Conditions for the Formation of Sellaite in Salt Sediments

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Abstract—The conditions for magnesium fluoride (sellaite) precipitation from seawater with a salinity of 35-105% were experimentally determined. It was found that the precipitation of MgF₂ at the salinity of 35, 70, and 105% occurs at a concentration of dissolved fluorine above 37, 46, and 51 mg/L, respectively. In isolated evaporite basins, the fluorine concentration required for the formation of sellaite is not reached at all stages of the evaporative thickening of seawater. Therefore, it is assumed that a high concentration of fluorine, sufficient for the precipitation of sellaite, arises as a result of the combined effect of evaporation and additional input of this element into salt-bearing basins with river runoff and/or the release of coprecipitated and sorbed fluorine during the post-sedimentary recrystallization of salt minerals.

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INTRODUCTION

Sellaite, MgF₂, and fluorite, CaF₂, are fluorine minerals that are quite rare in salt deposits. While there are sufficiently reliable experimental data concerning the conditions for the formation of sedimentary fluorite (Kazakov and Sokolova, 1950), the conditions for the formation of sellaite are still not clear. It was noted that sellaite, as a primary mineral in evaporite deposits, occurs together with potassium salts (Steward, 1963), which are deposited at the later stages of thickening of seawater with the highest concentration of magnesium ions in solution. The latter, at first glance, should facilitate the separation of the solid MgF_2 phase from the brine; however, the formation of strong MgF⁺ complexes, whose contribution also increases with an increase in the concentration of dissolved magnesium, prevents this process. In addition, since the product of CaF2 solubility is 160 times less than that for MgF_2 (Lur'e, 1989), it can be expected that only a small part of the fluorine remains in a dissolved state until the stage of precipitation of potassium salts and participates in the formation of sellaite, while the bulk of fluorine is precipitated in the form of fluorite in the earlier stages of thickening of seawater. This work is aimed at clarifying the conditions for the formation of sellaite in evaporite deposits based on experimental modeling of the deposition of fluoride mineral phases from seawater of normal and increased salinity.

MATERIALS AND METHODS

Research methods. In the experiments, we used artificial seawater with salinities of 35, 70, and 105%

containing components of the basic salt composition according to (Popov et al., 1979), but replacing sodium bicarbonate with sodium chloride in order to prevent precipitation of the CaCO₃ solid phase. The upper limit of the salinity of seawater was limited to 105% in order to exclude the possibility of the formation of nonfluoride solid phases (gypsum, halite, etc.), whose presence could affect the concentration of fluorine in the solution as a result of coprecipitation and sorption processes. Portions of solid NaF salt weighing from 25 to 300 mg were added to plastic test tubes to 40-mL aliquots of artificial seawater of different salinities, making it possible to create a high total fluorine content in the experiments, which significantly exceeds its maximum possible concentration in solution. After 3 weeks of daily stirring of the suspensions on a shaker for 8-10 h at room temperature, the solutions were filtered through a membrane filter with a pore size of $0.22 \,\mu m$. The concentration of fluorides was determined by direct potentiometry in the filtrate and samples of the initial seawater (Savenko, 1986), as well as the content of magnesium and calcium by capillary electrophoresis with a dilution of highly mineralized solutions 1 : 100-1 : 200 (Komarova and Kamentsev, 2006). The measurement error did not exceed $\pm 3\%$.

RESULTS AND DISCUSSION

From the data given in Table 1 it follows that for each salinity value there is a slight increase in the equilibrium concentration of dissolved fluorides with an increase in the weight of the NaF sample. This is associated with a change in the compositions of the initial

Seawater salinity, %	NaF content, mg/L	Equilibrium concentrations				$\Delta \left[\operatorname{Ca}^{2+} \right] + \Delta \left[\operatorname{Mg}^{2+} \right]^*$	$\left[Mg^{2+} \right]^{**}$
		F ⁻ , mg/L	F⁻, mM	Mg ²⁺ , mM	Ca ²⁺ , mM	$\frac{\Box}{\Delta [F^-]}$	$\begin{bmatrix} Ca^{2+} \end{bmatrix}$
35	0	0	0	54.5	10.55	—	—
	625	53.0	2.79	49.0	7.72	0.69	6.35
	1250	64.1	3.37	44.9	7.33	0.49	6.13
	1875	75.8	3.99	40.7	6.65	0.44	6.12
	2500	89.2	4.70	36.5	5.32	0.42	(6.86)
Mean						0.51 ± 0.12	6.20
70	0	0	0	109.7	21.05	—	—
	1250	56.0	2.95	100.8	16.45	0.50	6.13
	2500	65.3	3.44	93.8	14.44	0.40	6.50
	3750	77.2	4.06	81.5	13.22	0.42	6.16
	5000	86.2	4.54	75.4	10.18	0.39	(7.41)
Mean			0.43 ± 0.05	6.26			
105	0	0	0	163.7	31.57	_	_
	1875	61.1	3.22	147.5	25.51	0.54	5.78
	3750	70.1	3.69	137.1	21.56	0.43	6.36
	5625	77.6	4.08	123.0	19.21	0.41	6.40
	7500	87.8	4.62	107.9	11.50	0.44	(9.38)
Mean						0.45 ± 0.06	6.18

Table 1. The variations in the composition of seawater of different salinity upon interaction with NaF

* Δ [Ca (Mg)] is the difference in molar concentrations of calcium (magnesium) in equilibrium with fluorine minerals and the initial seawater of the corresponding salinity; Δ [F⁻] is the difference between the molar concentrations of fluorine in equilibrium seawater and in the added portion of NaF; **, when calculating the mean values of the [Mg²⁺]/[Ca²⁺] ratio, the last experiments in each series, which were carried out with the maximum additions of NaF, were not taken into account.

solutions caused not only by the precipitation of CaF_2 and MgF₂ solid phases but also by the dissolution of residual NaF until the saturation state for this solid phase is reached. In experiments with the same NaF additions, the concentration of dissolved fluorides is approximately at the same level in the entire studied range of seawater salinity. The molar ratio of the sum of changes in the calcium and magnesium contents to the change in the fluorine concentration is 0.4-0.5, which is close to the stoichiometry for fluorides of alkaline earth elements and indicates the simultaneous precipitation of fluorine in the form of $\mbox{Ca}\mbox{F}_2$ and MgF₂. Direct determination of sellaite is complicated, because precipitates of calcium and magnesium fluorides are represented by finely dispersed X-ray amorphous phases, which remain so for at least 4-5 months.

If simultaneous precipitation of calcium and magnesium fluorides occurs, then due to small differences in the activity coefficients of Ca^{2+} and Mg^{2+} ions, the ratio of the concentration values of these elements in solution should be constant and closely correspond to the ratio of the solubility product of these phases:

$$\frac{L_{MgF_{2}}^{0}}{L_{CaF_{2}}^{0}} = \frac{\left[Mg^{2^{+}}\right]\gamma_{Mg^{2^{+}}}}{\left[Ca^{2^{+}}\right]\gamma_{Ca^{2^{+}}}} \approx \frac{\left[Mg^{2^{+}}\right]}{\left[Ca^{2^{+}}\right]}$$

In fact, in the experiments we carried out the molar ratio $[Mg^{2+}]/[Ca^{2+}]$ is constant and equals 6.2 ± 0.2 (Table 1). According to the reference data (Lur'e, 1989), the values of $L^0_{MgF_2}$ and $L^0_{CaF_2}$ are 6.5×10^{-9} and 4.0×10^{-11} , respectively, which leads to a significantly larger $[Mg^{2+}]/[Ca^{2+}]$ ratio equal to 162. Such discrepancies are not critical and can be associated with differences in the solubility product of crystalline and freshly precipitated solid phases. As an example, a 5–8 times excess of the solubility product of precipitated CaF₂ over that for the crystalline phase was previously established for normal seawater and solutions that imitated the pore waters of marine sediments (Savenko, 1983).

The experimental results show a linear dependence of dissolved fluoride equilibrium concentration on the amount of precipitated MgF₂, that equals the difference between the initial and equilibrium magnesium concentration in the solution (Fig. 1). Extrapolation to a zero difference of the magnesium concentration values allows one to determine the fluoride concentration at which the precipitation of MgF₂ begins. In this case, the extrapolation points correspond to the minimum changes in the initial solutions caused by the addition of NaF. For seawater with salinities of 35, 70, and 105‰, the concentrations of fluorides at the beginning of the MgF₂ precipitation were 1.93, 2.42,



Fig. 1. The dependence of the equilibrium concentration of dissolved fluorides ([F]) on the difference between the values of the initial and equilibrium concentration of magnesium ($-\Delta$ [Mg]), corresponding to the amount precipitated MgF₂, for seawater with the salinity of 35 (*1*), 70 (*2*), and 105‰ (*3*)

and 2.70 mM, respectively (37, 46, and 51 mg/L). The contents of dissolved fluorides in natural seawater of the corresponding salinity were 1.3, 2.6, and 3.9 mg/L, which is much lower than the concentration values at which precipitation of MgF_2 is possible. Moreover, even with a 9–10-fold thickening of normal seawater, when potassium salts, that is, sylvite and carnallite, begin to move, the natural increase in the concentration of dissolved fluorides to 14–16 mg/L turns is insufficient for precipitation of MgF₂.

The conclusion about the impossibility of the formation of sellaite during the evaporative concentration of seawater is valid only for isolated evaporite basins that do not have additional sources of fluorine. At the same time, for many modern and ancient evaporite basins an important part of the water-salt balance is the river runoff, in which the share of fluorides in the total mineralization is much higher than in seawater. As an example, the share of fluorine in the composition of sea salts is 0.0037% (Popov et al., 1979), while for the salts of the worldwide river runoff it averages 0.12% (Gordeev, 2012). Therefore, with a significant contribution of river runoff to the water-salt balance of evaporite basins and evaporation exceeding the freshwater inflow, the concentration of dissolved fluorides can reach the values required for precipitation of MgF_2 . As well, the formation of sellaite at the stage of post-sedimentary changes in salt deposits is not excluded. Local areas with a high concentration of fluorides may occur due to recrystallization of salt minerals with the release of previously absorbed impurities, including fluorine. Unfortunately, the minimal information on fluorine in salt deposits does not allow one to prefer one of these mechanisms of sellaite genesis. Data on the fluorine content in the main minerals of salt deposits and information on the distribution coefficients of fluorine between these minerals and parent liquors are needed to solve this problem.

CONCLUSIONS

Sellaite formation in salt basins can occur only at high values of the concentration of dissolved fluorine in brine (>50 mg/L), which are not achieved with autonomous evaporative thickening of seawater. The concentration of fluorine required for the formation of sellaite may arise due to the inflow of a significant volume of river waters into evaporite basins, where the share of fluorides in the total mineralization is much higher than that in seawater. Another process that increases the fluorine content in brine may be the recrystallization of salt minerals during their post sedimentary changes, leading to the release of fluorides previously absorbed in the processes of sorption and coprecipitation.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

- Gordeev, V.V., *Geokhimiya sistemy reka-more* (Geochemistry of River–Sea System), Moscow: IP I.I. Matushkina, 2012.
- Kazakov, A.V. and Sokolova, E.I., Conditions of the formation of fluorite in sedimentary rocks (the fluorite system), in *Tr. Inst. geol. nauk. Geol. Ser. Vyp. 114. (№ 40)* (Trans. Inst. Geol. Sci. Ser. Geol. Vol. 114, no. 40), Moscow, 1950, pp. 22–64.
- Komarova, N.V. and Kamentsev, Ya.S., Prakticheskoe rukovodstvo po ispol'zovaniyu sistem kapillyarnogo elektroforeza "KAPEL" (Practical Guidance on the Use of "Kapel" Capillary Electrophoresis System), St. Petersburg: Veda, 2006.
- Lur'e, Yu.Yu., *Spravochnik po analiticheskoi khimii* (Handbook on Analytical Chemistry), Moscow: Khimiya, 1989.
- Popov, N.I., Fedorov, K.N., and Orlov, V.M., *Morskaya* voda (Seawater), Moscow: Nauka, 1979.
- Savenko, V.S., Features of fluorine geochemistry in mud waters of sediments of highly productive oceanic area, *Geokhimiya*, 1983, no. 12, pp. 1791–1795.
- Savenko, V.S., Vvedenie v ionometriyu prirodnykh vod (Introduction to Natural Water Ionometry), Leningrad: Gidrometeoizdat, 1986.
- Steward, F.H., Marine evaporites (Chapter Y), in Data of Geochemistry (6th ed.). U. S. Geol. Surv. Prof. Pap. 440-Y, Washington, 1963.

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