

Marine Phosphorite Deposits and the Nitrogen Cycle

High denitrification rates may have enhanced phosphorite precipitation in ancient oceans.

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In recent years considerable effort has been devoted to determining if phosphorites are forming in the oceans today. Known phosphorite deposits on the ocean floor are of limited areal extent and have yielded little evidence to support present-day formation (1). Exceptions are deposits on the continental shelves of southwestern Africa (2) and Peru (3), associated with muds having exceptionally high concentrations of organic matter, and phosphorite on a log dredged from the Gulf of Tehuantepec (4). Most marine phosphorite deposits occur in areas of intensive coastal upwelling and at depths roughly corresponding to the depth at which the oxygen (O_2) minimum layer in the ocean comes in contact with the ocean floor. (The O_2 minimum layer in the ocean is the stratum usually observed between 200 and 1500 meters in which vertical profiles of dissolved O_2 exhibit a minimum.)

Berner (5) has also noted an apparently high rate of accumulation of phosphorus in metalliferous sediments from the East Pacific Rise. Although others have proposed a volcanogenic source for several of the heavy metals in these deposits, Berner suggests that normal seawater may be the source for phosphorus. His estimate of the rate

of accumulation of phosphorus in rise crest sediments between $10^\circ S$ and $30^\circ S$ suggests that as much as 15 percent of the total world influx to the oceans of dissolved phosphorus from rivers may accumulate over this limited area of the ocean floor.

Kramer (6) and Roberson (7) have suggested that seawater is saturated or even supersaturated with respect to hydroxyapatite and carbonate fluorapatite. Arrhenius (8) has concluded that seawater is undersaturated with respect to phosphatic minerals at depth but is saturated in some shallow waters, and that carbonate fluorapatite precipitates where aided by the flux of organic material to shallow-water sediments, particularly in areas of coastal upwelling.

The high concentration of magnesium in seawater, however, may inhibit the precipitation of phosphorites, according to Martens and Harriss (9). Until more reliable data are available on such inhibitory effects and complex formation of phosphorus, it may not be possible to determine precisely the degree to which seawater is saturated (10). The results of the work of Kolodny and Kaplan (1), however, strongly suggest that, even though seawater may be near, or even in excess of, saturation values with respect to carbonate fluorapatite, the precipitation of this mineral in today's ocean is of minor quantitative importance.

Phosphorus and Nitrogen in Seawater

The distribution of phosphorus in the oceans and its relationship to the distribution of nitrogen indicate that biological removal of these two essential nutrients in the surface layer may limit phosphorus precipitation. The ratio of nitrogen [we are here considering only combined nitrogen, not dissolved molecular nitrogen (N_2)] to phosphorus throughout the deep ocean approximately equals the 16:1 atomic ratio of nitrogen to phosphorus in living marine organisms (11). Both nutrients usually exhibit extremely low concentrations in the photic zone of the ocean, primarily because of phytoplankton uptake. Although nitrogen more commonly appears to be the limiting nutrient, the concentration of phosphorus in the surface layer of the ocean is often only slightly in excess of the biological demand.

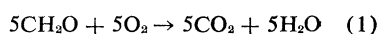
Under what conditions might the phosphorus content of the surface layer be increased such that the precipitation of carbonate fluorapatite is enhanced? Because phosphorus is closely linked to nitrogen in the biological cycle, it is often useful to include the one element in any discussion of the other. The problem we plan to examine is the following: might a reduction in the availability of combined nitrogen, that is, a reduction of the nitrogen/phosphorus ratio below its current value of 16:1, allow for an increase in the concentration of phosphorus in the surface layer of the oceans to the point where carbonate fluorapatite would precipitate?

Before considering the mechanism whereby combined nitrogen concentrations in the ocean may be lowered, let us consider briefly its present cycle. The major input of nitrogen to the ocean appears to be via the atmosphere (Table 1). Much of this nitrogen may be combined nitrogen that is produced on land by nitrogen-fixing bacteria and the decay of organic matter. At the present time a significant amount may also be introduced by man's activity (12). Emery *et al.* (13) have suggested that

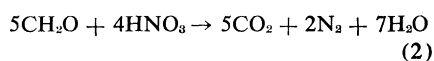
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the fraction of the input in excess of that lost to the sediments, the amount necessary to maintain a steady state, may be balanced by the reduction of NO_3^- to N_2 by the activity of denitrifying bacteria. Marine denitrification occurs largely in environments where O_2 concentrations are less than ~ 0.1 milliliter per liter of seawater (14), and denitrification appears to proceed to, or almost to, completion before sulfate reduction begins (15). Generalized equations for these three types of respiration are as follows:

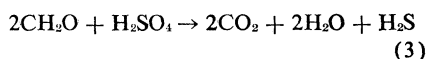
Oxygen respiration:



Denitrification:



Sulfate reduction:



Codispoti (14) and Cline (16) have recently shown that denitrification rates within the O_2 minimum layer of the eastern tropical North Pacific, where the O_2 concentrations are often less than 0.05 ml/liter, are of the order of magnitude needed to maintain nitrogen at a steady state. Thus, the cycle of combined nitrogen may be controlled largely by a series of biological processes, its input from the continents and atmosphere and from a possibly lesser amount of marine nitrogen fixation being balanced largely by marine denitrification in O_2 -deficient marine environments.

Under what conditions then could the concentration of combined nitrogen in the ocean be lowered below its present value? We propose that the necessary conditions may be met by a significant increase in the areal extent of that portion of the O_2 minimum layer within which O_2 concentrations are less than ~ 0.1 ml/liter. The consequences of such an increase can be summarized as follows:

1) An increase in denitrification in the O_2 minimum layer will occur. When this overwhelms the total influx of combined nitrogen, the nitrogen concentration will decrease throughout the ocean and biological productivity in the surface layer will decrease, owing to this decrease in the concentration of combined nitrogen.

2) Muds with high concentrations of organic matter may accumulate where-

ever water within which O_2 concentrations are less than approximately 0.1 ml/liter intersects the sea floor and dilution by terrigenous sediment is minimal. Muds currently accumulating under these conditions contain as much as 14 percent organic carbon (2).

3) The concentration of phosphorus will increase in the surface layer of the ocean after which the least soluble phosphate salt, possibly $\text{Ca}_{10}(\text{PO}_4\text{CO}_3)_6\text{F}_{2-3}$, will precipitate, in association with these muds but at a somewhat shallower depth. This increase in the concentration of phosphorus in the surface water may result from its decreased use in biological activity. For a discussion of the relationship between the concentration of an element in seawater and its reactivity and residence time, see Goldberg *et al.* (17). It is not possible to say how much of an increase over the present concentration of phosphorus may be required before surface seawater reaches saturation (10). Since carbonate fluorapatite is currently accumulating on the sea floor (2-4) on a very limited scale, perhaps only a slight increase in the phosphorus concentration in the near-surface waters may be required to considerably enhance the precipitation of this salt.

4) A decrease in the pH of seawater occurs within and adjacent to the O_2 minimum layer. In the O_2 minimum layer the pH is 7.4 to 7.9, whereas in surface water the pH is frequently greater than 8 (18). The upwelling of water with low pH and high PO_4^{3-} concentrations into the warm surface layer may promote the precipitation of phosphorites instead of other precipitates (19). In addition, the high biological activity associated with such upwelling (that is, high relative to that in other areas of the ocean at that time) would tend to supply the organic matter necessary to maintain the O_2 minimum layer and, at the same time, provide for the accumulation of organic-rich muds.

Variation of the Nitrogen/Phosphorus Ratio in Ancient Oceans

Although the processes that maintain the marine nitrogen/phosphorus atomic ratio at a value close to the requirements of organisms may be in balance today, it is possible that this has not always been the case. A warming trend, for example, could increase the marine

denitrification rate because of decreased O_2 solubilities. A temperature increase of $\sim 2^\circ\text{C}$ decreases the O_2 solubility values by about 5 percent. Some rough calculations indicate that such a decrease, occurring in the regions of major marine denitrification, could cause a substantial increase in the marine denitrification rate. For example, NO_3^- removals in the O_2 -deficient waters of the eastern tropical North Pacific are generally less than 10 microgram-atoms per liter, corresponding to 25 microgram-atoms per liter of O_2 (Eqs. 1 and 2), or about 5 percent of the O_2 solubility. Thus, we might expect a 2°C warming to cause a considerable increase in the maximum NO_3^- removal values. In addition, a glance at O_2 distributions (20) indicates that, with a 2°C warming, the volume of O_2 -deficient seawater would increase considerably. If it were not compensated, the present estimate for marine denitrification alone, $\sim 10^{14}$ grams of nitrogen per year (14), would be sufficient to remove all the combined NO_3^- from the ocean in $\sim 10^4$ years. Therefore, climatic changes could conceivably have significant effects on the combined nitrogen inventory of seawater.

Dilution of seawater caused by the melting of continental ice may be one possible compensating factor to increased denitrification. Such melting should dilute the oceans and increase the O_2 solubilities. However, dilution with today's quantity of ice would increase solubilities by less than 1 percent.

Ultimately, any impoverishment of combined nitrogen, caused by increased denitrification, should cause marine nitrogen fixation rates to rise or should cause respiration rates at depth in the ocean to decrease because of reduced primary productivity, or both. Over geologic time the nitrogen/phosphorus ratio may be maintained reasonably constant by such feedback mechanisms in the nitrogen cycle, aided by the increased phosphorite precipitation which, according to our proposal, should accompany increased denitrification.

These processes, however, may not be closely coupled. A good portion of the denitrification occurs in waters well below the depth of upwelling into the local photic zone. As a consequence, much of the reduced primary productivity may first occur years hence and in a different region of the ocean. In addition, Ryther and Dunstan (21) have suggested that marine nitrogen fixation

is not effective in increasing the nitrogen concentration in the short run. One can envision, therefore, a time lag before reduced primary production in the region of denitrification and marine nitrogen fixation could redress the imbalance between the nitrogen/phosphorus ratio required by organisms and available in seawater.

Therefore, increased denitrification rates could temporarily create an imbalance and lower primary production throughout the ocean. This reduction would eventually become apparent in the waters immediately above the region of denitrification. This would reduce respiration at depth and help nitrogen fixation to drive the system back toward a balance. The crucial point is that, because of the possible time lag, a period of increased denitrification could overlap, or be closely followed by, a period of higher phosphorus concentrations in the surface water of the ocean. We believe that this would be a very favorable period for the accumulation of phosphorite deposits.

Obviously several somewhat different versions of this scenario could be advanced on the basis of various assumptions about the rates of input of phosphorus to the ocean, the vertical circulation in the ocean, and the rate of denitrification in the O_2 minimum layer during periods of extensive phosphorite accumulation. An alternative mechanism, the invasion of the continents by shallow seas with depths roughly corresponding to the depth of the O_2 minimum layer, may allow for the accumulation of extensive organic-rich muds and significant increases in the rates of denitrification without any global temperature change. This would suggest a correlation between periods of maximum transgression, as discussed by Damon (22), and the ages of extensive phosphorite deposits (Fig. 1). However, the point we want to make is that an increase in the areal extent of the O_2 minimum layer, by whatever means, may have so altered the nutrient cycles in the ocean as to enhance the precipitation of phosphorus from the surface layer of the oceans.

Ancient Phosphorite Deposits

Phosphorite deposits occur in sedimentary rocks of all ages from Precambrian to Recent. However, as noted

Table 1. Combined nitrogen and phosphorus budgets in the ocean (13) (in millions of metric tons).

Component	Nitrogen	Phosphorus
Reserve in ocean	920,000	120,000
Annual use by phytoplankton	9,600	1,300
Annual contribution by river, dissolved	19	2
Annual contribution by river, suspended	0	12
Annual contribution by rain	59	0
Annual loss to sediments	9	13

by Bushinskii (23), major phosphorite deposits of marine origin have accumulated during only a few intervals of geologic time. These intervals are shown in Fig. 1. More than 95 percent of the world's commercial production of sedimentary phosphorus is from rocks of these ages, as estimated from a publication by the British Sulfur Corporation (24). These deposits are usually associated with black shales, the main exception being the Miocene deposits of the eastern United States which account for approximately one-third of the world's production. Although Upper Devonian–Lower Mississippian deposits are significantly less important than deposits of other ages shown, these rocks contain widely scattered low-grade deposits, associated with black shales that have an areal distribution unequaled except perhaps by black shales of the Upper Cretaceous–Lower Tertiary. Deposits of ages other than those shown also occur but are usually quite minor or areally limited [for example, an Upper Triassic deposit in the Shublik formation of northern Alaska (25)].

Thus, during possibly six short intervals of geologic time phosphorite deposits accumulated from ancient oceans on a global scale.

Gulbrandsen (26) and Bushinskii (23) have recently presented excellent reviews of the different hypotheses that have been advanced to account for the origin of deposits formed in the geologic past. We will only briefly note the more frequently mentioned associations of phosphorites. In addition to occurring with black shales (27), they contain uranium in a reduced valence state (28). Consequently, they are considered to have formed under reducing conditions or in association with nearby reducing conditions. Their frequent association with the remains of fish debris has been cited as evidence that they accumulated in areas of high biological activity such as occur in regions of coastal upwelling. Mansfield (29) has also noted their association with unconformities and with volcanic debris.

The mechanism we have advanced for the formation of marine phosphorite

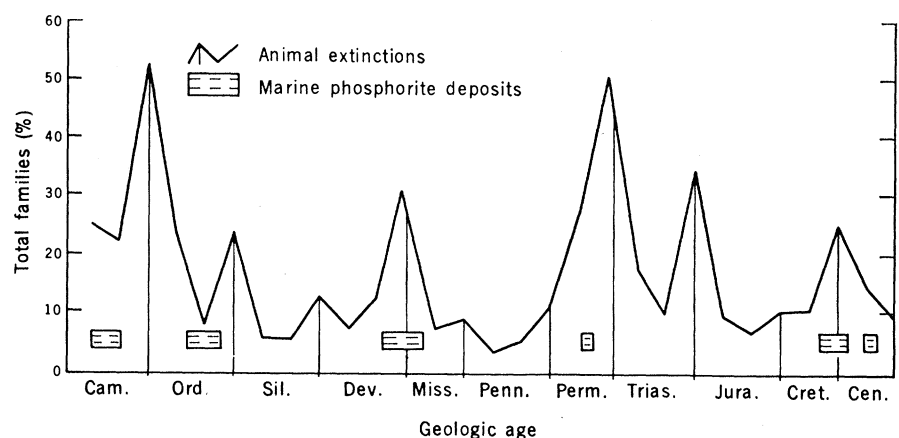


Fig. 1. Episodes of extinction in the animal kingdom (32), and approximate ages of extensive marine phosphorite deposits (24). The last appearances of animal families through geologic time are given in percentages. Main episodes of extinction occurred near the close of the Cambrian, Devonian, Permian, Triassic, and Cretaceous periods (32). The size of the symbol designating the age of phosphorite deposits is not intended as an estimate of their relative economic importance nor of their amount of total phosphorus.

deposits, when applied to ancient deposits, may account for their association with carbonaceous shales and the very broad areal distribution of deposits of any one age. The mechanism does not prohibit, and in fact favors, local enhancing complications such as coastal upwelling. We want to emphasize, however, that the accumulation of major phosphorite deposits may have required a significant change in global nutrient budgets.

Consider, for example, the Upper Permian Phosphoria formation, in the northwestern part of North America. It contains approximately 7×10^{11} metric tons of phosphorus, or six times the total amount of phosphorus in the ocean today (Table 1), extending over an area of 3.5×10^5 square kilometers (26, 30). This must represent a conservative estimate of the amount initially deposited and certainly of the amount deposited throughout the oceans during the time required for the accumulation of this formation. Gulbrandsen (26) has estimated a minimum required time of 2.1×10^5 years. A more conservative estimate of accumulation rate has been made by Cressman and Swanson (31) in considering only the Retort member of the Phosphoria formation in southwestern Montana. They estimate that roughly 1.3×10^6 years were required to deposit 1.6×10^{10} metric tons of phosphorus over an area of 20,300 square kilometers, corresponding to an accumulation of roughly 1 percent of the current river input of dissolved phosphorus for that period of time, over only 0.006 percent of the current surface area of the ocean.

As McKelvey *et al.* (30) suggest, open circulation with the ocean was required to form such a deposit. We suggest that this apparently accelerated rate of accumulation of phosphorus may have resulted in a lowering of the phosphorus concentration in the deep ocean, in contrast to the surface layer of the ocean where its concentration may have increased slightly. As noted above, this would aid in reestablishing the nitrogen/phosphorus ratio of the deep-ocean reservoir. When the lowered phosphorus concentration of the deep ocean again corresponded to the lowered nitrogen concentration, that is, when the nitrogen/phosphorus ratio of the deep ocean again approached the biological demand of organisms living in the surface layer, phosphorite pre-

cipitation on a large scale probably ceased.

Of possibly considerable significance is an apparent relationship between the age of marine phosphorite deposits and the times of maximum evolutionary change. Newell (32), Flessa and Imbrie (33), Tappan and Loeblich (34), and others have noted changes in the numbers of groups of organisms with time, from the Cambrian to the present (Fig. 1). Several of the phosphorite and black shale deposits, specifically those of Devonian, Permian, and Cretaceous ages, apparently accumulated during times of the mass extinction of organisms, although there are obvious exceptions to this relationship (Fig. 1).

Bramlette (35) has suggested that a decrease in the supply of nutrients from land may have caused the drastic faunal extinctions at the end of the Cretaceous. Since phosphorite was precipitating in shallow seas that covered large areas of the continents at that time, it seems unlikely that phosphorus would have been in short supply. However, this may not have been the case for combined nitrogen. We can only speculate on whether a possible increase in denitrification, producing lower concentrations of combined nitrogen in seawater, may have decreased biological productivity in ancient oceans such as to contribute to the mass extinction of groups of organisms.

Summary

We have attempted to demonstrate a possible relationship between phosphorite deposition and an increase in marine denitrification. The studies of others indicate that major phosphorite deposits are often associated with black shales and accumulated during only a few epochs of geologic history. Some of these epochs were also marked by mass extinctions of organisms. Such events are not as precisely nor as strongly correlated as we would like. Nevertheless, the correlations are strong enough to encourage further consideration of the effects of possible changes in the rate of denitrification within ancient oceans on the origin of phosphorite deposits, the extinctions of marine organisms, variations in the overall level of biological activity, and temporal fluctuations in the organic carbon content of sedimentary rocks (36).

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