

Golubev S.V., Savenko A.V. Solubility and stability of magnesium phosphates in sea water

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There is an opinion, that formation of calcium phosphates in sea water is preceded by a precipitation of magnesium phosphates, which transform subsequently to apatite. This attractive hypothesis has no reliable basis. In the present study, an experimental investigation of stability (solubility) of diverse magnesium phosphates (newberite $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, bobierite $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and struvite $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is carried out in order to clarify their participation in the processes of oceanic phosphorite formation.

In order to avoid the transformations in magnesium phosphates and precipitation of calcium phosphates, we used an artificial 35 % calcium-free sea water with addition of some amount of solid magnesium phosphates. The constant ionic strength of the solution was controlled by addition of equivalent amount of NaCl.

In study of stability of magnesium phosphates in sea water, we used an artificial 35 % sea water with normal calcium concentration. Some amount of solid phase was added into the solution as well.

Struvite is found to be unstable both in the calcium-free and in the normal sea water. In all experiments the phosphorus concentration is lower than the ammonia concentration. Decrease of the phosphorus concentration in the normal sea water occurs in all experiments at the constant calcium content in the solution.

The calculated value of the negative logarithm to the base 10 of the solubility constant in power of stoichiometric coefficients for struvite and newberite increases more than by unit if pH increases from 7.4 to 8.2. That points to instability of the phases. At the same time, the value calculated for $\text{Mg}_3(\text{PO}_4)_2$ is approximately constant, 12.06 ± 0.05 . These facts allow a conclusion that solubility of unstable struvite is accompanied by the precipitation of $\text{Mg}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$.

The value of the negative logarithm to the base 10 of the solubility constant in power of stoichiometric coefficients for newberite is constant at $\text{pH} < 7.0$ (3.25 ± 0.05). This value increases up to 4.8 if pH increases from 7.0 to 8.0 in more alkalic solutions. The values for bobierite and hydroxyl-apatite vary within 2-3 units, that implies an impossibility of the formation of these phases. This value is constant for octa-calcium-phosphate $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$ (29.05 ± 0.05), that corresponds to formation of this phase.

Since we experimentally found the transformation of newberite $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and struvite $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ in sea water into bobierite $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, the solubility of the later phase is studied in detail.

We experimentally studied the solubility of both synthetic bobierite ("approach to equilibrium from below") and phases, precipitated from the calcium-free sea water with the initial phosphorus concentration 10 mmole/l ("approach to equilibrium from above").

According to our experiments, the solubility of bobierite at $\text{pH} = 8.0$ is about 15 mg/l. That is only slightly larger than the solubility of newly precipitated calcium phosphates, which at the same pH is about 10 mg/l [2]. Thus, pore water of sediments of highly productive regions containing up to 10-40 mg/l [3], can be oversaturated with respect to both calcium phosphates and magnesium phosphates. However, experimental results on the kinetics of precipitation show [1, 4] that the induction periods of precipitation of magnesium phosphates are several orders of magnitude higher than the induction periods of precipitation of calcium phosphates. That prevents from precipitation of magnesium phosphate phases. In the process of aging of newly precipitated calcium phosphates, a decrease of their solubility by order of magnitude takes place [2]. Therefore, magnesium phosphates become more unstable with respect to the apatite phases. Thus, magnesium phosphates do not precipitate in the formation of marine phosphorites.

Conclusions.

1. Struvite in sea water transforms to bobierite.
2. Newberite is stable in sea water at $\text{pH} < 7$; in more alkalic environment it transforms to octa-calcium-phosphate in normal sea water, or to bobierite in calcium-free sea water.
3. Magnesium phosphates do not participate in the formation of marine phosphorites.

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