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Review

Fluorite genesis in sedimentary basins: A review

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Abstract: The available data on the dissolved fluoride content and the saturation degree by fluorite in waters of the world ocean and large continental reservoirs were critically reviewed. It was shown that evaporative concentrating of dissolved salts in the autonomous marine basins cannot cause chemogenic fluorite precipitation, which can occur only with additional supply of fluoride from external sources (river runoff, volcanic exhalations, and terrigenous aerosols). The contribution of external fluoride sources should be at least 1.5–4 times of the mass of fluoride supplied with seawater. As such, saturation of waters by CaF_2 and the fluorite formation is possible in large drying continental reservoirs of the arid zone that have no direct connection with the world ocean. An assumption about a two-stage mechanism of authigenic fluorite formation in carbonate rocks was made. At the first stage, freshly formed finely dispersed carbonate sediments uptake fluoride from seawater as a result of sorption and coprecipitation. In the second stage, during the recrystallization of the primary solid phase, its partial purification occurs, which is accompanied by the release of some of the uptaken fluoride into the pore solutions. This causes an increase in the dissolved fluoride concentration in the pore waters to values sufficient for fluorite precipitation.

Keywords: fluorite; sedimentary rocks; genesis; ocean; continental water reservoirs; saturation degree; mechanism of formation

1. Introduction

The most abundant fluoride minerals in sedimentary rocks are fluorite and fluoride-containing apatite. The abundance of other sedimentary fluoride minerals is much less, since their formation requires conditions that rarely occur in modern and ancient sedimentary basins. While numerous researchers are devoted to the genesis of sedimentary apatite, which forms the basis of phosphorites, one of the major sources of phosphate raw materials, there are not so many works concerning the genesis of sedimentary fluorite. Furthermore, the greatest uncertainty exists in relation to the sources of fluoride and the physicochemical mechanisms of sedimentary fluorite formation. Our aim of this study was to clarify these problems taking into account new data on the fluoride geochemistry in the waters of the world ocean and large continental reservoirs, as well as experimental data on the CaF_2 solubility in natural waters of different chemical compositions.

2. Fluoride distribution in waters of modern sedimentary basins

The world's largest sedimentary basin is the world ocean, the main reservoir of free water on Earth and regulator of the global hydrological cycle. With the exception of small continental water reservoirs, where fluoride concentrations are determined by local factors (mainly the fluoride content of the catchment rocks), all large land water reservoirs in humid areas generally have low fluoride concentrations (<0.5 mg/L). This prevents the formation of sedimentary fluorite, as evidenced by the low fluoride content in sedimentary rocks formed in humid climate [1]. Moreover, endorheic water reservoirs in arid areas may contain more than 1 mg/L of fluoride. Since fluorite does not form in continental water reservoirs in humid climate, they are not considered further.

It is advisable to divide modern large sedimentary basins into three large groups depending on the ratio of nourishment sources (primarily, the participation of the world ocean waters). The first group includes the world ocean and seas with a minor contribution of dissolved and solid terrigenous material entering them with river runoff or with continental aerosols. The mineralization and salt composition of the water reservoirs of this group are determined by the water evaporation and are described with good approximation within the framework of a simple model of "sea salts + variable amount of H_2O". The second group consists of water reservoirs with significant mass exchange with the world ocean and with land, from where dissolved substances are transferred as part of river runoff. This group includes, for example, the desalinated inland Baltic and Black seas. The third group unites continental water reservoirs that have never had, or had only in the distant past, a direct connection with the world ocean and are now influenced by factors of continental origin. Examples of water reservoirs of this group are the seas-lakes: Aral and Caspian.

2.1. Waters of the world ocean

The fluoride concentration in the open oceanic waters is quite constant and is approximately 1.3 mg/L with salinity of 35‰ and a F/Cl mass ratio equal to $(6.8 \pm 0.2) \times 10^{-5}$ [2–11]. Rare deviations from the given range of the F/Cl ratio are apparently associated either with an abnormally high content of suspended matter when using the spectrophotometric method for fluoride determination or with sampling in coastal waters, where the influence of terrigenous material and anthropogenic sources of pollution is most pronounced.

It has been repeatedly suggested that submarine volcanism may be the cause of significant changes in fluoride concentrations in seawater. However, the few data [12,13] indicate approximately the same and lower fluoride content in underwater hydrothermal vents of mid-ocean ridges compared to seawater. In areas of modern island-arc volcanism, seawater in the immediate vicinity of active submarine volcanoes is barely enriched with fluoride [14]. Additionally, more intense, but also local and short-term changes in fluoride concentration, were observed in the coastal seawater near Heimaey Island interacting with molten lava [15]: The fluoride concentration ranged from 1.3 to 2.0 mg/L in 26 of 32 seawater samples, from 2.0 to 3.0 mg/L in five samples, and it was 4.8 mg/L in one sample. Therefore, modern volcanism does not cause strong, extended and long-term fluoride anomalies in the world ocean.

2.2. Waters of desalinated inland seas

The water reservoirs of the second group (the Baltic and Black seas) are characterized by lower fluoride content than the open ocean waters due to the diluting effect of river runoff. The fluoride concentration in these decreases as desalination continues, reaching minimum values in the estuarine coastal areas (0.4–0.5 mg/L) with an increase in the F/Cl mass ratio in the same direction from $(7–8) \times 10^{-5}$ at Cl = 16–17‰ to $\sim 25 \times 10^{-5}$ at Cl ≈ 1.8‰ [16,17].

2.3. Waters of large arid continental reservoirs

Table 1. Fluoride concentration in waters of large continental reservoirs of the arid zone and their saturation degree by CaF_2 at 22 ± 3 °C.

Water reservoir, year of sampling (horizon)	Mineralization, g/L	Fluoride concentration[1], mg/L		Saturation degree Ω_{CaF_2}	Reference
		natural	in equilibrium with CaF_2		
Caspian Sea, 1981	13.0	3.1	11.0–12.0	0.067–0.079	[18]
Aral Sea, 1980	16.2	4.1	8.7–9.5	0.19–0.22	[18,19]
Aral Sea, 2014–2015:					
Small Aral Sea, 0 m	10.2	2.54	4.85	0.27	[20]
Lake Tshchebas, 0 m	85.9	21.0	21.7	0.94	“
Western basin of the Large Aral Sea, 0 m	136.8	38.2	38.1	1.01	“
Chernyshev Bay, 0 m	153.4	38.1	38.7	0.97	“
The same, 5 m	212.3	37.2	47.8	0.61	“
The same, 7 m	288.1	28.7	49.1	0.34	“
The same, 10 m	306.1	28.6	48.3	0.35	“
Lake Issyk Kul, 2015	5.96	2.3	10.5	0.048	[20,21]
Dead Sea, 2017	333.1	5.3	30.3	0.031	[22]
Lake Urmia, 2017	404.0	10.5	369	0.0008	“

Note: [1] The relative error of potentiometric determinations of the fluoride concentrations given here and in Tables 2–4 was ±3%.

The fluoride content in all studied large water reservoirs in arid areas exceeds its concentration in seawater (Table 1). In the modern, greatly dried up Aral Sea, divided into several isolated water bodies with mineralization from 86 to 306 g/L, the fluoride content reaches 21–38 mg/L. For instance, 35 years ago, the fluoride concentration and mineralization of the Aral Sea waters were 4.1 mg/L and 16.2 g/L [19]. Such high modern fluoride concentrations suggest that sedimentary fluorite may be deposited in continental endorheic basins of the arid zone.

3. Saturation degree by CaF_2 of waters of modern sedimentary basins

Precipitation of solid phase A_mB_n is possible only when the saturation degree of the solution $\Omega_{A_mB_n}$ is greater than 1:

$$\Omega_{A_mB_n} = \frac{a_A^m a_B^n}{a_{A(sat)}^m a_{B(sat)}^n} = \frac{[A]^m[B]^n \bar{\gamma}_A^m \bar{\gamma}_B^n}{[A]_{(sat)}^m [B]_{(sat)}^n \bar{\gamma}_{A(sat)}^m \bar{\gamma}_{B(sat)}^n} = \frac{[A]^m[B]^n \bar{\gamma}_A^m \bar{\gamma}_B^n}{L_{A_mB_n}^0} > 1, \qquad (1)$$

where a_i, $[i]$, and $\bar{\gamma}_i$ are the activity, total concentration, and total activity coefficient of the dissolved component i, respectively; $L_{A_mB_n}^0$ is the thermodynamic solubility product of the solid phase A_mB_n; and *sat* is the index denoting a saturated solution. The equilibrium state of the solid phase is shown by $\Omega_{CaF_2} = 1$. Since dissolution of CaF_2 in seawater and other natural waters practically does not change the calcium ions concentration and the total activity coefficients of dissolved components, the saturation degree by fluorite Ω_{CaF_2}, with a good approximation, is equal to the square of the ratio of fluoride concentrations in the studied solution in a natural state and in equilibrium with CaF_2:

$$\Omega_{CaF_2} = \frac{a_{Ca^{2+}} a_{F^-}^2}{a_{Ca^{2+}(sat)} a_{F^-(sat)}^2} = \frac{[Ca^{2+}][F^-]^2 \bar{\gamma}_{Ca^{2+}} \bar{\gamma}_{F^-}^2}{[Ca^{2+}]_{sat}[F^-]_{sat}^2 \bar{\gamma}_{Ca^{2+}(sat)} \bar{\gamma}_{F^-(sat)}^2} \approx \left(\frac{[F^-]}{[F^-]_{sat}}\right)^2. \qquad (2)$$

In the future, relation (2) will be used to determine Ω_{CaF_2}.

3.1. Seawater

The experimental data presented in Table 2 show that the solubility of CaF_2 in seawater increases with increasing temperature, and, for freshly precipitated phases, is several times greater than that for crystalline fluorite. The beginning of CaF_2 precipitation occurs at a fluoride content of 18–29 mg/L, while the equilibrium fluoride concentration with crystalline fluorite is in the range of 6.6–15 mg/L. The observed differences in the CaF_2 solubility are apparently associated with the well-known fact of the significant dependence of solid phase's solubility on the stage of their aging, degree of dispersion, and amount of impurities. In any case, natural seawater is greatly undersaturated by calcium fluoride.

3.2. Products of seawater evaporative concentrating

Table 2. Saturation degree of seawater by CaF_2.

Mineralization, g/L (salinity)	Fluoride concentration, mg/L		Saturation degree	Reference
	natural	in equilibrium with CaF_2[1] (temperature)	Ω_{CaF_2}	
35.8 (35‰)	1.33	7.0 (0°C)	0.036	[23]
35.8 (35‰)	1.33	12.0 (15°C)	0.012	“
35.8 (35‰)	1.33	13.5–15.1 (22 ± 3°C)	0.008–0.010	[24]
35.8 (35‰)	1.33	*23.4–29.4* (22 ± 3°C)	0.002–0.003	“
35.8 (35‰)	1.33	6.6	0.041	[25]
35.7	1.36	7.40 (22 ± 3°C)	0.034	[26]
39.6	1.50	7.19 (22 ± 3°C)	0.044	“
39.6	1.50	*18.3* (22 ± 3°C)	0.007	“

Note: [1] Roman font is crystalline CaF_2 and italics is precipitated CaF_2 (aging time from 3 weeks to 3 months).

Syngenetic fluorite is most often found in deposits of the early stages of the evaporation process when carbonates and gypsum are precipitated [27]. Therefore, information on the CaF_2 solubility in the products of seawater evaporative concentrating formed at these stages (before the stage of halite precipitation) is of interest.

To calculate the saturation degree of solutions by CaF_2 using experimentally determined values of the equilibrium fluoride concentration, it is necessary to know its actual content at different stages of salinization. Such information for modern water reservoirs is extremely limited, which is one of the major difficulties preventing reliable assessments of the conditions of fluorite chemogenic formation. However, taking into account the fact that, during evaporative concentrating, chlorides remain in solution until the halite precipitation begins, the dissolved fluoride concentration at a given chlorinity can be determined from the F/Cl ratio in the initial seawater:

$$[\mathrm{F}^-]_{br} = \frac{[\mathrm{F}^-]_{sw}}{[\mathrm{Cl}^-]_{sw}}[\mathrm{Cl}^-]_{br} = k_{\mathrm{F/Cl}}[\mathrm{Cl}^-]_{br}, \tag{3}$$

where the indices *sw* and *br* denote belonging to the initial seawater and brine (water concentrated in the evaporation process); and $[\mathrm{F}^-]_{sw}/[\mathrm{Cl}^-]_{sw} = k_{\mathrm{F/Cl}} = 6.7\times10^{-5}$ is the F/Cl ratio in the seawater of normal salinity. The obtained fluoride concentration is the maximal, since some of it can coprecipitate with autochthonous chemogenic phases: Calcium carbonate and gypsum. From (2) and (3), the equation for the maximum saturation degree of brine of the marine evaporite basin by CaF_2 follows:

$$\Omega_{\mathrm{CaF_2}}^{\max} = \left(\frac{k_{\mathrm{F/Cl}}[\mathrm{Cl}^-]_{br}}{[\mathrm{F}^-]_{sat}}\right)^2 = 4.50\times10^{-9}\left(\frac{[\mathrm{Cl}^-]_{br}}{[\mathrm{F}^-]_{sat}}\right)^2. \tag{4}$$

Our experiments [26], the results of which are presented in Table 3, confirmed the significantly higher solubility of freshly precipitated CaF_2 than crystalline fluorite (Figure 1) and showed that the condition $\Omega_{\mathrm{CaF_2}}^{\max} \ll 1$ is maintained in the studied range of brine mineralization (35.7–344 g/L).

Increasing the mineralization of seawater to the value at which gypsum precipitation begins causes a relatively small increase in the saturation degree. In brines formed at the stage of gypsum precipitation (before the start of halite precipitation), further growth of the equilibrium with CaF_2 fluoride concentration with an increase in mineralization is accompanied by a decrease in the saturation degree by this mineral (Figure 2).

Table 3. Solubility of CaF_2 in seawater and products of its evaporative concentrating at 22 ± 3 °C.

Mineralization, g/L	$[F^-]_{sat}$ mg/L	$[Cl^-]$	$[SO_4^{2-}]$	$[Na^+]$	$[K^+]$	$[Mg^{2+}]$	$[Ca^{2+}]$	$\Omega^{max}_{CaF_2}$
Natural crystalline CaF_2 (fluorite) before gypsum precipitation								
35.7	7.40	19830	2710	11030	409	1330	412	0.032
39.6	7.19	21970	3060	12140	461	1460	470	0.042
71.4	8.87	39660	5420	22050	818	2660	824	0.090
79.1	8.68	43940	6110	24280	923	2930	939	0.115
107.2	10.1	59490	8140	33080	1230	3990	1240	0.155
118.7	11.0	65910	9160	36410	1380	4390	1410	0.163
158.2	14.0	87880	12220	48550	1840	5850	1880	0.178
Precipitated CaF_2 before gypsum precipitation								
39.6	18.3	21970	3060	12140	461	1460	470	0.007
79.1	21.0	43940	6110	24280	923	2930	939	0.020
118.7	27.3	65910	9160	36410	1380	4390	1410	0.026
158.2	41.7	87880	12220	48550	1840	5850	1880	0.020
Natural crystalline CaF_2 (fluorite) at the stage of gypsum precipitation before halite precipitation								
158.1	13.7	88220	12360	47560	1490	7140	1290	0.187
202.7	17.1	113350	15340	61440	1910	9630	1010	0.199
251.4	24.2	141240	18690	76340	2310	12090	699	0.153
296.8	37.7	168890	21200	89360	2760	14250	307	0.091
344.5	52.2	196480	24360	103740	3220	16480	198	0.064

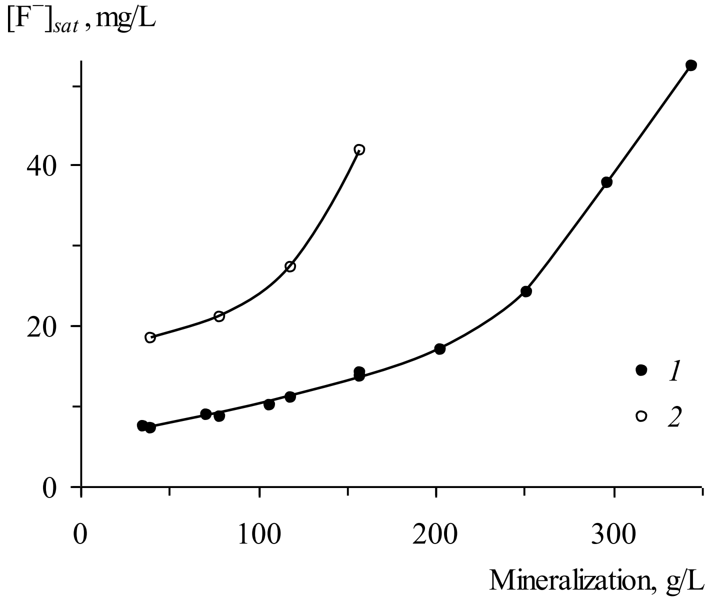

Figure 1. Relationship of the fluoride concentration in equilibrium with CaF_2 on the mineralization of seawater brine: (*1*) Natural crystalline CaF_2 (fluorite) and (*2*) precipitated CaF_2.

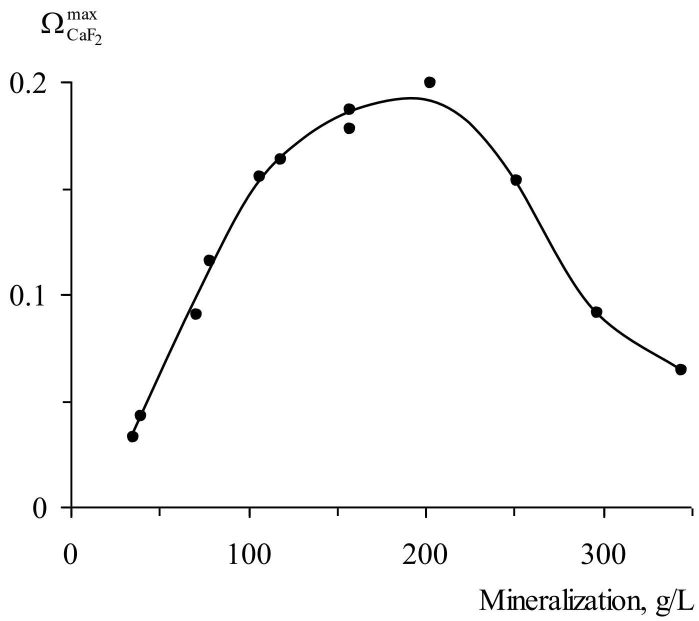

Figure 2. Relationship of the saturation degree by CaF_2 on the mineralization of seawater brine.

When fluorite is deposited, the fluoride content in the brine must correspond to the equilibrium concentration with this mineral $[F^-]_{sat}$. Furthermore, the maximum fluoride amount that could accumulate in the brine as a result of evaporation of seawater ($[F^-]_{br}$), according to (3), is equal to $k_{F/Cl}[Cl^-]_{br}$. The difference between these values can be used to determine the contribution of additional external sources of fluoride

$$\Delta[\mathrm{F}^-] = [\mathrm{F}^-]_{sat} - k_{\mathrm{F/Cl}}[\mathrm{Cl}^-]_{br}, \tag{5}$$

from which follows their proportion in the total amount of this element:

$$\beta_{\mathrm{F}^-} = 1 - \frac{k_{\mathrm{F/Cl}}[\mathrm{Cl}^-]_{br}}{[\mathrm{F}^-]_{sat}}. \tag{6}$$

As the experimental data showed, in the studied range of brine mineralization, the proportion of external fluoride sources exceeds the proportion of seawater fluoride, with the largest contribution of the latter (40–45%) occurring in the brine mineralization of 120–240 g/L (Figure 3). Geological observations agree with this conclusion.

Therefore, it can be argued that, in drying sea basins, which have limited water exchange only with the open ocean or none at all, the aqueous environment at the carbonate–gypsum stages of the evaporation process is strongly undersaturated by CaF_2. This means that the chemogenic formation of sedimentary fluorite is impossible under these conditions, which requires the supply of significant amounts of dissolved fluoride from external sources. Such sources may include the influx of river waters [23,28,29], the entry of volcanic exhalations and hydrothermal solutions [30–33], and the deposition of continental aerosols containing water-soluble components [34].

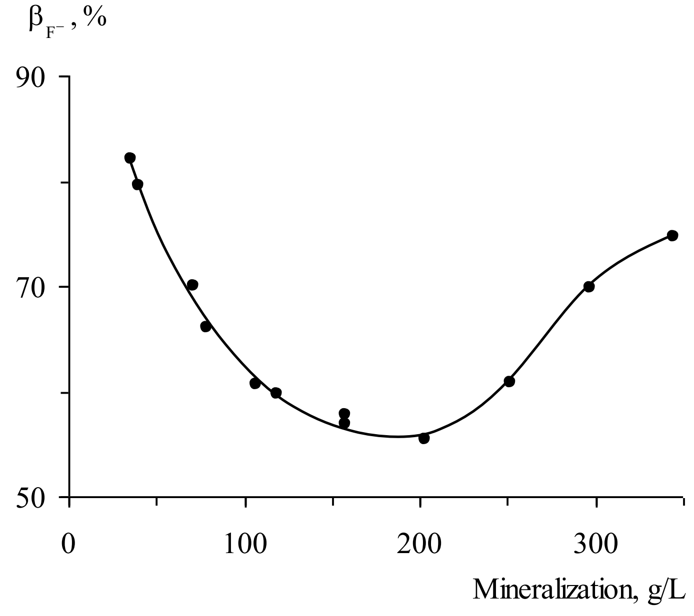

Figure 3. Contribution of external fluoride sources required for the formation of chemogenic CaF_2 in salinizing sea basins with different brine mineralization.

3.3. Waters of large continental reservoirs

Surface waters of large catchments in a humid climate are severely undersaturated with CaF_2 [35] and are, therefore, not considered here.

Large continental water reservoirs in the arid zone (for example, the Caspian Sea and the Aral

Sea before its drying up) are also undersaturated by fluorite to a varying degree (Table 1), but it has been found [20] that, in some residual basins formed as a result of the Aral Sea drying up (Figure 4), the state of saturation by CaF_2 is achieved (see Table 1). In the Small Aral Sea with relatively low mineralization (10.2–11.2 g/L), which brings the runoff of the Syr Darya River, the fluoride content is significantly less than the equilibrium concentration of 4.85 mg/L and is in the range of 2.54–3.16 mg/L. With an increase in mineralization from 86–105 g/L in Lake Tshchebas to 137–144 g/L in the western basin of the Large Aral Sea and to 150–159 g/L in the upper mixed layer of the meromictic Chernyshev Bay, a proportional increase in the fluoride concentration from 21.0 to 42.4 mg/L occurs, which, within the measurement accuracy, corresponds to the equilibrium values. A further increase in mineralization in the deep horizons of Chernyshev Bay to 306 g/L with developing anoxia is accompanied by a decrease in the fluoride concentration to 28.6 mg/L and an increase in the undersaturation by fluorite (Figure 5). In addition to the fluoride concentration decrease, a decrease in calcium concentration in the deep waters of Chernyshev Bay is observed, which is apparently associated with the precipitation of calcium carbonate and sulfate, which are among the major components of bottom sediments [36]. The removal of dissolved fluoride is caused by its coprecipitation with carbonate–sulfate mineral phases, since, under conditions of water saturation by fluorite, a decrease in the calcium concentration should lead to an increase in the fluoride content.

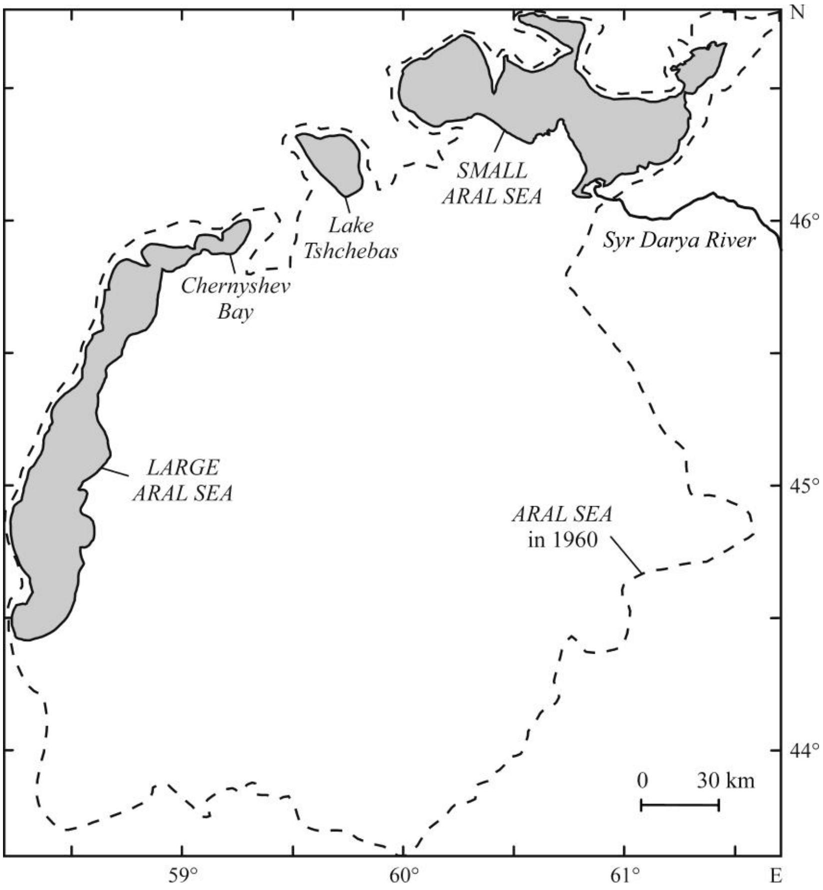

Figure 4. Location of residual basins formed as a result of the Aral Sea drying up in 2014–2015.

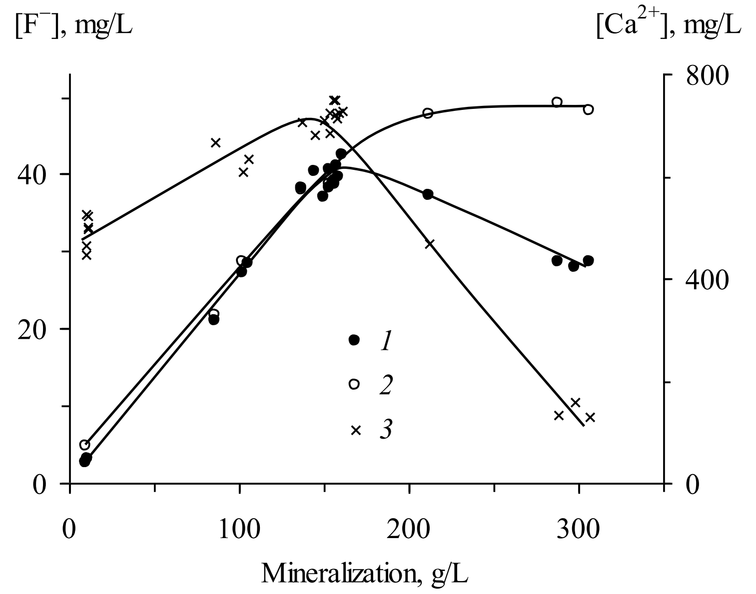

Figure 5. Relationships of natural (1) and equilibrium with CaF_2 (2) concentrations of fluoride and concentration of calcium (3) on the mineralization of waters of the Aral Sea residual basins in 2014–2015.

Thus, the most favorable conditions for the fluorite formation are realized in shallow evaporite basins of the second and third types: (ii) Basins with limited water exchange with the open ocean, containing fluoride supplied with seawater and with river runoff or from other external sources; and (iii) basins of internal runoff of arid territories.

4. Physicochemical mechanism of fluorite formation in sedimentary basins: The role of Mg

Any genetic hypothesis of fluorite formation in sedimentary basins must take into account and explain the preferential fluorite occurrence in magnesium enriched carbonate rocks. Since high-magnesian carbonates are formed mainly in salinized water reservoirs in the early stages of the evaporation process [27], the increased fluoride content in them may be due to the evaporative concentrating of seawater fluoride with some participation of external sources of this element. In this case, the deposition of magnesian carbonates, synchronous with the fluorite formation, is an accompanying process. Another, alternative explanation enables the possibility of a specific uptake of dissolved fluoride by magnesian carbonates, which should be significantly higher than its uptake by ordinary limestones. An experimental study of the fluoride coprecipitation with carbonate sediments [37,38] confirms the dependence between the content of fluoride and magnesium in the solid phase. However, the composition of the model solutions used in these studies did not correspond to that of natural waters.

We conduct long-term, 9-year, experiments to study the fluoride behavior during the interaction of seawater with the major sedimentary carbonate minerals, which were represented by synthesized samples of calcite, aragonite, and dolomite, as well as natural dolomite from the Domodedovo deposit (Moscow Region), crushed to a size of <20 μm. The specific surface areas of the samples are 0.45, 0.43, 0.48, and 0.40 m^2/g, respectively. The experimental results are presented in Table 4.

As shown in Figure 6, the fluoride uptake (x_F, μg/g) linearly depends on its final concentration in seawater ($[F^-]$, mg/L):

$$x_F = k[F^-], \quad (7)$$

and according to the value of proportionality coefficient k (Table 5), the studied carbonate minerals are arranged in the following order: dolomite >> calcite > aragonite.

Table 4. Changes in pH value, concentration of dissolved fluoride, and fluoride uptake after 9 years of interaction between carbonate minerals and seawater with a salinity of 35‰ at 22 ± 3 °C.

Mass ratio mineral/seawater m, g/L	pH	$[F^-]$ mg/L	$-\Delta[F^-]$	Specific fluoride uptake x_F, μg/g
0	7.90	1.29	–	–
Calcite (synthesis)				
6.25	7.81	1.28	0.01	2.2
12.5	7.81	1.26	0.03	2.2
25	7.80	1.24	0.05	2.1
50	7.80	1.19	0.09	1.9
100	7.79	1.12	0.17	1.7
200	7.78	0.99	0.30	1.5
Aragonite (synthesis)				
6.25	7.87	1.28	0.01	1.7
12.5	7.84	1.27	0.02	1.7
25	7.82	1.25	0.04	1.6
50	7.81	1.22	0.07	1.5
100	7.82	1.16	0.13	1.3
200	7.83	1.09	0.20	1.0
Dolomite (synthesis)				
6.25	7.92	0.90	0.39	63.0
12.5	7.92	0.69	0.60	48.1
25	7.92	0.46	0.83	33.3
50	7.92	0.22	1.06	21.3
100	7.91	0.11	1.18	11.8
Dolomite (natural)				
6.25	7.87	1.14	0.15	24.0
12.5	7.88	1.04	0.24	19.6
25	7.90	0.93	0.36	14.5
50	7.93	0.75	0.54	10.8
100	7.96	0.50	0.79	7.9

Table 5. The proportionality coefficient *k* in equation (7) for carbonate minerals at fluoride uptake from natural seawater with a salinity of 35‰ containing 1.29 mg F/L.

Mineral	Proportionality coefficient *k* in equation (7)	Correlation coefficient *r*	x_F (μg/g) at [F$^-$] = 1.3 mg/L
Calcite (synthesis)	1.6	0.930	2.1
Aragonite (synthesis)	1.2	0.739	1.6
Dolomite (synthesis)	71.6	0.986	93.1
Dolomite (natural)	18.0	0.918	23.4

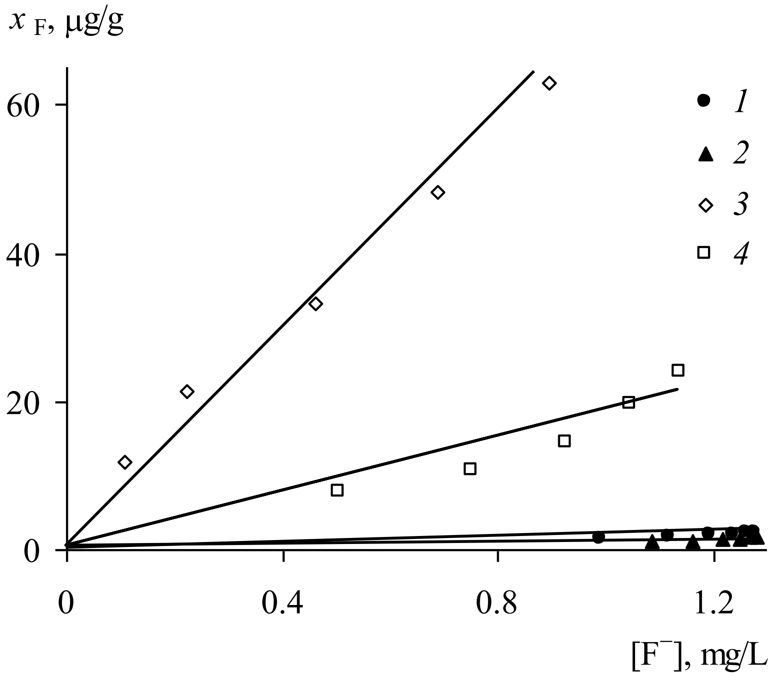

Figure 6. Relationship of the fluoride uptake by carbonate minerals on the final fluoride concentration in seawater: (1) Calcite (synthesis), (2) aragonite (synthesis), (3) dolomite (synthesis), and (4) dolomite (natural).

The less intense fluoride uptake by natural dolomite compared to the chemically pure synthesized phase is due to the initial presence of fluoride in it (~680 μg/g). The significantly greater fluoride accumulation in dolomite relative to calcite and aragonite is qualitatively consistent with experiments [37,38] on the fluoride coprecipitation with calcium carbonates of varying degrees of magnesiality (quantitative differences may be caused by the fact that the volume of the solid phase participates in the coprecipitation process).

The reason for the relationship between the amount of magnesium in carbonate minerals and the fluoride content in them is not clear. It should be only noted that the MgF^+ complex is much stronger in aqueous solutions than CaF^+ [39]. It can be assumed that a similar proportion is fulfilled during adsorption for the bonds between magnesium and calcium ions of the solid phase and fluoride ions in the solution. In this case, the fluoride adsorption on magnesian carbonates should be higher than on pure calcium carbonate, which is established experimentally.

P. Möller et al. [40] used the fact that a significant proportion of dissolved fluoride is present in the MgF^+ form to explain the mechanism of sedimentary fluorite deposition in dolomite rocks. According to their ideas, the partial removal of magnesium ions from the solution during the dolomite formation leads to a decrease in the MgF^+ concentration and an increase in the concentration of free F^- ions, which creates conditions for fluorite precipitation:

$$\begin{gathered} 3Ca^{2+} + 2MgF^+ + 4HCO_3^- = 2CaMg(CO_3)_2 + Ca^{2+} + 2F^- + 4H^+ = \\ = 2CaMg(CO_3)_2 + CaF_2 + 4H^+. \end{gathered} \tag{8}$$

Reaction (8) describes an important, but not the only possible process of the sedimentary fluorite formation. The occurrence of fluoride in carbonate minerals can also be associated with adsorption on the surface of formed particles or (and) entry into the crystal lattice of the solid phases during their release from the solution (in the process of coprecipitation). The adsorption value increases with increasing specific surface area of the solid phase and is generally higher for freshly formed precipitates with a large specific surface. During coprecipitation, the presence of defects in the crystal lattice, which are also more numerous in newly formed phases, facilitates the entry of chemical elements that are not coherent with its structure. After the separation of finely dispersed sediments with a defective crystal lattice from the solution, the lattice gradually becomes ordered, and the dispersion degree decreases. Over time, this leads to the removal of some of the initially coprecipitated and adsorbed components from the solid phase and an increase in their concentration in the pore solution.

The primary dolomite phase, protodolomite, is characterized by an exceptionally high defectiveness of the crystal lattice. This ensures the capture of large quantities of various impure elements at the stage of sediment formation and their influx into the pore waters during subsequent autolysis (purification as a result of recrystallization) of protodolomite, as well as calcite and aragonite. If the concentrations of chemical elements in pore waters increase to the state of supersaturation by certain compounds, new minerals are formed at the stage of diagenesis. In this way, fluorite may be formed in carbonate rocks, primarily in dolomites. This hypothesis is supported by the fact that the bulk of fluorite in carbonate rocks is formed after sedimentation at the bottom of the reservoir.

5. Conclusions

Seawater and products of its evaporative concentrating with a small contribution of fluoride influx from external sources (river runoff, volcanic exhalations, and terrigenous aerosols) are not saturated by CaF_2. This excludes the chemogenic fluorite formation in isolated marine evaporite basins or basins with an insignificant fluoride supply from the outside. The fluorite formation in marine basins is possible at the carbonate–gypsum stages of the evaporation process if the fluoride influx from external sources is at least 1.5–4 times greater than the fluoride contribution of marine origin.

In the waters of large continental reservoirs of the arid zone, the fluoride content is much higher than in seawater. In some cases, for example, in the most saline residual basins of the modern drying Aral Sea, a state of saturation by CaF_2 is reached, and conditions for the formation of sedimentary fluorite arise.

The presence of magnesium in sedimentary carbonate minerals promotes the fluoride accumulation in them. Based on the intensity of the dissolved fluoride removal from seawater, carbonate minerals are arranged in the following order: dolomite >> calcite > aragonite, and the fluoride uptake by dolomite is 40–60 times higher than by calcite and aragonite. Moreover, magnesium is an important factor controlling the fluoride content in sedimentary carbonate rocks.

The association of fluorite with dolomites may be due to two successive processes. Initially, the dissolved fluoride is taken up by the freshly precipitated protodolomite phase, which is highly dispersed and characterized by the greatest defectiveness of the crystal lattice, favoring the capture of impurities, including fluoride. The subsequent transformation of protodolomite into dolomite at the stage of early diagenesis is accompanied by a decrease in the dispersion degree and ordering of the crystal lattice. This leads to the removal of some previously uptakes of fluoride from the dolomite, which passes into the pore solutions and creates supersaturation by CaF_2, which is necessary for fluorite formation.

Author contributions

The authors jointly carried out the research and wrote the manuscript.

Use of AI tools declaration

The authors declare they have not used Artificial Intelligence tools in the creation of this article.

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Conflict of interest

The authors declare no conflicts of interest in this paper.

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