

Solubility of Struvite in Seawater

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It has been frequently argued that magnesium which prevents direct apatite crystallization from seawater, can be removed by struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) precipitation in porous waters (Hirschler et al., 1990; Lucas, Prevot, 1985; Prevot et al., 1989). The absence of experimental data about solubility and stability of struvite in seawater makes difficult the real estimation of this hypothesis.

Solubility of struvite was investigated in the artificial seawater solutions without Ca. Reagent grade chemicals and distilled water were used to prepare the artificial seawater solutions. These solutions comprise all major components of seawater except of Ca, which was not included because of possible Ca phosphate precipitation. The pH was adjusted by addition of small volumes of acid (HCl) or base (NaOH). All solutions were filtered through a membrane filter before the experiments. Solutions were analysed for dissolved Mg by volumetric titration with EDTA. Phosphorus was analysed by the standard molybdate blue spectrophotometric method with an uncertainty $\pm 5\%$. Ammonium was analysed by spectrophotometry with Nessler reagent with a detection limit of 0.05 ppm and an uncertainty $\pm 5\%$. pH was measured using a glass electrode and KCl-saturated Ag/AgCl reference electrode with an uncertainty $\pm 1\%$. The experiments were conducted under thermostated conditions at $20 \pm 1^\circ\text{C}$.

At the end of each experiment, the solid was collected on a membrane filter, washed in distilled water, dried at room temperature, and stored for subsequent analysis. The solid products were characterized by X-ray Diffraction Spectroscopy (XRD) and their chemical composition was determined by wet chemical analysis.

Experiments were conducted at different water/solid mass ratios (100 - 6500). At high values of these ratios the composition of solutions can give an information about

stability of struvite. At low values of these ratios concentrations of dissolved magnesium, ammonium and phosphorus are controlled by solubility of struvite that allows to determine thermodynamic solubility of struvite (L^0). The activity coefficients of aqueous species were calculated using Davies equation. According to our experimental data $pL^0 = 13.08 \pm 0.02$. At high values of water/solid mass ratios the value of pL^0 increases up to 14.0 that allows to make a conclusion about instability of struvite. XRD analysis of solid phases in experiments at high values of water/solid mass ratios showed the presence of bobbierite $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. Chemical analysis of these phases revealed the presence of Mg and phosphate with Mg/P molar ratio of 1.50 ± 0.05 which is close to the one for bobbierite. As a result of this investigation and our experimental data about unseeded precipitation of calcium and magnesium phosphates from modified seawater solutions (Golubev et al., 1999), no magnesium (ammonium) phosphate can be inorganically precipitated in modern marine environments of phosphorites formation which is in agreement with available natural observations (Baturin, 1978).

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