

SOLUBILITY OF CaF₂ IN SEAWATER AND INTERSTITIAL WATERS OF MARINE SEDIMENTS

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In spite of poverty of information about presence of fluorite in marine phosphorites its concentration can reach high amounts - 2-3% [Krasilnikova et al., 1961]. It is known that accumulation of fluoride occurs in interstitial waters of marine sediments containing phosphate material in zones with high biological productivity: at the shelves of South America and South-West Africa [Shishkina, 1972; Baturin, 1978], however conditions of CaF₂ formation remain unclear.

The average concentration of fluoride in interstitial waters is near 2.7 mg/l: it is two times higher than in seawater. In interstitial waters of marine sediments in zones with high biological productivity concentration of fluoride can increase up to 8-11 mg/l [Shishkina et al, 1972].

Solubility of CaF₂ is defined not only total concentrations of calcium and fluoride, but the concentration of magnesium due to its formation of complex with fluoride. Concentration of calcium and fluoride can vary in wide interval changing the saturation state of solution with respect to CaF₂. The aim of this study is experimental investigation of solubility of CaF₂ in solution imitating seawater and interstitial waters of marine sediments.

Reagent grade chemicals and distilled water were used to prepare solutions with different concentration of calcium and magnesium containing all other components found in natural seawater. All solutions after addition solid phase (CaF₂) were stirred many times. After 6 mounts all solutions were filtered through a membrane filter. Solutions were analysed for dissolved Ca and Mg by titration. Fluoride-ion was analysed using fluoride-electrode; total concentration of soluble F was determined using "method of addition". The results of all experiments are presented in table 1.

Total concentration of fluoride $[\Sigma F]$:

$$[\Sigma F] = [F^-] + [CaF^+] + [MgF^+] = [F^-] \{1 + K_{CaF^+} [Ca^{2+}] + K_{MgF^+} [Mg^{2+}]\},$$

where K_{CaF^+} и K_{MgF^+} - the constants of stability of complexes CaF⁺ and MgF⁺.

Using equation for solubility $L_{CaF_2} = [Ca^{2+}][F^-]^2$ we can write next equation:

$$[\Sigma F][Ca^{2+}]^{0.5} = L_{CaF_2}^{0.5} \{1 + K_{CaF^+} [Ca^{2+}] + K_{MgF^+} [Mg^{2+}]\}, \quad (1)$$

and for constant of sum of calcium and magnesium concentration:

$$[\Sigma F][Ca^{2+}]^{0.5} = L_{CaF_2}^{0.5} \{1 + K_{CaF^+} [Me^{2+}] + K_{MgF^+} (1 - K_{CaF^+}) [Mg^{2+}]\}, \quad (2)$$

where $[Me^{2+}] = [Ca^{2+}] + [Mg^{2+}]$.

Table 1

№	$[\Sigma F]$, mkM	$[\Sigma Mg]$, mM	$[\Sigma Ca]$, mM
1	89.5	0	39.75
2	107.9	6.40	33.40
3	139.2	15.10	23.85
4	184.4	23.60	15.70
5	277.2	31.10	7.75
6	726.8	37.35	0.95
7	194.9	0	10.43
8	236.8	12.55	8.15
9	314.9	23.95	6.05
10	430.3	35.35	4.30
11	598.5	45.75	2.40
12	969.9	57.23	0.90

The equations (1) and (2) we can write like $y = a + b \cdot x$, where for (1):

$$y = [\Sigma F][Ca^{2+}]^{0.5} / (1 + K_{CaF^+} [Ca^{2+}]); \quad a = L_{CaF_2}^{0.5};$$

$$x = [Mg^{2+}] / (1 + K_{CaF^+} [Ca^{2+}]); \quad b = K_{MgF^+} L_{CaF_2}^{0.5},$$

and for (2): $y = [\Sigma F][Ca^{2+}]^{0.5}; \quad a = L_{CaF_2}^{0.5} (1 + K_{CaF^+} [Me^{2+}]);$
 $x = [Mg^{2+}]; \quad b = K_{MgF^+} (1 - K_{CaF^+}).$

The figures 1 and 2 show conformity of our experimental data with equation

$$y \cdot 10^{-5} = a + b x \cdot 10^{-3}.$$

According to our experimental data $L_{CaF_2} = 2.90 \cdot 10^{-10}$. Conversion to termodinamical solubility gives $L^0 = 3.05 \cdot 10^{-11}$, ($pL^0 = 10.52$). This value is with good agreement with reference data ($pL^0 = 10.40$ [Lurie, 1971]). Using experimental results the diagram of correlation between concentration of equilibrium with CaF₂ fluoride and concentration of magnesium in seawater can be got (fig. 3).

As it is seen from fig. 3, solubility of CaF₂ in magnesium free seawater 1.5 times lower than in normal seawater. Interstitial waters of marine sediments (with normal concentration of magnesium – 53 mM) in zones with high biological productivity containing 8-11 mg F/l can be supersaturated with respect to CaF₂.

In the result of change of magnesium concentration in interstitial waters of marine sediments due to formation of dolomite or magnesium silicates [Initial reports of the deep sea drilling project, 1978, 1979, 1980, 1981] the saturation state of solutions with re-

spect to CaF_2 decreases. On the base of our experimental data we can conclude that precipitation of CaF_2 can take place not only in interstitial waters of marine sediments in zones with high biological productivity but due to the extraction of magnesium in marine sediments.

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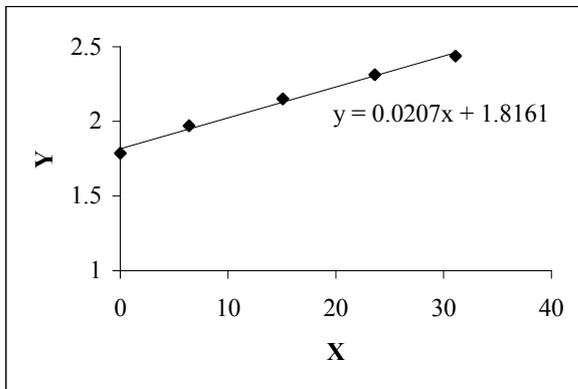


Fig. 1

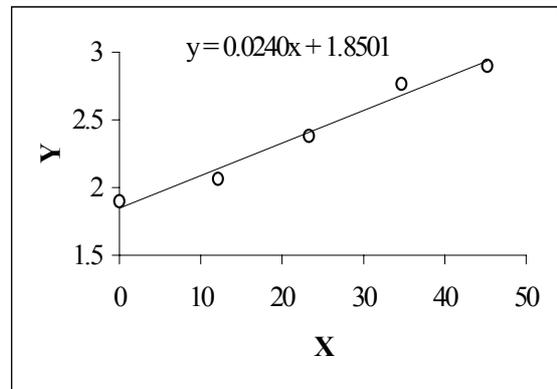


Fig. 2

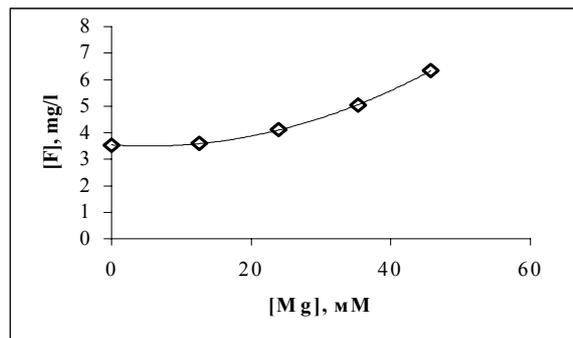


Fig. 3