–Bottom Boundary in the Coastal Zone of Peru, *Okeanologiya*, 1980, vol. 20, no. 4, pp. 645–650.

Boyle, E.A., Paired Carbon Isotope and Cadmium Data from Benthic Foraminifera: Implications for Changes in Oceanic Phosphorus, Oceanic Circulation, and Atmospheric Carbon Dioxide, Geochim. Cosmochim. Acta, 1986, vol. 50, no. 2, pp. 265–276.

Bray, J.T., Bricker, O.P., and Troup, B.N., Phosphate in Interstitial Waters of Anoxic Sediments: Oxidation Effects during Sampling Procedure, *Science*, 1973, vol. 180, no. 4093, pp. 1362–1364.

Broecker, W.S., Ocean Chemistry during Glacial Time, *Geochim. Cosmochim. Acta*, 1982, vol. 46, pp. 1689–1705.

Bruevich, S.V. and Vinogradova, E.G., Chemical Composition of Underground Solutions of the Caspian Sea, *Gidrokhim. Mat.*, 1947, vol 13, pp. 129–186.

Bruevich, S.I. and Zaitseva, E.D., Biogenic Elements in Underground Solutions of the Pacific Ocean, *Tr. Inst. Okeanol. Akad. Nauk. SSSR*, 1964, vol. 47, pp. 56–90.

Bruland, K.W., *Chemical Oceanography*, London: Academic, 1983, pp. 157–220.

Burnett, W.C., Geochemistry and Origin of Phosphorite Deposits from off Peru and Chile, *Bull. Geol. Soc. Am.*, 1977, vol. 88, no. 6, pp. 813–823.

Bushinskii, G.I., The Origin of Marine Phosphorites, *Litol. Polezn. Iskop.*, 1966, no. 3, pp. 15–23.

Colman, A.S. and Holland, H.D., The Global Diagenetic Flux of Phosphorus from Marine Sediments to the Oceans: Redox Sensitivity and the Control of Atmospheric Oxygen Levels, *Marine Authigenesis: from Global to Microbial*, Glenn C.R., Prevot-Lucas L., and Lucas J., Eds., *SEPM Spec. Publ.*, 2000, no. 66, pp. 53–75.

Compton, J., Mallinson, D., Glenn, C., *et al.*, Variations in the Global Phosphorus Cycle, *Marine Authigenesis: from Global to Microbial*, Glenn, C.R., Prevo-Lucas, and Lucas J., Eds., *SEPM. Spec. Publ.*, 2000, pp. 35–51.

Cook, P.J. and McElhinny, M.W., A Reevaluation of the Spacial and Temporal Distribution of Sedimentary Phosphate Deposits in the Light of Plate Tectonics, *Econ. Geol.*, 1979, vol. 79, no. 2, pp. 315–330.

Edel'shtein, K.K., Discharge of Phosphorus with Urban Waste Water in the Oceanic Coastal Zone, *Okeanologiya*, 1998, vol. 38, no. 2, pp. 216–220.

Emel'yanov, E.M. and Romankevich, E.A., *Geokhimiya Atlanticheskogo okeana. Organicheskoe veshchestvo i fosfor* (Geochemistry of the Atlantic Ocean: Organic Material and Phosphorus), Moscow: Nauka, 1979.

Feely, R.A., Massoth, G.J., Baker, E.T., *et al.*, The Effect of Hydrothermal Processes on Midwater Phosphorus Distribution in the North East Pacific, *Earth Planet. Sci. Lett.*, 1990, vol. 96, nos. 3–4, pp. 305–318.

Filipek, L.H. and Owen, R.M., Diagenetic Controls on Phosphoru in Outer Continental Shelf Sediments from the Gulf of Mexico, *Chem. Geol.*, 1981, vol. 33, pp. 181–204.

Filippelli, G.M. and Delaney, M.L., The Oceanic Phosphorus Cycle and Continental Weathering during the Neogene, *Paleoceanography*, 1994, vol. 9, pp. 643–652.

Föllmi, K.B., The Phosphorus Cycle, Phosphogenesis, and Marine Phosphate-rich Deposits, *Earth Sci. Rev.*, 1996, no. 4, pp. 55–124.

Föllmi, K.B. and von Breymann, M., Phosphates and Glauconites of Sites 798 and 799, *Proc. Ocean Drill. Progr.: Sci. Results*, 1992, Leg 127/128, pp. 63–74.

Föllmi, K.B., Weissert, H., and Lini, A., Nonlinearities in Phosphogenesis and Phosphorus-Carbon Coupling and Their Implications for Global Change, *Interactions of C*, *N*, *P*, and

 S Biogeochemical Cycles and Global Change, Wollast R., Mackenzie F.T., and Chou L., Eds., NATO ASI Ser., 1993, vol. 14, pp. 447–474.

Froelich, P.N., Bender, M.L., and Heath, G.R., Phosphorus Accumulation Rates in Metalliferous Sediments on the East Pacific Rise, *Earth Planet. Sci. Lett.*, 1977, vol. 34, pp. 351–359.

Froelich, P.N., Bender, M.L., Luedtke, N.A., *et al.*, The Marine Phosphorus Cycle, *Am. J. Sci.*, 1982, vol. 282, pp. 474–511.

Gaioty Zapadnoi Patsifiki i ikh rudonosnost' (Guyots of the Western Pacific and Their Ore Potential), Moscow: Nauka, 1995.

Glenn, C.R. and Arthur, M.A., Sedimentary and Geochemical Indicators of Productivity and Oxygen Contents in Modern and Ancient Basins: The Holocene Black Sea as the "Type" Anoxic Basin, *Chem. Geol.*, 1985, vol. 48, pp. 325–354.

Gordeev, V.V., *Rechnoi stok v okean i cherty ego geokhimii* (River Runoff into the Ocean and Features of Its Geochemistry), Moscow: Nauka, 1983.

Gordeev, V.V., Chemistry of Hydrothermal Solutions in Basins of the Back-Arc Spreading (Woodlark and Manus), *Metallogeniya sovremennykh i drevnikh okeanov* (Metallogeny of Recent and Ancient Oceans), Moscow: TsNIGRI, 1992, pp. 181–183.

Gorshkov, V.G., Tenfold Intensification of Production of Dissolved Organic Matter in the Ocean over the Industrial Era, *Dokl. Akad. Nauk SSSR*, 1991, vol. 320, no. 2, pp. 492–497.

Gorshkov, V.G. and Makar'eva, A.M., Changes in the Global Cycle of Carbon Based on Measurements of the O_2/N_2 Ratio in the Atmosphere and Partial Pressure of CO_2 near the Ocean–Atmosphere Interface, *Geokhimiya*, 2002, no. 5, pp. 526–535.

Gusarova, A.N. and Bordovskii, O.K., Assessment of Primary Production of the World Ocean Based on the Dynamics of Phosphate and Silica, *Dokl. Akad. Nauk*, 1993, vol. 330, no. 5, pp. 634–637.

Heggie, D.T., Skyring, G.W., O'Brian, G.W., *et al.*, Organic Carbon Cycling and Modern Phosphorite Formation on the East Australian Continental Margin: An Overview, *Phosphorite Research and Development*, Notholt, G.J. and Jarvis I., London: *Geol. Soc. Spec. Publ.*, 1990, no. 52, pp. 87–117.

Hein, J.R., Yeh, H.W., Gunn, S.H., *et al.*, The Major Cenozoic Episodes of Phosphogenesis Records in Equatorial Pacific Seamounts Deposits, *Paleoceanography*, 1993, vol. 8, no. 2, pp. 293–311.

Holland, H.D., *The Chemical Evolution of the Atmosphere* and Oceans, Prinston: Prinston Univ. Press, 1984.

Honjo, S., Manganini, S.J., and Cole, J.J., Sedimentation of Biogenc Matter in the Deep Ocean, *Deep-Sea Res.*, 1982, vol. 29, no. 5, pp. 609–625.

Ingall, E.D. and Jahnke, R., Evidence for Enhanced Phosphorus Regeneration from Marine Sediments Overlain by Oxygen Depleted Waters, *Geochim. Cosmochim. Acta*, 1994, vol. 58, pp. 303–316.

Jahnke, R.A., Emerson, S.R., Roe, K.K., and Burnett, W.C., The Present Day Formation of Apatite in Mexican Continental Margin Sediments, *Geochim. Cosmochim. Acta*, 1983, vol. 47, pp. 259–266.

Jensen, H.S., Mortensen, P.B., Andersen, F.O., *et al.*, Phosphorus Cycling in a Coastal Marine Sediment, Aarhus Day, Denmark, *Limnol. Oceanogr.*, 1995, vol. 40, pp. 908–917.

Kester, D.R. and Pytkovicz, R.M., Determination of the Apparent Dissociation Constants of Phosphoric Acid in Seawater, *Limnol. Oceanogr.*, 1967, vol. 12, no. 2, pp. 243–252.

Khimiya okeana (Chemistry of the Ocean), vol. 1: Chemistry of the Oceanic Water, Bordovskii, O.K. and Ivanenkov, V.N., Eds., Moscow: Nauka, 1979.

Kholodov, V.N., Vendian and Cambrian Metallogeny in Eyrasia. Communications I and II, *Litol. Polezn. Iskop.*, 1970, no. 2, pp. 130–147; no. 4, pp. 29–44.

Kholodov, V.N., Epochs of Phosphorite Formation and Biogeochemistry of Phosphorus, *Litol. Polezn. Iskop.*, 1997, no. 6, pp. 563–577.

Kim, D., Schuffert, J.D., and Kastner, M., Francolite Authigenesis in California Continental Slope Sediments and Its Implications for the Marine P Cycle, *Geochim. Cosmochim. Acta*, 1999, vol. 63, nos. 19/20, pp. 3477–3485.

Klump, J.V. and Martens, C.S., Biogeochemical Cycling in an Organic Rich Coastal Marine Basin. II. Nutrient Sediment-Water Exchange Processes, *Geochim. Cosmochim. Acta*, 1981, vol. 45, pp. 101–121.

Knauer, G.A., Martin, J.H., and Bruland, K.W., Fluxes of Particulate Carbon, Nitrogen, and Phosphorus in the Upper Water Column of the Northwest Pacific, *Deep-Sea Res.*, 1979, vol. 26, no. 1, pp. 97–108.

Koblents-Mishke, O.I., Kabanova, Yu.G., and Volkovinskii, V.V., New Data on the Volume of Primary Production in the World Ocean, *Dokl. Akad. Nauk SSSR*, 1968, vol. 183, no. 5, pp. 1189–1192.

Krom, M.D. and Berner, R.A., The Diagenesis of Phosphorus in a Nearshore Marine Sediment, *Geochim. Cosmochim. Acta*, 1981, vol. 45, pp. 207–216.

Kurnosov, V.B., *Gidrotermal'nye izmeneniya bazal'tov v Tikhom okeane i metallonosnye otlozheniya* (Hydrothermal Alterations of Basalts in the Pacific Ocean and Metalliferous Sediments), Moscow: Nauka, 1986.

Lisitsyn, A.P., *Osadkoobrazovanie v okeanakh* (Sedimentation in Oceans), Moscow: Nauka, 1974.

Lisitsyn, A.P., *Protsessy okeanskoi sedimentatsii* (Processes of the Oceanic Sedimentation), Moscow: Nauka, 1978.

Lisitsyn, A.P., Paleooceanology, in *Okeanologiya. Geologiya* okeana. Geologicheskaya istoriya okeana (Oceanology. Ocean Geology: Geological History of the Ocean), Moscow: Nauka, 1980, pp. 386–405.

Lukashin, V.N., Isaeva, A.B., Serova, V.V., and Nikonova, G.G., Geochemistry of Organic Matter and Its Flows in the Eastern Equatorial Atlantic, *Geokhimiya*, 2002, no. 3, pp. 306–318.

Mach, D.M., Ramirez, A., and Holland, H.D., Organic Phosphorus and Carbon in Marine Sediments, *Am. J. Sci.*, 1987, vol. 278, pp. 429–441.

Mackenzie, F.T., Ver, L.M., Sabine, C., *et al.*, C, N, P, S Global Biogeochemical Cycles and Modeling of Global Change, *Interactions of C, N, P, and S Biogeochemical Cycles and Global Change*, Wollast, R. *et al.*, Eds., New York: Springer, 1993, pp. 1–61.

Martens, C.S., Berner, R.A., and Rosenfeld, J.K., Interstitial Water Chemistry of Anoxic Long Island Sound Sediments. 2. Nutrient Regeneration and Phosphate Removal, *Limnol. Oceanogr.*, 1978, vol. 23, no. 4, pp. 601–617.

Martin, J.M. and Meybeck, M., Elemental Mass-Balance of Material Carried by World Major Rivers, *Mar. Chem.*, 1979, vol. 7, pp. 173–206.

McNickol, A.P., Lee, C., and Druffel, E.R.M., Carbon Cycling in Coastal Sediments. I. A Quantitative Estimate of the Remineralization of Organic Carbon in the Sediments of the Buzzard Bay, MA, *Geochim Cosmochim Acta*, 1988, vol. 52, pp. 113–136.

Meybeck, M., Carbon, Nitrogen, and Phosphorus Transport by World Rivers, *Am. J. Sci.*, 1982, vol. 282, pp. 401–450.

Milliman, J.D. and Meade, R.H., World-Wide Delivery of River Sediment to the Ocean, *J. Geol.*, 1983, vol. 91, no. 1, pp. 1–21.

Moody, J.B., Chaboudy, L.R., and Worsley, T.R., Pacific Pelagic Posphorus Accumulation during the Last 10 M.Y., *Paleoceanography*, 1988, vol. 3, pp. 113–136.

Nissenbaum, A., Presley, B., and Kaplan, I.R., Early Diagenesis in a Reducing Fjord, Saanich Inlet, British Columbia. 1. Chemical and Isotopic Changes in the Major Components of the Interstitial Water, *Geochim. Cosmochim. Acta*, 1972, vol. 36, no. 9, pp. 1007–1027.

Rabouille, C., Mackenzie, F.T., and Ver, L.M., Influence of Human Perturbation on Carbon, Nitrogen, and Oxygen Biogeochemical Cycles in the Global Coastal Ocean, *Geochim. Cosmochim. Acta*, 2001, vol. 65, no. 21, pp. 3615–3645.

Reimers, C.E., Ruttenberg, K.C., Canfield, D.E., *et al.*, Porewater pH and Authigenic Phases Formed in the Uppermost Sediments of the Santa Barbara Basin, *Geochim. Cosmochim. Acta*, 1996, vol. 60, no. 21, pp. 4037–4057.

Romankevich, E.A., *Geokhimiya organicheskogo veshchestva v okeane* (Geochemistry of Organic Matter in the Ocean), Moscow: Nauka, 1977.

Romankevich, E.A., Vetrov, A.A., and Korneva, G.A., Geochemistry of Organic Carbon in the Ocean, *Biogeochemical Cycling and Sediment Ecology*, Gray, J.S., Ambrose, W., and Szaniawska, A., Eds., Dordrecht: Kluwer, 1999, pp. 1–27.

Ronov, A.B., *Osadochnaya obolochka Zemli* (Sedimentary Cover of the Earth), Moscow: Nauka, 1960.

Ronov, A.B., *Stratisfera ili osadochnaya obolochka Zemli* (Stratisphera or Sedimentary Cover of the Earth), Moscow: Nauka, 1993.

Ronov, A.B. and Korzina, G.A., Phosphorus in Sedimentary Rocks, *Geokhimiya*, 1960, no. 8, pp. 667–687.

Ronov, A.B., Yaroshevskii, A.A., and Migdisov, A.A., *Khimicheskoe stroenie zemnoi kory i geokhimicheskii balans glavnykh elementov* (Chemical Structure of the Earth's Crust and Geochemical Balance of Major Elements), Moscow: Nauka, 1990.

Ruttenberg, K.C., Development of a Suquential Extraction Method for Different Forms of Phosphorus in Marine Sediments, *Limnol. Oceanogr.*, 1992, vol. 37, pp. 1460–1482.

Ruttenberg, K.C., Reassessment of the Oceanic Residence Time of Phosphorus, *Chem. Geol.*, 1993, vol. 107, pp. 405–409.

Ruttenberg, K.C. and Berner, R.A., Authigenic Apatite Formation and Burial in Sediments from Non-Upwelling, Continental Margin Sediments, *Geochim. Cosmochim. Acta*, 1993, vol. 57, pp. 991–1007.

Ruttenberg, K.C. and Goni, M.F., Phosphorus Distribution, C : N : P Ratios, and $o^{13}C_{oc}$ in Arctic, Temperate, and Tropical Coastal Sediments: Tools for Characterizing Bulk Sedimentary Organic Matter, *Mar. Geol.*, 1997, vol. 139, pp. 123–145.

Ryther, J.H., Photosynthesis and Fish Production in the Sea, *Science*, 1970, vol. 166, no. 3901, pp. 72–76.

Savenko, V.S., On Physicochemical Mechanism of the Formation of Marine Phosphorites, *Dokl. Akad. Nauk SSSR*, 1979, vol. 249, no. 4, pp. 972–976.

Savenko, V.S., Basic Regularities of the Phosphorus Behavior in Pore Waters of Marine and Oceanic Sediments, *Litol. Polezn. Iskop.*, 1990, no. 5, pp. 33–49.

Savenko, V.S., Is the Ocean a Source of Carbon Dioxide?, *Geokhimiya*, 1995, no. 11, pp. 1634–1642.

Savenko, V.S., Global Hydrological Cycle and Geochemical Balance of Phosphorus in the Ocean, *Okeanologiya*, 2001, vol. 41, no. 3, pp. 379–385.

Savenko, V.S. and Zakharova, E.A., Phosphorus in the River Discharge, *Dokl. Akad. Nauk*, 1995, vol. 345, no. 5, pp. 682–685.

Savenko, V.S. and Zakharova, E.A., Basic Regularities of Phosphorus Behavior in the River Discharge, *Vodn. Resursy*, 1997, vol. 24, no. 2, pp. 159–168.

Schuffert, J.D., Jahnke, R.A., Kastner, M., *et al.*, Rates of Formation of Modern Phosphorite off Western Mexico, *Geochim. Cosmochim. Acta*, 1994, vol. 58, pp. 5001–5010.

Schuffert, J.D., Kastner, M., and Jahnke, R., Carbon and Phosphorus Burial Associated with Modern Phosphorite Formation, *Mar. Geol.*, 1998, nos. 1–4, pp. 21–31.

Sevast'yanova, E.S., Dispersed Phosphorus in the Recent Marine and Oceanic Sedimentary Basin, *Extended Abstract* of *PhD* (*Geol.–Miner*.) *Dissertation*, Moscow: Inst. Oceanol. Akad. Nauk SSSR, 1983.

Shatsky, N.S., Phosphorus-Bearing Formations and Classification of Phosphorite Deposits, in *Soveshchanie po osadochnym porodam* (Conference on Sedimentary Rocks), Moscow: Akad. Nauk SSSR, 1955, issue 2, pp. 7–100.

Shishkina, O.V., Biogenic Elements in Mud Waters and the Role of Exchange in the Transport of Phosphates into the Bottom Water, *Dokl. Akad. Nauk SSSR*, 1971, vol. 201, no. 3, pp. 707–710.

Sokolov, A.S., Phosphorus in the Stratisphere, *Dokl. Akad. Nauk*, 1995, vol. 344, no. 3, pp. 370–373.

Sokolov, A.S., Causes of the Activation of Vendian–Cambrian Phosphorite Formation, *Dokl. Akad. Nauk*, 1999, vol. 369, no. 6, pp. 799–801.

Sorokhtin, O.G. and Ushakov, S.A., *Global'naya evolyutsiya* Zemli (Global Evolution of the Earth), Moscow: Mosk. Gos. Univ., 1991.

Sorokin, Yu.I., *Ekosistema korallovykh rifov* (Ecosystem of Coral Reefs), Moscow: Nauka, 1990.

Steeman-Nielsen, E. and Jensen, A., Primary Oceanic Production of Organic Matter in the Oceans, *Galathea Rep.*, 1957, vol. 1, pp. 49–136.

Strakhov, N.M., Climate and Phosphate Accumulation, *Geol. Rudn. Mestorzhd.*, 1960, no. 1, pp. 3–15.

Strakhov, N.M., *Tipy litogeneza i ikh evolyutsiya v istorii Zemli* (Types of Lithogenesis and Their Evolution in the Earth's History), Moscow: Gosgeoltekhizdat, 1963.

Tsunogai, S., Uematsu, M., Noriki, S., *et al.*, Sediment Trap Experiment in the Western North Pacific, *Geochem. J.*, 1982, vol. 16, no. 3, pp. 129–147.

Tunnicliff, V., Botros, M., De Burgh, M.E., *et al.*, Hydrothermal Vents of Explorer Ridge, Northeast Pacific, *Deep-Sea Res.*, 1986, vol. 33, no. 3, pp. 401–412. Turekian, K.K. and Wedepohl, K.H., Distribution of the Elements in Some Major Units of the Earth'S Crust, *Bull. Geol. Soc. Am.*, 1961, vol. 72, no. 1, pp. 175–192.

Ushakov, S.A. and Yasamanov, N.A., *Dreif kontinentov i klimaty Zemli* (Drift of Continents in the Earth's History), Moscow: Mysl', 1984.

Van Cappellen, P. and Ingall, E.D., Benthic Phosphorus Regeneration, Net Primary Production, and Ocean Anoxia: A Model of the Coupled Marine Biogeochemical Cycles of Carbon and Phosphorus, *Paleoceanography*, 1994, vol. 9, pp. 677–692.

Vedernikov, V.I. and Starodubtsev, E.G., Primary Production and Chlorophyll in the Southeastern Pacific Ocean, *Tr. Inst. Okeanol. Akad. Nauk SSSR*, 1971, vol. 89, pp. 33–42.

Vink, S., Chambers, R.M., and Smith, S.V., Distribution of Phosphorus in Sediments from Tomales Bay, California, *Mar. Geol.*, 1997, vol. 139, pp. 157–179.

Vinogradov, A.P., Average Content of Chemical Elements in Rocks, *Geokhimiya*, 1962, no. 7, pp. 555–571.

Vinogradov, A.P., *Vvedenie v geokhimiyu okeana* (Introduction to Ocean Geochemistry), Moscow: Nauka, 1967.

Vinogradov, M.E., Shushkina, E.A., Kopelevich, O.V., and Sheberstov, S.V., Photosynthetic Production of the World Ocean Based on Satellite and Field Data, *Okeanologiya*, 1996, vol. 36, no. 4, pp. 566–575.

Volkov, I.I. and Yagodinskaya, T.A., Transitional Group of Elements: Phosphorus, Rare Earth Elements, and Yttrium, *Litologiya i geokhimiya osadkov Tikhogo okeana* (Lithology and Geochemistry of Sediments in the Pacific Ocean), Kholodov, V.N., Ed., Moscow: Nauka, 1979, pp. 203–224.

Volkov, I.I., Sevast'yanova, E.S., and Yagodinskaya, T.A., Phosphorus in Sediments of the Northwestern Pacific Ocean, *Geokhimiya*, 1974, no. 9, pp. 1297–1309.

Wefer, G., Suess, E., Balzer, W., *et al.*, Fluxes of Biogenic Components from Sediment Trap Deployment in Circum-Polar Waters of Drake Passage, *Nature* (London), 1982, vol. 299, no. 5879, pp. 145–147.

Wheate, C.G., Feely, R.A., and Mottle, M.J., Phosphate Removal by Oceanic Hydrothermal Processes: An Update of the Phosphorus Budget in the Oceans, *Geochim. Cosmochim. Acta*, 1996, vol. 60, pp. 3593–3608.

Zaitseva, E.D., Alkalinity and Biogenic Elements in Ground Waters of the Northeastern Black Sea, *K poznaniyu diageneza osadkov* (The Congition of Sediment Diagenesis), Moscow: Akad. Nauk SSSR, 1959, pp. 51–71.

Zanin, Yu.N., Climatic Aspects of the Evolution of Phosphate Accumulation in the Phanerozoic, *Problemy evolyutsii geologicheskikh protsessov* (Problems of the Evolution of Geological Processes), Bogolepov, K.V. and Zharkov, M.A., Eds., Novosibirsk: Nauka, 1981, pp. 122–133.

Zanin, Yu.N., The Weathering and Phosphorite Genesis, *Geol. Geofiz.*, 2001, vol. 42, no. 4, pp. 589–595.