

PHYSICOCHEMICAL MECHANISM OF FORMATION OF RECENT DIAGENETIC PHOSPHORITES IN THE OCEAN

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Authentic recent oceanic phosphorites have been found in the areas with the highest biological productivity. For these regions maximum intensity of sedimentation flow of phosphorus as biogenic detritus is typical. Elevated concentrations of the element in sea-floor sediments have been revealed [1]. Available literature data [2–6] have shown that only in that sites concentrations of dissolved phosphorus are sufficient for precipitation of calcium phosphate. Active plankton development leads to phosphorus concentrating from undersaturated seawater of apatite. Biogenic detritus inherits high phosphorus concentration from organisms. Due to the shallow depth, the main part of detritus reaches the ocean floor without substantial phosphorus removal. High rates of sedimentation bring to burial of significant quantity of biogenic detritus accumulated in bottom sediments. This leads to phosphorus release from the sediment column in conditions of decomposition of organic matter. As a result, concentrations of dissolved mineral phosphorus in pore water reach 10–30 mg/l or more [7], which is sufficient for precipitation of dispersed amorphous apatite.

On the other hand, mechanism of phosphorus concentrating from dispersed micro nodules of apatite phases to ore deposits is still unanswered question. According to the field data, in pore water of bottom sediments deposited in high productive ocean areas parallel growth in carbonate alkalinity and mineral phosphorus concentrations have happened with depth [7]. Recently, this fact was interpreted as a consequence of increased solubility of dispersed calcium phosphates as a result of durable carbonate-phosphate-calcium complexes formation [8, 9]. However, direct evidence of existence of such complexes is still not found. Together with this, it's been known that isomorphous substitution $\text{CO}_3^{2-} \rightarrow \text{PO}_4^{3-}$ is closely related to increase in equilibrium concentrations of dissolved phosphorus in conditions of the constant activities of other ions.

Solubility of different apatite phases has been analyzed in order to investigate mechanism of phosphorus diagenetic changes. Laboratory studies have been conducted in 0.05 N NaNO_3 – NaHCO_3 – Na_2CO_3 solutions and saturated of CaCO_3 artificial seawater with salinity of 35‰ and variable carbonate alkalinity. Five samples of apatite were used: laboratory synthesized at the temperature of 25°C hydroxyapatite and fluorapatite, natural samples of Khibine apatite, oceanic coprolite and phosphorite. Time of exposure has been 2.5 month. The solid/liquid mass ratio has been 1 : 100.

The obtained results (figure) have shown that increase in alkalinity and pH for all analyzed samples enriches its solubility. In diluted solutions NaNO_3 – NaHCO_3 – Na_2CO_3 with Ca^{2+} concentration less than 0.05 mM just as in seawater solubility of apatite phases has increased sharply with elevation of carbonate alkalinity. So, the presence of calcium is not the necessary requirement for increasing of apatite solubility in carbonate solutions. It may be postulated that if carbonate-phosphate-calcium complexes do exist, their role is much less than it was assumed in [8, 9].

The data for apatite solubility in seawater are described by relationship between concentration of dissolved mineral phosphorus ($P_{\min}$, μM) and the value of alkalinity (Alk, mM):

$$P_{\min} = a \text{Alk}^b. \quad (1)$$

The equation was theoretical derived in [8] in case when carbonate-phosphate-calcium complexes are dominant form of dissolved mineral phosphorus. Experimentally determined values of exponent b for alkalinity ranges from 0.61 to 0.75. These values and the theoretical (calculated) value of $b = 0.72$ [8] are found to be in general agreement. However, this coincidence can not be considered as conclusive evidence for confirming a hypothesis about diagenetic mobilization of phosphorus as carbonate-phosphate-calcium complexes. Enhanced apatite solubility in carbonate solutions can be caused by alteration of solid phase.

As a rule the ocean phosphorites are presented as fluorcarbonateapatite, having isomorphous $\text{CO}_3^{2-} \rightarrow \text{PO}_4^{3-}$ substitution [12]. The degree of this substitution has to depend on carbonate alkalinity in pore water: the more the latter, the higher the former. The release of dissolved phosphate results from apatite carbonatization. So, the increase in carbonate alkalinity in the substratum of sediment

columns should be attended by dissolving of dispersed calcium phosphates following redepositing them in overlying deposits.

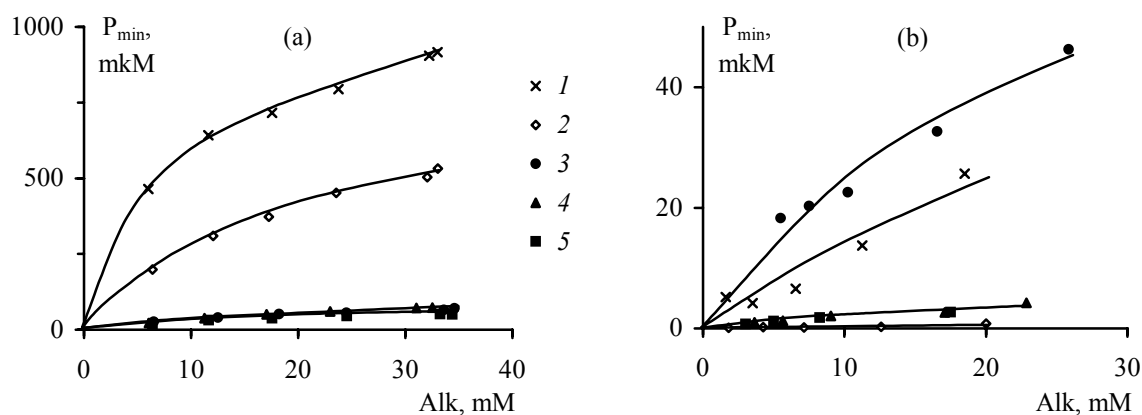


Fig. The relationship between solubility of apatite phases in diluted solution $\text{NaNO}_3\text{--NaHCO}_3\text{--Na}_2\text{CO}_3$ (a) or saturated of CaCO_3 artificial seawater with salinity of 35‰ (b) and value of alkalinity. 1 – hydroxyapatite, 2 – fluorapatite, 3 – Khibine apatite, 4 – oceanic coprolite, 5 – oceanic phosphorite.

Carbonate alkalinity of pore water is known to increase as moving from the border water–bottom. It's been more typical for sediments with high initial concentration of organic carbon from areas with high biological productivity. In that direction solubility of apatite phase is raised. Favorable conditions for phosphorus mobilization and growth of dissolved phosphate concentration are established. So, vertical alkalinity gradients in bottom sediments at the stage of paleodiagenesis create the same gradients of apatite phase solubility. And this leads to dissolved phosphorus flow from the substratum of sediment column to border line water–bottom. Near this boundary (in the low apatite solubility zone) geochemical barrier for diagenetic upflow is generated. Under favorable conditions repeated cyclical process of redeposition can be led to formation of ore shoot of phosphorite nodules.

Suggested mechanism is alternative to hypothesis about phosphorus mobilization as carbonate-phosphate-calcium complexes. In both cases rise in carbonate alkalinity leads to increased concentration of dissolved phosphates. However, in our hypothesis necessary condition of phosphorites formation is primary precipitation of dispersed calcium phosphate. This happens only in high-productive ocean areas where modern oceanic phosphorites have been found.

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