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CONDITIONS OF THE FORMATION OF FLUORITE IN SEDIMENTARY ROCKS
(The Fluorite System)

By A. V. Kazakov and E. I. Sokolova

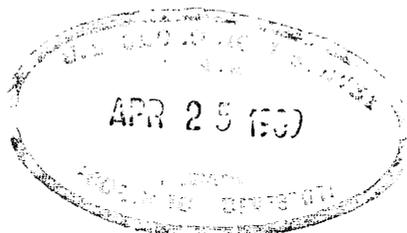
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TRANSLATOR'S ABSTRACT

The formation of fluorite in sedimentary rocks has been investigated by studies of fluorite equilibria in different solutions. Determinations at different temperatures were made on the solubility of crystalline CaF_2 in chemically pure water, in aqueous solutions of components of sea water-- CaSO_4 , NaCl , Na_2SO_4 , and MgSO_4 --at different concentrations, and in the sea water itself at degrees of salinity varying from normal to a 15-fold concentration. Conclusions are reached on the effects of the various salts and on the consequent possibilities of fluorite precipitation in basins of different types. Facies conditions of fluorapatite and fluorite deposition are derived for successive states of evaporation of saline basins, and the use of the fluorine-phosphorus coefficient as a facies index is suggested. Literature is reviewed.

V. L. S.

CONDITIONS OF THE FORMATION OF FLUORITE IN SEDIMENTARY ROCKS
(The fluorite system)

By

A. V. Kazakov and E. I. Sokolova (1)

I. GEOLOGIC CONDITIONS OF DEPOSITS OF SEDIMENTARY FLUORITE

A. First stage of geologic investigations (1809-1925)

The development of investigations on the origin of sedimentary fluorite falls distinctly into several stages. The first stage covers the period from 1809 to 1925 and can be characterized by a decided preponderance of genetic hypotheses of a biolitic type (C. Andrée, Ia. V. Samoilov, A. E. Fersman), and by a quest for a relation to magmatic, fumarolic, and hydrothermal processes (A. P. Karpinskii, B. P. Krotov, A. Knop, and others).

Fluorite in sedimentary rocks was first discovered and described in an exposure on the banks of the Ratovka River near the town of Vereia, Moscow province, by G. Fisher von-Waldheim, who was also the first to give it the name of "ratovkite". As is now known, this friable, earthy mineral can be assigned to sediments of the Kashira horizon of the Middle Carboniferous (C_2^k). In 1848 the field observations were repeated by Professor Roulié; the chemical analyses were carried out and rendered more precise by R. Herman.

(1) A co-editor of this paper is A. G. Bergman, Ph.D. in chemical sciences.

In 1841, I. Lagusen reported new discoveries of ratovkite in the region of the upper Volga River, within the Staritsk and Zubtsovsk districts. Ratovkite was referable here to the same Kashira horizon.

The English geologist V. Mackie (1901), who investigated the halogenic Triassic sediments of England and Germany, found in them an abundant accumulation of fluorite and ascribed to it a typical sedimentary halogenic origin resulting from the drying of relict basins.

Almost half a century after the studies of Roulié and Lagusen, Russian geologists and lithologists again became interested in fluorite of sedimentary rocks. As a result, special geologic studies were organized in 1912-14 for the investigation of fluorites in the region of the upper Volga River (Sergeev, 1912, 1914) on the initiative of A. E. Fersman. However, the origin of ratovkite remained completely uncertain.

In 1915 an investigation of ratovkite in the Moscow province was reported by A. P. Karpinskii, who concluded that ratovkite is genetically connected with deep magmatic intrusions (emanation of fluorine). At about the same time Professor Ia. V. Samoilov (1910, 1915) advanced his biolitic theory of the formation of sedimentary fluorite (fixation of fluorine and phosphorus by the skeletons of biologic organisms.)

In 1916 the deposits of ratovkite on the upper Volga River were studied by the academician A. E. Fersman in association with V. I. Kryzhanovskii and L. A. Kulik. As a result of this work, Fersman arrived at a genetic concept; his hypothesis occupied a middle position and aimed to reconcile the conflicting views of A. S. Sergeev and A. P. Karpinskii on the one hand ("emanation of fluorine compounds" connected with processes of "tectonic, magmatic, and hydrothermal character, which

developed along the periphery of the Moscow sea" --Fersman, 1922, p. 152), and of Ia. V. Samoilov on the other hand (biolitic origin of phosphorites as the primary form of fluorine compounds, with a subsequent separation from them of fluorine and its fixation as ratovkite).

The unsoundness of these genetic concepts will become apparent in the course of the present paper. Fersman eventually reached, in essence, such a conclusion when he wrote in his work of 1934: "Really, the nature of the formation of the so-called ratovkite has remained far from clarified."

In 1917 B. P. Krotov published a paper in which he connects the genesis of ratovkite in the Southern Urals (right bank of Lakla River at its issue into Ai River, limestones C.) with juvenile waters containing SiF_4 . The scheme of the reaction is:



Eventually B. P. Krotov (1928) abandoned this genetic scheme and adopted the hypothesis of a sedimentary formation of ratovkite in saline relict basins.

B. Second stage of geologic investigations (1926 - 1945)

The second stage of the development of geologic-lithologic research on sedimentary fluorite is already characterized by prevalence of hypotheses of a sedimentary origin of ratovkite and a more precise knowledge of the condition of facies, as exemplified by the work of A. P. Ivanov (1926), B. P. Krotov (1928), L. V. Pustovalov (1937), G. I. Bushinskii (1936), V. P. Baturin (1938), L. M. Miropol'skii (1939, 1941), and others.

A. P. Ivanov reported in his geological-stratigraphic paper, summarizing data on the Carboniferous of the Moscow area, that there are numerous occurrences of ratovkite in the basin of the Upper-Vom' River (Tver' province) which can be referred to the Kashira horizon (C_{II}^2). As an experienced field geologist, Ivanov is one of the first Russian investigators to arrive at the conclusion of a sedimentary origin of ratovkite: "with the discovery of a colorless, fluorine-containing mineral in C_2 (Kashira horizon) the origin of ratovkite ceases to be a riddle and must be considered as one of the particular cases of the secondary deposition of minerals from compounds already contained in sedimentary strata" (Ivanov, 1926, p. 139).

It is also necessary to note the valuable work of B. P. Krotov (1928), who described Upper Permian fluorites in paragenetic association with gypsum-bearing dolomites and arrived at the conclusion of a probable chemogene origin of fluorites from evaporating sea waters.

In the same year, 1928, I. I. Ginsburg published a note on the discovery of fluorite in the limestones of the western fringe of the Don Basin.

In 1936 the papers of N. S. Zaitsev and G. I. Bushinskii described for the first time fluorite occurrences in the Ozerski district, discovered in exposures along the Oka River and referable to the Kashira horizon of the Middle Carboniferous. The fluorite is found here in the form of lenses of red fluoritic sandstone. These red sediments were studied and described geologically and lithologically as early as 1929 by V. S. Iablokov, who characterized them as polymict, texturally slantingly schistose, and containing much fluor spar. G. I. Bushinskii gave no genetic hypothesis for the fluorites of the Ozerski district,

saying: "the local conditions of the concentration of fluorine are not clear." In 1936 N. A. Uspenskii discovered fluorite in a gypsum-celestite deposit in the Kaslinsk district of the Cheliabinsk region, in Permian sediments. The fluorite occurs here in the form of inclusions in syngenetic celestite concretions.

In the same year, 1936, a report was published by Ia. Ia. Iarzhemskii, who detected fluorite in dolomitized portions of the subsalt strata of Middle Cambrian age in the Priangar'e region of Siberia.

The next year, 1937, saw the publication of the comprehensive work of L. V. Pustovalov dealing with ratovkite in the region of the upper Volga River and presenting results of field observations and lithologic studies. This work gives also the materials of geologist E. A. Moldavskaja (who continued to investigate ratovkite in subsequent years). The author reached the conclusion that the sediments of the Kashira horizon in the upper Volga region had a cyclic character and that the maximum primary concentration of fluorite is to be referred to the upper dolomitic sediments of each cycle. The infinitesimally small crystals of fluorite are syngenetic with the enclosing rock and constitute the first chemical sediment of a saline basin. Larger crystals of fluorite are mostly of secondary origin, being formed by a recrystallization of the small, syngenetic, highly dispersed crystals of fluorite in the upper parts of each sedimentary cycle.

Of particular value are Pustovalov's observations on the cyclic character of accumulations of sediments and of correlations between the content of fluorine and of phosphorus in sediments (the "fluorine-phosphorus scissors"). At the beginning of each cycle the sediments are relatively high in phosphorus and very low in fluorine; at

the end they contain very little phosphorus and much fluorine. Regrettably, these interesting relations between fluorine and phosphorus were not duly clarified and interpreted.

At about the same time L. V. Pustovalov and his associates discovered fluorite in the dolomitic rocks of Upper Permian age in the region of Sterlitanak and the Orenbursk Steppe.

In the same year, 1937, V. P. Baturin found fluorite in the area of the salt dome in the Emba River, where it is present in insoluble residues of the Kungur limestones and dolomites of the Urals-Emba region; in 1938 and 1940 E. N. Egorova (VSEGEI) established the existence of a heightened content of fluorine (from 0.6 to 1.4 percent) in this same region. The fluorite is concentrated here principally in the heavy fraction, together with celestite (80.3 percent). The source of the fluorine, according to the author, is sea water.

Increased concentrations of fluorine were found in recent years by Iu. V. Morachevskii in the insoluble residues of some potassium salts.

These investigations were lately broadened by M. G. Valiashko (of the Vsesoiuznyi Nauchnoissledovatel'skii Institut Galurgii), who pointed to the following distribution (concentration) of fluorine in the salt strata of Lake Inder:

Halite	0.001-0.0001% F.
Sylvite.	mostly 0.02-0.03% F of total amount of salt.
Cap-rock	secondary concretions of fluorite.
Borates: (a) ascharite -	up to 1% and even 10% F;
(b) calcium borates -	0.0X% F.

In 1939 and 1941 L. M. Miropol'skii reported finding fluorite in the Kazan' ($P_2^{\text{Kaz.2}}$) anhydrites of the Cheboksary district, the Kungur (P_1^{K}) dolomites of the lower ranges of the Kama River, and the Artinsk ($P_2^{\text{Art.}}$) gypsum-bearing dolomites and Upper Carboniferous (C_3) gypsum-bearing dolomites within the basin of the Kama River, mainly in drill cores. The fluorite occurs in paragenetic association with celestite and chalcedony. Miropol'skii correctly refers the fluorite of sedimentary rocks to chemogene formations of halogenic facies deposited from sea water of high concentration.

In 1940 M. S. Shvetsov reported the presence of small crystals of fluorite in the Carboniferous strata of the Moscow area, as observed in cores from Moscow and Dvinsk structural boreholes.

V. P. Florenskii (1941) detected fluorite in the Kungur halogenic strata of the Tuimazy oil deposit. The maximum fluorite concentration occurs in dolomitic interstratifications underlying the anhydrite-dolomite strata. The size of the fluorite grains is mostly 0.1 - 0.3 mm., $Nm = 1,435 \pm 0.002$.

V. P. Maslov, who in 1944 studied the sediments of the Middle Carboniferous in the area of Rzhev and Staritsa, definitely stressed in 1945 the paragenetic association of fluorite, developed in the sediments of the Kashira horizon, with gypsum (both primary and secondary) and with dolomite and opal-chalcedony.

The recently published comprehensive work of A. N. Churakov (1947) stands somewhat in a class by itself. Its author, adhering to the views of A. P. Karpinskii and V. I. Vernadskii, expresses himself in favor of a direct genetic relation between sedimentary fluorite and the volcanogenic-fumarolic processes connected "with the alkaline

fluorine-bearing rocks bordering the Russian table lands." On our part, we do not deny, of course, the important role of the volcanogenic-fumarolic processes as powerful sources of the propulsion of chlorine and fluorine on their way to the world's oceans. But we pursued a different objective in our work. The salt content of the world's oceans is determined by a shifting equilibrium in their salt balance, established during geologic time and showing on the average a fluorine content of 1 mg./lt. in the sea water of normal salinity. This salt content of oceans is very stable and does not change practically over the entire globe either in the horizontal or in the vertical direction. Therefore, without asking ourselves the question of the origin of the salt in the water of the oceans and more particularly the question of the sources of fluorine, we investigated a more restricted problem: Is sedimentation of fluorite in sea basins possible, under what geologic-lithologic conditions does this process develop, and where is its place in the solar diagram of evaporation?

C. General geologic conclusions on sedimentary fluorites

The review of literature on fluorite, presented above, makes it possible to approach closer to reconstructing the hydrochemical conditions of the origin of sedimentary fluorite and to determining the character of the distribution of respective facies. We summarize the conclusions reached by investigators.

1. Sedimentary fluorites cannot be referred to any definite period in the earth's history and are not related to any specific paleobiologic development of organic life. Sedimentary fluorites have been identified in sediments dating from the Cambrian to the lower Cretaceous inclusive. (See Table 1).

TABLE 1.

Deposits of sedimentary fluorite,
its paragenetic association and facies

/ Geologic Age	Location	Paragenetic association, facies	Author, Year of investigation
Cr ₁ Valanzhim	(a) Lower Cretaceous: Alps	Dolomites	Andrée, 1909
J ₁ Lower Lias	(b) Jurassic: Switzerland	Dolomites and dolomitized limestones; cement of red conglomerates; barite concretions	Duparc, 1898
T	(c) Triassic: England, Germany	Sandstones (cement); barite and halogenic facies	Mackie, 1901
P ₂ ^{kaz2}	(d) Permian: Cheboksary	Anhydrites with dolomite	Miropol'skii, 1941
P ₂	"	Gypsum-bearing dolomites	
P ₂	Belgium, Liège area	Red-brown limestone schists	Krotov, 1928
P ₁ ^k	Urals-Emba region	Salt domes	Baturin, 1938
P ₁ ^k	" "	Potassium salts, borates	Egorova, 1938
P ₁ ^k	Basin of middle Kama River	All halogenic sediments	-
P ₁ ^{Art} + P ₁ ^k	" "	Gypsum-bearing dolomites	Miropol'skii, 1941
C ₃	(e) Carboniferous: Urals	Limestones	Zaitsev, 1883
C ₃	Basin of middle Kama River	Limestones	Miropol'skii, 1941
C ₂	Urals; Zigan River, Saknarsk district	Adhesions on cracks in dolomitized limestone	Krestovnikov, 1936 (verbal communic.)

(TABLE 1 continued on following page)

TABLE 1 (continued)
Deposits of sedimentary fluorite, its paragenetic association and facies

Geologic Age	Location	Paragenetic association, facies	Author Year of investigation
C ₂ ^{pod}	Moscow basin	Limestones	-
C ₂	Upper Volga region - Rzhev, Staritsa, Zubtsov	Limestones, dolomites, dolomitized palygorskite	Lagusen, 1871 Pustovalov, 1937
C ₁ ^k	Zubtsov, Rzhev	Limestones, dolomitized	Maslov, 1945 Bushinskii, 1936
C ₁ ^k	Vereia	Palygorskite, dolomitized limestones	Sergeev, 1912
C ₂ ^k	Ozerki on the Oka River	Red fluoritic sandstone	Zaitsev, 1936 Bushinskii, 1936
C ₂ ^k	Oksko-Tsninskii embankment	Dolomitic facies	Trofimov, Kalmykov
C ₂	Donbas, Elenovskie pits	Along cracks in limestones	Orlovskii, 1934 Ginsburg, 1928
C ₁	Urals	In cracks and cavities in limestones	Krotov, 1917
C ₁	"	Limestones, bauxites	Smol'ianinov, 1928
C ₁	England, western Cumberland	Fluorite, red sandstones, barite	Lewis, 1931
D ₃ ¹	(f) Devonian: Urals	Bituminous limestones; upper horizons, along cracks	Krestovnikov, 1936 (verbal communic.)
D	England, Cardiff	Red fluoritic sandstone, barite	Heard & Davies, 1924
S ₂	(g) Silurian: U.S.A., Ohio; Ontario	Gypsum-bearing dolomites, celestite. Halogenic facies of a relict basin	Morrison, 1935

2. Attention is particularly drawn to the fact that fluorite can be referred to the saline facies of relict basins, namely, to dolomites and dolomitized limestones, gypsum, red rocks, anhydrites, potassium-magnesium salts, and celestite. There is a distinct antipathy between phosphorus and fluorine (phosphate facies preclude the formation of fluorite, and vice versa).

3. In the region of the upper Volga and the Oka rivers the fluorites of the Kashira horizon are disposed along the southwestern rim of the shallow, periodically salinified Kashira waterbasin (Rzhev, Staritsa, Vereia, Ozerki-Kashira, Oksko-Taninskii embankment - northward from the line Kasimov-Elat'ma). Intensive processes of halogenesis (gypsum, anhydrite, halite, less frequently fluorite) developed to the north and northeast of this zone, in the direction of the depression along the axis of the Moscow syncline. On the other hand, toward the south and southeast, nearer to the shore line, there occurred a considerable desalinification of the water in the basin; this part is characterized mostly by fragmentated organogenic limestones and by shoreline sand-and-clay sediments devoid of fluorite.

4. Sedimentary fluorite is a new and sensitive mineral index of the presence of halogenic facies, which can be used with the method of determining the "fluorine-phosphorus coefficient" proposed by us. The relatively slight solubility of fluorite (together with a sensitive reaction to F') makes it also suitable for solving questions regarding the time relation to halogenic facies of those sediments which do not contain any visible mineral remnants of halogenesis (gypsum and marls, the latter multicolored).

While the conditions of the formation of fluorite have become clearer in the light of geologic field observations, the details of the process of sedimentation of fluorite and of its paragenetic association with other products of halogenesis, their position in the "solar diagram" of evaporation of sea water, their relation to phosphorus and other fluorides, and also the geochemical history of fluorine in the weathered crust, -- these details still remain uncertain in many respects. The questions which they pose are the subject of our investigation.

To gain a more accurate knowledge of the conditions of the formation of fluorite in sedimentary rocks, we carried out systematic laboratory investigations of the systems of fluorite equilibria (as precipitated phases) in different solutions. Determinations were made of the isotherms (0-10-20 and 100° C) of the solubility of crystalline CaF_2 in chemically pure H_2O , in aqueous solutions of different concentrations of CaSO_4 , NaCl , Na_2SO_4 , and MgSO_4 (basic components of sea water), and in the sea water itself at various stages of concentration (evaporation) from a normal salinity to a 15-fold evaporation by volume (the field of anhydrite sedimentation).

II. THE SOLUBILITY OF FLUORIDES

(General comparative characterization)

Before presenting the results of our experimental investigations on the systems of fluorite equilibria, it is of interest to give a brief comparative outline of the solubility of fluorides. This problem is treated in the works of 44 authors. (See table 2).

The figures and other data cited from the literature will be classified by us under four basic groups of fluorides:

- I. Simple fluorides of metals and metalloids of various valency.
- II. Complex compounds of fluorides (of the type of cryolite, etc.)
- III. Fluosilicates of the type of K_2SiF_6 (hieratite)
- IV. Titanofluorides

Many minerals containing fluorine (See table 2) are not included in this scheme because the literature gives no data on their solubility.

Substantial advances in precision as to the solubility of NaF and KF were reported in the new publications of I. V. Tananaev and his associates, who studied the systems NaF-HF-H₂O and KF-HF-H₂O.

Among the conclusions reached by investigators we note the following:

(a) The existence of double salts of the type of NaF·HF, KF·HF, KF·2HF, KF·3HF, KF·4HF, and KF·5HF in the precipitated phases is established.

(b) In the presence of HF the solubilities of NaF and KF decline considerably because of the effect of a common ion and the formation of complexes; their minimum solubilities correspond to the figured points of the following systems:

Fluoride	Isotherm, t° C.	o/o fluoride	o/o HF	Precipitated phase	System
NaF	$\left\{ \begin{array}{l} 0 \\ 20 \\ 40 \end{array} \right.$	$\left\{ \begin{array}{l} 0.32 \\ 1.46 \\ 2.58 \end{array} \right.$	$\left\{ \begin{array}{l} 15.30 \\ 12.60 \\ 10.94 \end{array} \right.$	NaF·HF	NaF-Hf-H ₂ O
KF	$\left\{ \begin{array}{l} 0 \\ 20 \\ 40 \end{array} \right.$	$\left\{ \begin{array}{l} 9.86 \\ 17.45 \\ 26.25 \end{array} \right.$	$\left\{ \begin{array}{l} 64.13 \\ 64.12 \\ 60.54 \end{array} \right.$	KF·4HF	KF-HF-H ₂ O

TABLE 2

Summation table of the solubility of fluorides

Fluoride	t°C	Solubility in H ₂ O			% HF	Author and year of investigation	Notes
		MF		F			
		%	gr./lt.	mg./lt.			
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Fluorides of the metals MF, - Group Ia							
LiF	18	0.26	2.7	-	-	Mylius, 1897	
	25	-	1.51	1110	-	Carter, 1928	
	?	-	2.60	-	-	Fredenhagen and Cadenbach, 1930	
	25	0.132	-	-	-	Fajans, 1931	
NaF	15	3.85	-	-	-	Fremy, 1856	
	18	4.22	-	-	-	Mylius, 1897	
	21	4.04	-	-	-	Ditte, 1896	
	25	4.03	-	-	-	Clarke, 1919	
	25	-	40.54	18340	-	Carter, 1928	
	25	4.03	-	-	-	Fajans, 1931	System NaF-HF-H ₂ O
	25	-	37.70	-	-	Campbell and Campbell, 1939	
NaF·HF	0	0.32*	-	-	15.30	Tananaev, 1938, 1941	
	20	1.46*	-	-	12.60	Same	
	40	2.58*	-	-	10.94	"	
KF	18	48.0	-	-	-	Mylius, 1897	
	21	49.1	-	-	-	Ditte, 1896	
KF·2H ₂ O	?	-	380	-	-	Fredenhagen and Cadenbach, 1930	Method of electrical conductivity
	25	-	405	-	-	Campbell and Campbell, 1939	System
3KF·4HF	0	9.86**	-	-	64.13	Tananaev, 1938, 1941	KF-KCl-H ₂ O
	20	17.45**	-	-	64.12	Same	
	40	26.25**	-	-	60.54	"	
RbF·H ₂ O	18	75.06	-	-	-	Lannung, 1934	
CsF	18	85.36	-	-	-	" 1934	

* Minimum solubilities of NaF in the system NaF-HF-H₂O** Minimum solubilities of KF in the system KF-HF-H₂O

(TABLE 2 continued on following page)

TABLE 2 (continued)
 Summation table of the solubility of fluorides

Fluoride	t°C	Solubility in H ₂ O			% HF	Author and year of investigation	Notes
		MF		F			
		%	gr./lt.	mg./lt.			
Fluorides of the metals of Group Ib - monovalent heavy metals*							
AgF	15	57.5	-	-	-	Gore, 1870	
Fluorides of the metals of Group IIIa							
MgF ₂	0.3	9.04·10 ⁻³	0.0904	-	-	Kohlrausch, 1909	
	18	8.71·10 ⁻³	0.0874	-	-	Kohlrausch, 1909	
	27	8.41·10 ⁻³	0.0841	-	-	Kohlrausch, 1909	
	25	-	0.130	80	-	Garter, 1928	
CaF ₂ cryst.	0.05	1.31·10 ⁻³	-	6.37	-	Kohlrausch, 1909	Indirect method of electrical conduction of aqueous solutions
	16.08	1.48·10 ⁻³	-	7.20	-	Kohlrausch, 1909	
	18.00	1.50·10 ⁻³	-	7.30	-	Kohlrausch, 1909	
	26.59	1.60·10 ⁻³	-	7.79	-	Kohlrausch, 1909	
	40.00	1.67·10 ⁻³	-	8.13	-	Kohlrausch, 1909	
CaF ₂ colloidal synthetic	17.47	1.62·10 ⁻³	-	-	-	Kohlrausch, 1909	
	18.80	1.63·10 ⁻³	-	-	-	Kohlrausch, 1909	
	26.11	1.62·10 ⁻³	-	-	-	Kohlrausch, 1909	
	18.00	1.80·10 ⁻³	0.018	-	-	Auméras, 1927	
CaF ₂ calcined 800°C.	18	1.51·10 ⁻³	0.0151	7.40	-	Mougnand, 1931	Average of 3 experiments
CaF ₂ freshly sedimented 100°C.	31	1.83·10 ⁻³	0.0183	8.91	-	" , 1931	Average of 4 experiments
	206-210	2.96·10 ⁻³ Autoclave	0.0296	14.41	-	Thugutt, 1936	Method of sedimentation of CaF ₂ in the presence of CaCl ₂

* There is an interesting regularity in the solubility of the halides of these elements: Solubility increases with a decrease in the atomic weight of the halogen. Fluorides have precisely a maximum solubility, which in itself is sufficient for pre-determining their non-existence as minerals in sedimentary rocks.

(TABLE 2 continued on following page)

TABLE 2 (continued)
Summation table of the solubility of fluorides

Fluoride	t°C	Solubility in H ₂ O			% HF	Author and year of investigation	Notes
		MF		F			
		%	gr./lt.	mg./lt.			
Fluorides of the metals of Group IIIa (continued)							
SrF ₂	0.26	1.135·10 ⁻²	0.1135	-	-	Kohlrausch, 1909	
	17.38	1.171·10 ⁻²	0.1171	-	-	Kohlrausch, 1909	
	18.00	1.173·10 ⁻²	0.1173	-	-	Kohlrausch, 1909	
BaF ₂	17.2	-	1.603	-	-	Kohlrausch, 1909	It is well to note the paper of I. A. Tananaev and S. N. Chrelashvili "On the Solubility, of CaF ₂ , MgF ₂ , BaF ₂ , and SrF ₂ ."
	18	-	1.605	-	-	Kohlrausch, 1909	
	25	-	1.21	260	-	Carter, 1930	
Fluorides of the metals of Group IIb and other divalent metals							
ZnF ₂	20	-	16.0	-	-	Kohlrausch, 1909	Solid phase ZnF ₂ ·4H ₂ O
	25	-	15.16	3280	-	Carter, 1928	
	20	-	16.2	-	-	Kurtenacker, 1933	
CdF ₂	25	about 4.3	43.6	-	-	Jaeger, 1901	
	25	-	6.22	1570	-	Carter, 1928	
	20	-	40.6	-	-	Kurtenacker, 1933	
	25	-	43.5	-	-	Kurtenacker, 1933	
HgF ₂	-	-	-	-	-	-	Noticeable hydrolysis

(TABLE 2 continued on next page)

TABLE 2 (continued)
Summation table of the solubility of fluorides

Fluoride	t°C	Solubility in H ₂ O			% HF	Author and year of investigation	Notes
		MF		F			
		%	gr./lt.	mg./lt.			
Fluorides of the metals of Group IIb and other divalent metals (continued)							
CuF ₂	25	0.075	0.750	280	-	Carter, 1928 Kurtenacker, 1933	System CuF ₂ -HF- -H ₂ O
	20	-	-	-	-		
MnF ₂	25	1.860	1.860	760	-	Carter, 1928	
CoF ₂	20	-	13.3	-	-	Costachescu, 1911 Carter, 1928 Kurtenacker, 1933	System CoF ₂ -H ₂ O
	25	-	14.15	5540	-		
	20	-	13.60	-	-		
NiF ₂	25	-	40.30	15840	-	Carter, 1928 Kurtenacker, 1933 Kurtenacker, 1933	Solid phase NiF ₂ -4H ₂ O
	10	2.49	-	-	-		
	20	2.50	-	-	-		
Fluorides of trivalent metals							
Fe ⁺⁺⁺ F ₃ *	25	2.30	-	-	0.52	Tananaev and Deichman 1945, 1946	Solid phase FeF ₃ ·H ₂ O + 4FeF ₃ ·2KF· ·H ₂ O
	25	0.005	-	-	2.89		
Fe ⁺⁺⁺ F ₃	25	0.001	-	-	4.00	" "	4FeF ₃ ·11KF· ·12H ₂ O
	25	-	0.91	460	-		
AlF ₃	25	-	-	3790	5.59	Carter, 1929 Tananaev and Abilov, 1942 Tananaev and Lel'chuk, 1947	
	25	-	-	-	-		
MnF ₃	25	-	1.860	-	-	Carter, 1928	

* Minimum solubility in the system FeF-KF-H₂O (selectively).

With an increase of valence, the positive electrical character of metals decreases and, correspondingly, the hydrolysis of their salts in aqueous solutions is intensified. This relation applies also to all trivalent metals (of Group III). Still more it applies to those fluorides (salts of weak acidity) in the case of which hydrolysis progresses very far, -- up to the formation of basic salts and even of the free hydroxides of the metal. Most resistant to hydrolysis is $Mn^{+++}F_3$. Heating facilitates hydrolysis.

From this viewpoint the above-cited figures on the solubility of the fluorides Fe^{+++} and Al (Carter) need to be made more precise. For example, the work of I. V. Tananaev and E. Deichman (1945) shows that the solubility of $Fe^{+++}F_3$ reaches 560% in chemically pure water at 25° C., whereas it declines to 0.0004% (4 mg./lt. FeF_3) in the presence of 1% NaF because of the formation of the complex, poorly soluble salt $2FeF_3 \cdot 5NaF$ and the effect of the excess of the common fluoride ion (NaF).

In the system FeF_3 -KF- H_2O , for example, we have at 25° C. the following equilibrium points (selectively):

% FeF_3	% KF	Precipitated phase
2.30	0.52	$FeF_3 \cdot 3H_2O + 2KF \cdot FeF_3 \cdot H_2O$ $11KF \cdot 4FeF_3 \cdot 12H_2O$
0.005	2.89	
0.001	4.00	

Relations close to these take place in the case of AlF_3 (Tananaev and Lel'chuk, 1947).

Fluorides of the metals of Group IV. - The halides of quadrivalent metals in aqueous solutions are still more unstable than the salts

of the metals of Group III. They are usually synthesized by the dry method. Exceptions are elements of lower periods (VI, VII) with a high atomic weight, for example lead (period VI, serial no. 82). The solubility of the fluoride of lead (PbF_4) at different temperatures is as follows:

$t^\circ\text{C}$	% PbF_4	gr./lt. PbF_4	mg./lt. F	Author, year
9	5.98×10^{-2}	about 0.598	-	Kohlrausch, 1909
18	6.41×10^{-2}	-	-	" 1909
26.6	6.91×10^{-2}	-	-	" 1909
25	-	0.66	100	Carter, 1928

The fluorides of the metals of Groups V - VIII have been investigated very little.

A. Complex compounds of fluorides

Fluorides, and generally the halides of the metals III, IV, and higher groups, have a well developed capacity for forming various complex compounds, among which we note first of all compounds of the type $x\text{MF} \cdot \text{RF}_3$, where $\text{R} = \text{Al}, \text{Fe} \dots, \text{Cr}$; $\text{M} = \text{Na}, \text{K}$; and $x = 3, 2, \text{ or } 1$. Such a structure is possessed by the natural mineral cryolite and by a number of other minerals of this group. These compounds are slightly soluble in water and apparently become partly hydrolyzed. We give below the data available in the literature.

Fluoride	$t^\circ\text{C}$.	%	gr./lt..	Author and year of investigation
Li_3AlF_6	20	1.070	-	Weinland and Koppen, 1899; Carter, 1928
Na_3AlF_6 (cryolite)	-	0.411	-	Treadwell and Köhl, 1926
"	20	0.285	151	Tananaev, 1939
K_2AlF_6	20	1.580	-	Tananaev, 1932
$\text{Ca}_3(\text{AlF}_6)_2$	-	easily dissoluble	-	Tananaev, 1932
$5\text{NaF} \cdot 2\text{FeF}_3$	-	-	-	Tananaev and Deichman

It is well to stress once more that the above-indicated figures on the solubility of fluorides refer to chemically pure H_2O as the dissolving agent.

In the case when a system contains common ions, the solubility of salts can change considerably. As regards cryolite, for example, an experimental paper was published in 1947 by I. V. Tananaev and Iu. L. Lel'chuk on the system $AlF_3-NaF-H_2O$ at $25^\circ C.$; according to these workers the equiponderant solubility of AlF_3 in this system is expressed by the following data (selected figured points): (1)

% AlF_3	% NaF	Precipitated phase	Notes
-	0		The "seasoning" period for the systems equals 8-12 hours, with continuous mixing
0.5284	0.060	} $11NaF \cdot 4AlF_3$ (cryolite)	
0.00088*	0.880		
0.0011	1.276		
-	1.381	$11NaF \cdot 4AlF_3 + 3NaF \cdot AlF_3$	
-	1.381	Field $3NaF \cdot AlF_3$	

* Corresponds to about 8.8 mg./lt. AlF_3 .

Analyzing samples of the crystals of natural Greenland cryolite and of synthetic cryolite, the authors ascribe to cryolite the formula $11 NaF \cdot 4AlF_3$, instead of the usually accepted formula $3NaF \cdot AlF_3$. Such a contention, based purely on calculations of analytical balances of F, seems to us at least premature. If consideration is given on the one hand to the regularity in the highly developed isomorphism of the fluoride-ion and hydroxylion in natural minerals (see Fig. 4), demonstrated and stressed by us, and on the other hand to the well developed capacity of fluor-aluminum for forming the basic fluorides of aluminum of the type $AlF(OH)_2$ and $AlF_2(OH)$, then the gross formula of cryolite $11NaF \cdot 4AlF_3$

(1) See also the previously published analytical-theoretical paper on this system by I. V. Tananaev and Sh. Talipov (1939).

can be harmonized with good probability into the formula $12\text{NaF} \cdot 3\text{AlF}_3 \cdot \text{AlF}_2(\text{OH})$ or $3\text{NaF} \cdot \text{AlF}_2(\text{OH})$.

In sedimentary rocks these compounds are unstable; the minerals of the cryolite group are to be referred to zones of pneumatolysis.

B. Salts of hydrofluoric quadrivalent metals

In a complete review reference should also be made to the salts of the hydrofluoric acids of quadrivalent metals, among which the most common and well investigated is the group of H_2MF_6 , where Me = Si, Ti, Zr, and others, and where the hydrogen is replaced by metals of the Groups I and II.

The fluosilicates of the alkalis contain no water, and the least soluble among them is the K-salt. The solubility of the fluosilicate metals of Group II decreases from the light metals to the heavy metals; the fluosilicate of Ba has the least solubility in water.

Fluoride	t°C	%	gr./lt.	Author and year of investigation
Na_2SiF_6	0		4.350	Carter, 1930
"	20		7.350	" 1930
K_2SiF_6	0		0.770	" 1930
Hieratite	16		1.320	" 1930
CaSiF_6	-		105.8	Carter, 1930
BaSiF_6	0		0.150	" 1930
"	16		0.190	" 1930
"	25		0.250	" 1930
CuSiF_6	20	59.08 † 0.11		Worthington, 1931
ZnSiF_6	20	49.94 † 0.23		
MgSiF_6	20	37.94 † 0.29		

The solubilities of the titanofluorides were determined in 1931-1932 by Ginsberg:

Fluoride	t°C	% fluoride	Author and year of investigation
Li ₂ TiF ₆	20-22	480	Ginsberg, 1931
Na ₂ TiF ₆	-	65 ± 5	" 1931
K ₂ TiF ₆	-	12 ± 1	" 1932
Rb ₂ TiF ₆	-	8 ± 1	" 1931
Cs ₂ TiF ₆	20-22	25 ± 1	" 1931-1932

As can be seen from the table, the titanofluorides are more soluble than the respective fluosilicates and thus offer little interest for our purposes (they do not occur as minerals in sedimentary rocks).

C. Conclusions

Among all the investigated fluorides the least soluble in water is CaF₂ (fluorite).

The fluorides of the other metals and metalloids possess a considerably greater solubility, which explains the universality of fluorine concentration in sedimentary rocks especially in the form of two minerals: fluorapatite and fluorite.

Of the minerals containing fluorine, the following few varieties are known to occur among sedimentary rocks:

No.	Minerals	Facies		
		Marine		Continental (salt lakes)
		Normally saline	Over-saline	
1	Apatite	†	-	-
2	Fluorite CaF ₂	-	†	-
3	Sellaite MgF ₂	-	† (?)	-
4	Schairerite	Group of sulfatochalodes		†
5	Sulfohalite			
6	Fluoborite			

III. THE SOLUBILITY OF FLUORITE IN CHEMICALLY PURE WATER - THE POLYTHERM

A. The characteristics and preparation of fluorite

A pure fluorite in large crystals was used in our experiments. It was obtained from the collection of the Mineralogical Institute of the Academy of Sciences of USSR and came originally from the region of the Tadzhik SSR. We pulverized it in an agate mortar, sifted it through a sieve of 0.25-mm. mesh, treated 100 gr. in a glass with hydrochloric acid (diluting 4 ml. HCl 37.23% to 100 ml. with H₂O) while mixing thoroughly, left it standing for half an hour to precipitate, and poured off the solution remaining above the sediment. This procedure was repeated twice. The sediment CaF₂ was next washed in distilled water, with decantation, until there was no reaction to Cl⁻ (AgNO₃), and the residue was dried in an oven at 30° C. The washed and dried CaF₂ was then placed in 10-gr amounts in bottles, --one sample per bottle, --and 200 ml. of distilled water was poured into each bottle. In all experiments the ratio of the solid phase (S) to the liquid phase (L) was: S:L=1:20. The bottles were put into a constant temperature bath and mixed to obtain an equilibrium more rapidly. From time to time samples taken of the liquid phase were analyzed for their content of fluorine.

In all our experiments, fluorine in the solutions was determined colorimetrically; zircon was determined by the alizarin method of Bear-Thompson and Taylor, with a preliminary removal of fluorine according to Willard-Winter in a number of cases.

B. Comparative solubility of alkaline-earth fluorides

The literature generally contains a relatively limited number of papers on this subject. We will review the principal ones among them, mainly in application to the subject of our investigation - fluorite.

1. Solubility

Table 3 gives the data obtained by Kohlrausch (1909) and by Campbell and Campbell (1939) on the solubility of fluorite.

TABLE 3

Solubility of fluorides in chemically pure water
(comparative table)

Fluoride	% content of F	t°C	Concen- tration of fluoride, mg./lt.	Concen- tration of fluoride - ion, mg./lt.	Author and year of investigat- ion	Method
CaF ₂ natural	48.67	18	15.0	7.3	Kohlrausch, 1908	Elec- trical conduct- ivity
CaF ₂ synthetic	48.67	18.8	16.3	-	" 1908	"
MgF ₂	60.98	18	87.4	53.3	" 1908	"
SrF ₂	-	-	-	-	-	-
BaF ₂	17.98	25	1910	343.4	Campbell, 1939	Chemical analysis
NaF	45.24	25	37 700	-	" 1939	"
KF	-	25	495 000	-	" 1939	"

It can be seen in Table 3 that, among the alkali and alkaline-earth fluorides, fluorite CaF₂ has the least solubility. The fluorides of magnesium, strontium, and barium possess a much higher solubility, owing to which usually they do not occur in sedimentary strata.

2. Factor of temperature

The dependence of the solubility of fluorides on temperature has been studied for CaF₂ and MgF₂ by Kohlrausch (1909), in part also by the Polish mineralogist Thugutt, and experimentally by us in 1944. The results are summarized in Table 4.

TABLE 4

Solubility of CaF_2 and MgF_2 in chemically pure water
(in mg./lt.), as a function of temperature

t°C	CaF_2 crystalline		CaF_2 synthetic	MgF_2	Author and year of investigation
	CaF_2	F	F	F	
0.05	13.1	6.37	-	90.4	Kohlrausch, 1909
16.1	14.8	7.20	-	-	" 1909
17.5	-	-	16.2	-	" 1909
18.0	15.0	7.3	-	87.4	" 1909
18.8	-	-	16.3	-	" 1909
26.1	-	-	17.2	-	" 1909
26.6	16.0	7.79	-	-	" 1909
27.0	-	-	-	84.1	" 1909
40.0	16.7	8.13	-	-	" 1909
100	-	30.0	-	-	Kazakov
206-210	29.6	14.41	-	-	Thugutt, 1936

Table 4 shows that the solubility of CaF_2 increases noticeably with a rise of temperature; the relationship is practically linear:

$$\left. \begin{array}{l} \pm 0.190 \text{ mg./lt. } \text{CaF}_2 \text{ per } \pm 1^\circ\text{C.} \\ \text{or } \pm 0.092 \text{ mg./lt. F per } \pm 1^\circ\text{C.} \end{array} \right\} \begin{array}{l} \text{within the interval} \\ \text{of } 0 - 26^\circ \text{C.} \end{array}$$

In the case of high-temperature hydrotherms the solubility of CaF_2 can be doubled (Thugutt). It is very interesting that, in contrast to fluorite, the solubility of MgF_2 markedly decreases with an increase of temperature.

The papers of Auméras (1927) and Mougnaud (1931) give figures on the solubility of CaF_2 in chemically pure water which are close to the data of Kohlrausch (see Table 5).

TABLE 5

Solubility of CaF_2 in chemically pure water
(summary of data in the literature)

Author and year of investigation	Solubility			Notes
	t°C.	CaF_2 mg./lt.	F mg./lt.	
Kohlrausch, 1893	18	14	6.82	} Precipitated "gelatinous" CaF_2
" 1908	17.5	16.2	7.88	
" 1908	18.8	16.3	7.93	
" 1908	26.1	17.2	8.37	
" 1908	0.05	13.1	-	
" 1908	16.1	14.8		} Pulverized fluorite (mineral).
" 1908	18.0	15.0		
" 1908	26.6	16.0		
" 1908	40.0	16.7		
Aumeras, 1927	25	18	8.77	
Mougnaud, 1931	18	18.3	8.91	Freshly precipitated By method of dis- solution
Jensen, 1937	-	14.3	7.20	
" 1937	-	16.4	7.98	By method of cry- stallization

There is interest for us in Jensen's paper published in 1937, in which the author gives wholly justifiably two figures of solubility (Table 5), - one obtained by the "method of dissolution", the other by the "method of crystallization" from an oversaturated solution (a mixture of aqueous solutions of HF and $\text{Ca}(\text{OH})_2$). The determination proper of the concentration of equiponderant solutions was carried out by the method of electrical conductivity. The size of the particles of sedimented CaF_2 in these experiments was of the order of 1-2 microns.

C. The polytherm of the solubility of crystalline CaF_2 in chemically pure water

We made experiments on the solubility of natural CaF_2 in chemically pure water at temperatures of 0, 10, 20, and 100°C. In our tests Nos. 7 and 8 special note was taken of the effect of an admixture of

powdered CaCO_3 . The time, during which the containers with the solutions were left standing for the dissolving of CaF_2 , was as long as 130 days at most. The results are summarized in Table 6 and Figure 1.

TABLE 6

Solubility of crystalline fluorite in chemically pure water at $t^\circ = 0-10-20-100^\circ\text{C}$. (A. V. Kazakov and E. I. Sokolova). Pulverization: 0.20 mesh; Solid:Liquid = 1:20.

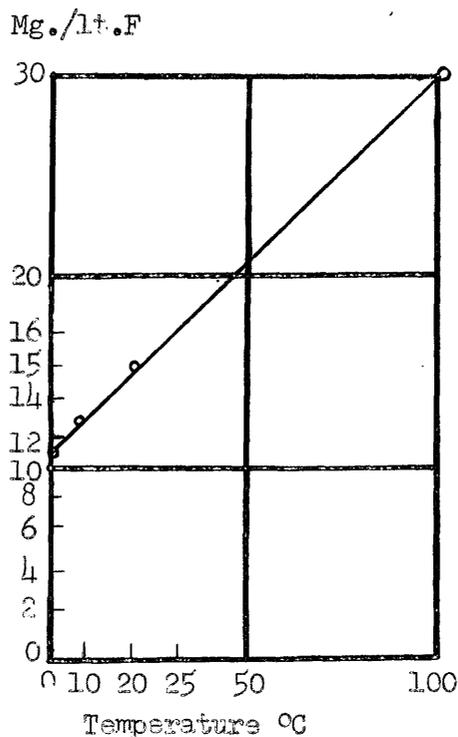
Duration of experiment, in days	Experiment No. 1, $t^\circ = 0^\circ\text{C}$.	Experiment No. 2, $t^\circ = 10^\circ\text{C}$.	Experiment No. 3, $t^\circ = 20^\circ\text{C}$.	Experiment No. 4, $t^\circ = 100^\circ\text{C}$.	
	F' mg./lt.	F' mg./lt.	F' mg./lt.	Duration of boiling	F' mg./lt.
10	10	9	-	30 min.	20
20	11	9	12	1 hour	27
30	12	9	-	2 hours	27
40	12	-	16	4 hours	30
50	-	13	16	6 hours	30
60	-	11	16		
70	-	12	-		
90	-	-	15		
100	-	13	-		
125	-	13	-		
140	-	13	-		
4 hours (boiling)	-	-	-		
Average equilibrium Corresponding quantity of CaO^* (by calculation)	11	13	15		30
	16.2	19.2	22.1		44.2

* For 25°C , by calculation: 15.9 mg./lt. F' and correspondingly 23.5 mg./lt. CaO .

Our experiments gave the solubility of fluorite in chemically pure water as ranging from 11 mg./lt. F at 0°C . to 15 mg./lt. F at 20°C . and 30 mg./lt. F at 100°C . Thus, the results which Kohlrausch obtained by the indirect method of electrical conductivity are decreased by almost half.

Figure 1

Solubility of crystalline CaF_2 in chemically pure water at temperatures from 0° to 100° C.



D. Experiments for the determination of the solubility of amorphous precipitated CaF_2 .

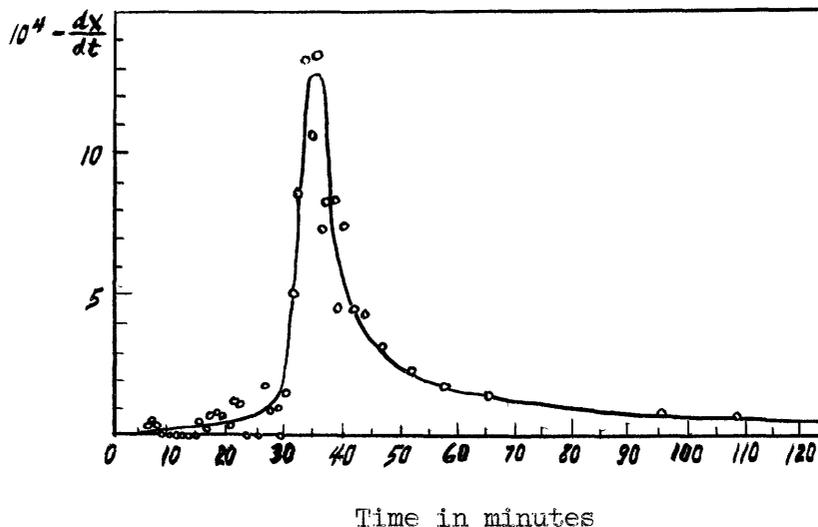
The literature contains a number of papers which report a greater solubility for highly dispersed CaF_2 (precipitated, amorphous) than for natural crystalline fluorite.

Paterna and Mazzuchelli (1904) have shown that the solubility of hydrosol and hydrogel particles has a ratio of 2.2 : 1 when the ratio between their radii is 1:10. Kohlrausch (1909) also noted this phenomenon:

t°C	% CaF_2	
	Crystalline	Synthetic colloidal
18	$1.50 \cdot 10^{-3}$	$1.62 \cdot 10^{-3}$
26.5	$1.60 \cdot 10^{-3}$	$1.72 \cdot 10^{-3}$

Our efforts to determine the solubility of samples of the highly dispersed precipitated CaF_2 at our disposal were unsuccessful because the given system $\text{H}_2\text{O}-\text{CaF}_2$ yielded a stable non-filterable hydrosol.

Figure 2
Kinetics of the crystallization of CaF_2 from supersaturated solutions (according to Towborg-Jensen, 1937)



IV. THE INFLUENCE OF CALCIUM SALTS ON THE SOLUBILITY OF FLUORITE

The literature contains a considerable number of papers on the influence of calcium salts upon the solubility of fluorite CaF_2 . The investigations have dealt mainly with the chlorides of calcium. The data on the role of gypsum are very limited, and there is no information on the effect of the bicarbonate of calcium. The decrease in the solubility of fluorite, produced by calcium salts, reflects a known law of the effect of common ions.

A. The influence of CaCl_2 on the solubility of fluorite

The earliest data on the influence of CaCl_2 in decreasing the solubility of fluorite CaF_2 are given in the description of the classic

method of Rose for the determination of fluorine by weight in the form of CaF_2 .

Paterno and Mazzuchelli (1904) point to the analogous effect of CaCl_2 and $\text{Ca}(\text{NO}_3)_2$. Dirwiddie (1916) recommends that, in the analysis of solutions for the presence of fluorine, the F-ions be precipitated by means of powdered gypsum. Treadwell and Köhl (1926) are the first to publish figures on the solubility of CaF_2 in aqueous solutions of CaCl_2 (see Table 7 and Figure 3).

TABLE 7

Solubility of CaF_2 in aqueous solutions of CaCl_2 (Treadwell and Köhl, 1926). Recalculated by A. V. Kazakov

Ca^{++} in C mol./lt.	0.00026	0.026	0.028	0.030	0.040	0.100
$\frac{F_0'}{F'}$	1	4.1	4.2	4.1	4.1	3.2
mg./lt. Ca^{++} mg./lt. CaO	20.4 14.56	1042 1459	1122 1571	1202 1683	1603 2244	4008 -
mg./lt. Ca^{++} (in the form CaCl_2)	0	1040	1120	1200	1600	4005
mg./lt. F'	11.0	2.68	2.62	2.68	2.68	3.44
gr./lt. CaCl_2	0	2.88	3.10	3.32	4.43	11.09

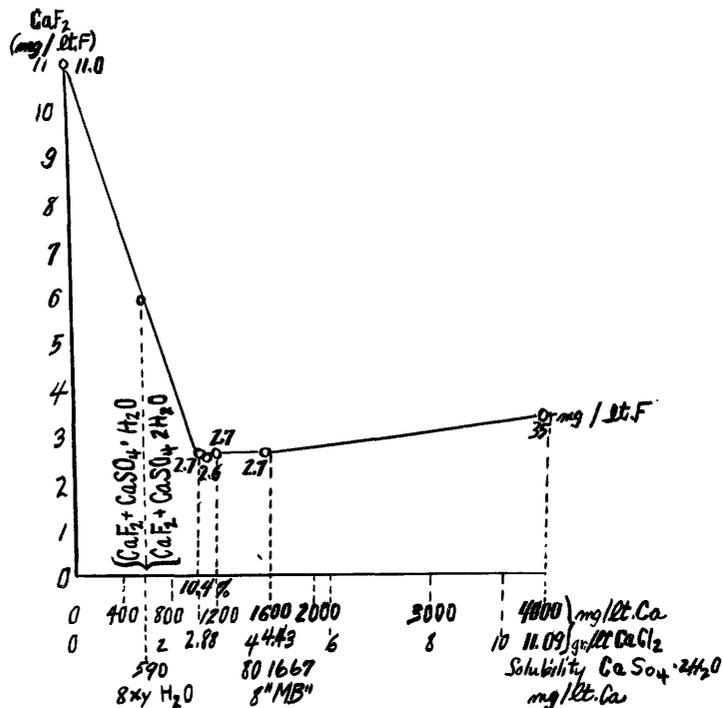
Note.--C mole/lt. is the excess (oversaturation) of Ca^{++} ions in g-mole/lt. (at expense of addition of CaCl_2); F_0' is the concentration of ions in the solution of CaF_2 in chemically pure water; F' is the concentration of ions in the solution of CaF_2 in the presence of CaCl_2 .

The minimum solubility of CaF_2 corresponds to Ca g-mole/lt. = 0.027, which equals $0.027 \times 40.08 = 1.0822$ gr./lt. Ca^{++} (or 1.515 gr./lt. CaO).

Carrière and Rouanet (1929) report in their paper a method for the determination of fluorine by weight in the form of CaF_2 in the presence of CaCl_2 at the temperature of boiling. The concentration of CaCl_2 in the system precipitated by the authors' procedure is equal to 6.937 gr./lt. CaCl_2 , or 3.505 gr./lt. CaO (as against the optimum concentration of 1.515 gr./lt. CaO , recommended by Treadwell).

Figure 3

Influence of calcium salts on the solubility of CaF_2 :
the system $\text{CaF}_2\text{-CaCl}_2\text{-H}_2\text{O}$ (according to Treadwell²
and Köhl, 1926)



B. The influence of $\text{Ca}(\text{OH})_2$ and HF on the solubility of fluorite (the system $\text{CaO-HF-H}_2\text{O}$, isotherm $25^\circ\text{C}.$)

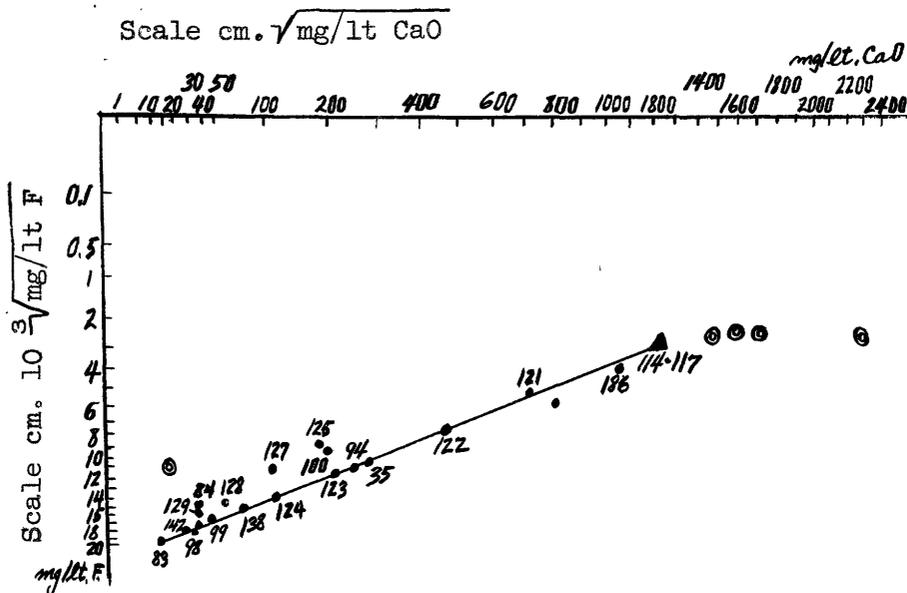
There are no experimental investigations of the equilibrated system $\text{CaO-HF-H}_2\text{O}$ in the literature. Studies were made only of parts of this system. Besides the determination of the solubility of CaF_2 in H_2O ,

there is also an indication that in the presence of HF the solubility of CaF_2 declines considerably, reaching values smaller than 0.01% CaF_2 ; however, the investigators give no other data.

In 1937 and 1939 A. V. Kazakov investigated the system $\text{CaO-HF-H}_2\text{O}$ at the temperature 25°C ., and in 1949 he studied the fluorapatite system. The results (27 experiments) are summarized in Fig. 4 of the present paper and in Fig. 2 of the paper of A. V. Kazakov "The fluorapatite system of equilibria in the conditions of formation of sedimentary rocks..." published in the present issue 114, no. 40, of the Trudy (see p. 23, TEI-385).

Figure 4

Influence of calcium salts on the solubility of CaF_2 :
the systems $\text{CaF}_2\text{-Ca(OH)}_2\text{-H}_2\text{O}$ at 25°C . and $\text{CaF}_2\text{-CaSO}_4\text{-H}_2\text{O}$ at 25°C .



The micro-texture of the bottom sediment of CaF_2

The bottom sediments in the segment of the $\text{CaO-HF-H}_2\text{O}$ system studied by us consisted of two phases: CaF_2 and Ca(OH)_2 . The microstructure of the precipitated CaF_2 (at $25^\circ\text{C}.$) is very interesting.

Judging from the investigation of A. V. Kazakov and E. I. Sokolova (1949), the order of the mixing of reagents $\left[\text{Ca(OH)}_2 \right] \rightleftharpoons \text{HF}$ has no noticeable effect upon the microstructure of the deposited CaF_2 , as distinguished from the system with P_2O_5 . We connect this characteristic with three features of the process of crystallization of CaF_2 in our system: (a) a protracted latent period of crystallization (see Fig. 2); (b) weakly developed adsorptive properties (see below) as regards the ions of Ca and F; and (c) absence in the system of any other fluoride than CaF_2 .

As to the given speed of crystallization, it had a noticeable effect on the degree of dispersion of CaF_2 , which should have been expected. This effect is shown by the following table:

Serial No. of experiments	Given speed of crystallization ($25^\circ\text{C}.$), mg./lt. of CaF_2 per hour	Size of grains of the sediment CaF_2 μ	Sedimentation and capacity for filtering
85	14.6	1-2	Settles well and gives an articulate, clear-cut Debye pattern. Colloidal, does not settle.
98	79 - 36	1-2	
84	800 - 2000	0.5	

A second specific characteristic of the sediments of CaF_2 in the system $\text{CaO-HF-H}_2\text{O}$ was a complete absence of aggregation of separate grains, which distinguishes it strongly from sediments of calcium phosphate.

C. The influence of gypsum and calcite on the solubility of fluorite

In 1945 we studied the system $\text{CaF}_2\text{-CaSO}_4\cdot 2\text{H}_2\text{O-H}_2\text{O}$. The results showed that the presence of gypsum decreases the solubility of fluorite. The experiments were conducted simultaneously by the method of dissolution and the method of crystallization of CaF_2 . In the latter case the system $\text{CaF}_2\text{+H}_2\text{O}$ was subjected to supersaturation (by a preliminary 2-hour boiling, increasing the content of F to 30 mg./lt.), whereupon gypsum was introduced. In both cases we obtained wholly comparable results (Table 8): (1) 6 mg./lt. F in the experiments with dissolution, and (2) 8 mg./lt. F in the experiments with crystallization. The solubility of fluorite in chemically pure water without gypsum was 12-15 mg./lt. F. The minimum solubility of fluorite (6 mg./lt. F) corresponded to a saturated solution of gypsum.

TABLE 8

Solubility of CaF_2 in a saturated solution of $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$. (Solid:Liquid = 1:20; $t^\circ = 10^\circ\text{C}$)
A. V. Kazakov and E. I. Sckolova, 1949.

Duration of experiments, in days	pH	F mg./lt.	Duration of experiments, in days	$t^\circ\text{C}$	pH	F mg./lt.
Experiment No. 5 (Method of dissolving CaF_2)			Experiment No. 6 (Method of crystallizing CaF_2)			
9	6.77	6	Preliminary 2-hour boiling of CaF_2 in H_2O	100	6.93	25
12	6.77	6	7	10	6.93	8
18	6.77	6	13	10	7.36	-
25	6.77	5	21	10	7.36	-
30	6.77	7	35	13	-	7
64	6.77	6	50	14	7.36	8
66	6.77	6	-	-	-	-
Average:	-	6	Average:	-	-	8

We also studied the simultaneous effect of gypsum and calcite, on the one hand (Experiment No. 7), and of gypsum, calcite, and CO_2 , on the other hand (Experiment No. 8). Both experiments were carried out by the method of crystallization. In the Experiment No. 9 we introduced CO_2 for 9 hours into the system $\text{CaF}_2 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CaCO}_3$; the pH of the system was equal to 6.71.

The alkalinity of the system $\text{Ca}(\text{OH})_2$, as judged by the phenolphthalein index, was increased to pH 8.20 and was maintained at this value (see Table 9 and Figure 4).

TABLE 9

Influence of gypsum and calcite (Experiment No. 7), and of gypsum, calcite, and $\dagger \text{CO}_2$ (Experiment No. 8) upon the solubility of CaF_2 in chemically pure H_2O (Institute of Geological Sciences, Acad. Sci. USSR, 1945)

Duration of experiment	Solid/Liquid	t°C	pH	F mg./lt.	Duration of experiment	Solid/Liquid	t°C	pH	F mg./lt.
Experiment No. 7					Experiment No. 8				
2 hours	1:20	100	6.77	25	2 hours	1:20	100	6.77	25
7 days	1:20	10	8.20	12	12 days	1:20	10	7.60	10
13 days	1:20	10	7.94	12	20 days	1:20	10	7.94	10
21 days	1:20	10	8.20	12	35 days	1:20	13	8.20	6
35 days	1:20	13	-	8.5	50 days	1:20	14	7.94	6
50 days	1:20	14	7.36	8		-	-	-	-

Our experiments Nos. 7 and 8 likewise showed a decreased solubility of fluorite in the presence of gypsum and calcite in the precipitated phase (common-ion effect of Ca).

D. General conclusions

1. Calcium salts (CaCl_2 , CaSO_4 , Ca(OH)_2 , and CaCO_3) reduce the solubility of CaF_2 in water, in full accord with the rule of the effect of common ions.

2. As a first approximation, the solubility of CaF_2 can be considered to be inversely proportional to the content of calcium cations (see Figure 4).

3. The lowest experimentally obtained figures for the solubility of CaF_2 in aqueous solutions of calcium salts are given in Table 10:

TABLE 10

Solubility of CaF_2 in aqueous solutions of calcium salts

Salts	Concentrations of CaO , in mg./lt.	$t^\circ\text{C}$.	Solubility of CaF_2 , in mg./lt.	Method of determination	Author and year
CaCl_2	1456-2240		2.68		Treadwell and Köhl, 1926
Ca(OH)_2	711	25	5.3	Method of crystallization Method of dissolving	Kazakov, 1937
	1211.7	25	2.6		
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}^*$	Saturated solution of gypsum	10	6.0	Method of dissolving and crystallization	Kazakov and Sokolova, 1949

* According to the data of P. P. Budnikov (1933), the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in chemically pure water is as follows:

Temperature	0°	18°	24°	32°	38°	41°	90°	Note
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	2.41	2.59	2.65	2.69	2.72	2.69	2.22	Calculated to ions and oxides by A. V. Kazakov
mg./lt. Ca	561.0	603.0	-	-	-	-	-	
mg./lt. CaO	784.7	843.3	862.8	875.8	885.6	-	-	
mg./lt. $\text{SO}_4^{=}$	1344.2	1444.7	-	-	-	-	-	

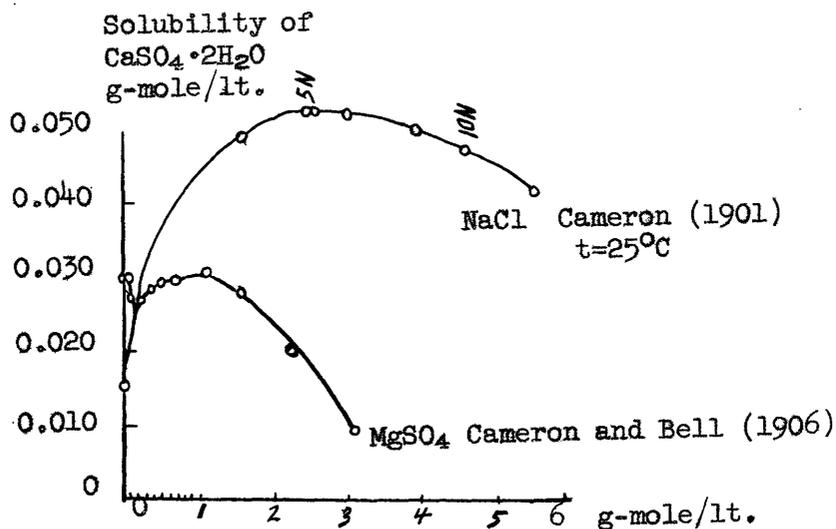
V. THE INFLUENCE OF SODIUM SALTS ON THE SOLUBILITY OF FLUORITE

The influence of sodium salts on the solubility of fluorite is much more complex than that of calcium salts, where the basic factor is the effect of the common cation of calcium. Our principal interest is, naturally, in the chloride and the sulfate of sodium, as they are the fundamental and prevalent forms of alkali salts in natural waters.

A. The system $\text{CaF}_2\text{-NaCl-H}_2\text{O}$

The literature contains no direct investigations of the influence of aqueous solutions of NaCl upon the solubility of CaF_2 . There are, however, indirect references in the papers of Cameron (1901), Orlov (1902), and Van-Goff on the system $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$, and in the paper of Cameron and Bell (1906) on the system $\text{CaSO}_4\text{-MgSO}_4\text{-H}_2\text{O}$ (Fig. 5).

Figure 5
Influence of sodium salts on the solubility of CaF_2 :
effects of NaCl and MgSO_4 on the solubility of gypsum



The introduction of NaCl into the system at first increases the solubility of gypsum. At a concentration of 2.5 mole/lit. NaCl (or 146.1 gr./lit. NaCl), calcium sulfate reaches its maximum solubility (3.5 times greater than its solubility in pure water). With a further increase of the concentration of NaCl, the solubility of calcium sulfate diminishes.

We studied the solubility of CaF_2 in aqueous solutions of NaCl for various concentrations from 10 to 300 gr./lit. NaCl at a temperature of about 10°C (see Table 11). Our results likewise showed that with an increase of the concentration of NaCl the solubility of fluorite gradually increases (Fig. 6) and reaches a maximum (about 18 mg./lit. F) with a concentration of 100 gr./lit. NaCl. A further increase of the concentration of NaCl leads to a diminution of the solubility of fluorite, which declines to 8 mg./lit. F in the field of saturation with halite.

The quantity of mg./lit. F was determined in all experiments by removal with subsequent application of the zirconium-alizarin method of colorimetry.

B. The system $\text{CaF}_2\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$

As distinguished from NaCl, sodium sulfate does not have any noticeable effect on the solubility of CaF_2 . The five experiments, conducted by us with aqueous solutions possessing concentrations of 10 - 25 - 100 - 200 - 270 gr./lit. Na_2SO_4 at a temperature of 14°C ., gave values of the solubility of crystalline CaF_2 hardly differing from its solubility in chemically pure H_2O (see Table 12 and Figure 6). The experiments were made by the method of dissolution with continuous mechanical stirring.

TABLE 11

Influence of NaCl on the solubility of fluorite.
(Solid:Liquid = 1:20; $t^{\circ} = 10^{\circ}\text{C}.$; $\text{pH} = 7.0 \pm 0.10$).

Serial No. of experiment	Duration of experiment, in days	Equiponderant concentrations	
		NaCl	CaF ₂
		gr./lt.	mg./lt.F
(1)	(2)	(3)	(4)
-	30	0	13
9	-	10	14
10	70	25	15
11	120	50	16
11-K*	60	50	16
12	38	100	18
14	70	200	16
14-K*	99	200	17
15	50	250	10
16	36	300	8

* Experiments by the method of crystallization of CaF₂ from super-saturated solutions (preliminary heating of systems to 100°C.)

Figure 6

Influence of sodium salts on the solubility of CaF₂:
the system CaF₂-NaCl-H₂O at 10°C. and the system
CaF₂-Na₂SO₄-H₂O at 14°C.

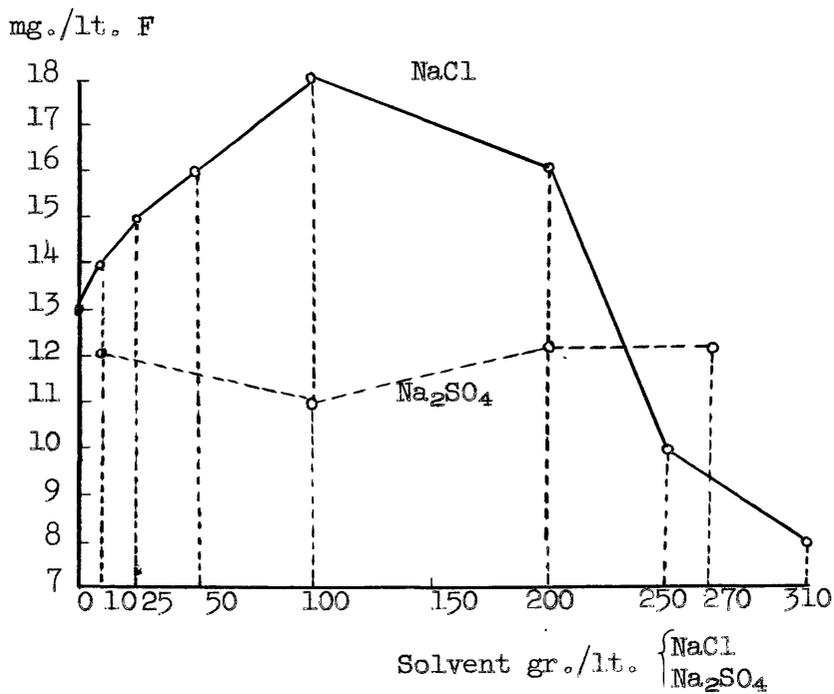


TABLE 12

Influence of Na_2SO_4 on the solubility of fluorite.
 (Solid:Liquid = 1:20; $t^\circ = 14^\circ\text{C}.$; $\text{pH} = 7.0 \pm 0.1$).

Serial No. of experiment	Duration of experiment, in days	Equiponderant concentrations	
		Na_2SO_4	CaF_2
		gr./lt.	mg./lt.F
(1)	(2)	(3)	(4)
17	15	10	13
18	30	25	12
19	39	100	11
20	40	200	12
21	39	270	12

VI. THE SYSTEM $\text{CaF}_2\text{-MgSO}_4\text{-H}_2\text{O}$

We must now consider the influence exerted on the solubility of fluorite by MgSO_4 , the fourth of the basic components of sea water. The literature gives no direct indications on this subject. The systematic experiments conducted by us (see Table 13 and Fig. 7) have revealed a very interesting and unexpected regularity: magnesium sulfate has a strong dissolving effect on fluorite at concentrations of > 10 gr./lt. MgSO_4 in the solution, but a quite insignificant dissolving effect at small concentrations (about 2 gr./lt. MgSO_4).

Taking into account general considerations regarding properties of magnesium salts and their capacity to form complex compounds, it seems justifiable to explain the pronounced increase of the solubility of CaF_2 in the system $\text{CaF}_2\text{-MgSO}_4\text{-H}_2\text{O}$ by a process of formation of complexes (at least in the solution) and, perhaps, by a partial exchange reaction $\text{CaF}_2 + \text{MgSO}_4 \rightleftharpoons \text{MgF}_2 + \text{CaSO}_4$, with the formation of a more soluble MgF_2 .

TABLE 13

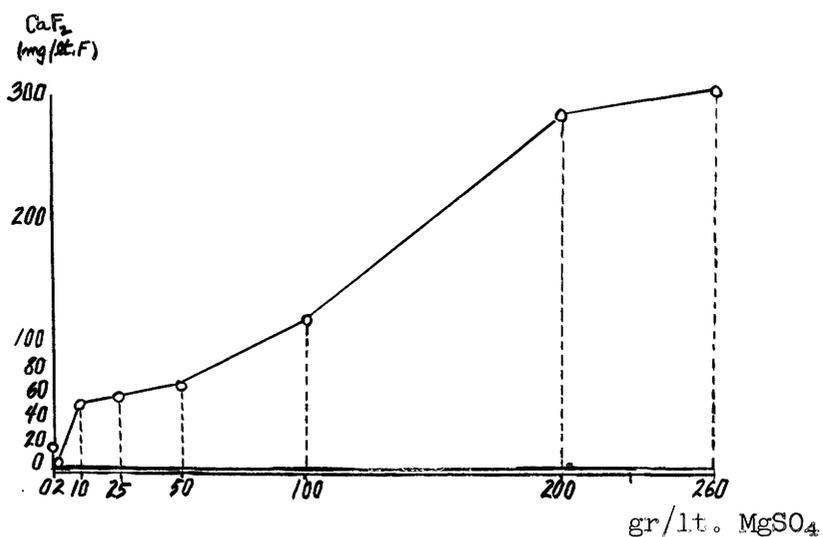
Influence of MgSO_4 on the solubility of fluorite.*
 (Solid:Liquid = 1:20; $t^\circ = 14^\circ\text{C}.$; $\text{pH} = 7.0 \pm 0.10$).

Serial No. of experiment	Duration of experiment, in days	Equiponderant concentrations	
		MgSO_4	CaF_2
		gr./lt.	mg./lt.F
22	90	2	3
23	83	10	50
24	70	25	55
25	8	50	66
26	45	100	110
27	50	200	280
28	78	260	300

* All equiponderant samples were filtered through membrane filters No. 2.

Figure 7

Influence of MgSO_4 on the solubility of CaF_2 at $14^\circ\text{C}.$



Though the investigation of this question is outside the scope of our present subject, from a geochemical standpoint it must be recognized at present as a pending problem in general chemistry. Let us note here that in our current work on the magnesite-dolomite system it is likewise not possible to clarify sufficiently the nature and mechanism of the formation of an alkali reserve in the system $\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$, in the presence of components of sea water, without taking into account a formation of magnesian complexes (a series of basic carbonates of magnesium, and so forth). One of the latest papers of Berton (1947) notes, for example, such complexes as: $\text{Mg}(\text{NO}_3)_2 \cdot \text{Mg}(\text{OH})_2$; $\text{Mg}(\text{NO}_3)_2 \cdot 4\text{Mg}(\text{OH})_2$; etc.

VII. THE INFLUENCE OF WEAK (ORGANIC) ACIDS AND AMMONIUM SALTS ON THE SOLUBILITY OF FLUORITE

Before considering the solubility of fluorite in sea water, we give the limited data available in the literature on the solubility of CaF_2 in some organic acids and ammonium salts.

The solubility of fluorite in aqueous solutions of acetic acid was studied in detail by Duparc (1925) and Mougnaud (1931). Their results are given in Table 14 and Figures 8 and 9.

TABLE 14

Solubility of CaF_2 in acetic acid (in gr./lt.)

t°C.	0.5	1	2
	30 gr./lt. CH_3COOH	60 gr./lt. CH_3COOH	120 gr./lt. CH_3COOH
40	0.153	0.175	0.192
60	0.178	0.203	0.229
80	0.206	0.237	0.267
100	0.229	0.264	0.300

Figure 8.--Influence of weak (organic) acids and ammonium salts on the solubility of CaF_2 : the system $\text{CaF}_2\text{-CH}_3\text{COOH-H}_2\text{O}$ at 40° to 100° C.

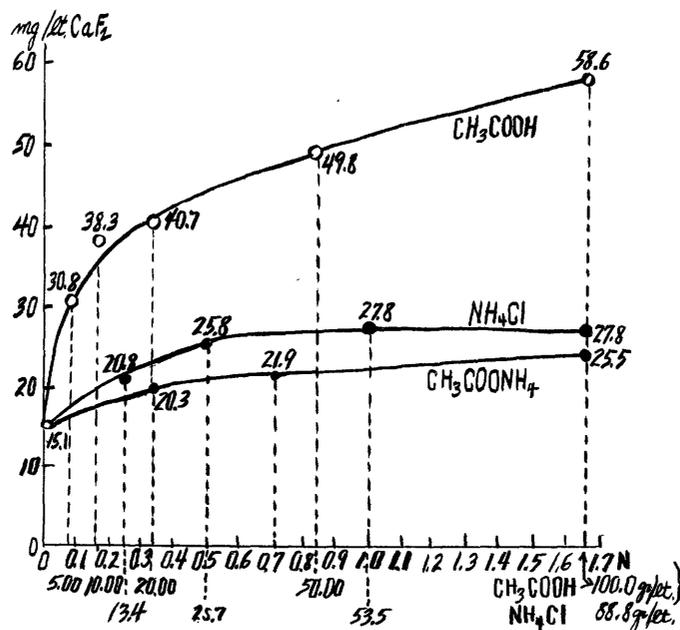
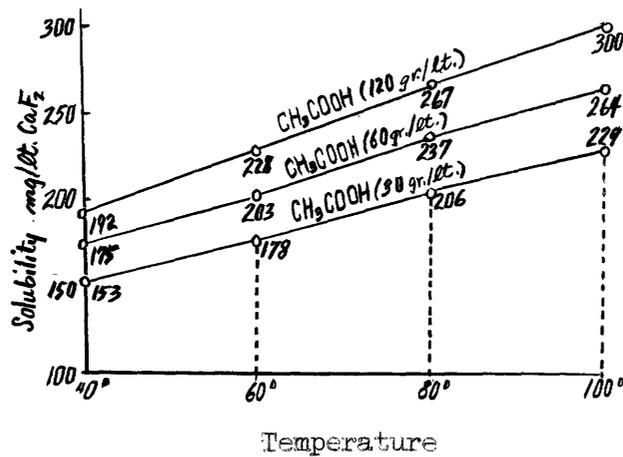


Figure 9.--Influence of weak (organic) acids and ammonium salts on the solubility of CaF_2 .

The systems: 1. $\text{CaF}_2\text{-CH}_3\text{COOH-H}_2\text{O}$; 2. $\text{CaF}_2\text{-NH}_4\text{Cl-H}_2\text{O}$;

3. $\text{CaF}_2\text{-CH}_3\text{COONH}_4\text{-H}_2\text{O}$; 4. $\text{CaF}_2\text{-CO}_2\text{-H}_2\text{O}$ (according to Mougnaud, 1931).

VIII. THE SOLUBILITY OF FLUORITE IN SEA WATER OF NORMAL SALINITY AT VARIOUS TEMPERATURES

Now that we have studied the behavior of fluorite in a number of saline solutions (components of sea water), we shall consider the conditions of equilibrium of fluorite in sea water of various concentrations. In this investigation, we used water to which known amounts of appropriate salts had been added in order to obtain the composition of sea water. The data of S. V. Bruevich (Table 15) served as the basis for this preparation.

TABLE 15

Composition of sea water of normal salinity
(according to data of S. V. Bruevich)

(Calculations based on dry salts)

Salts	Content in gr./lt.	Calculations based on oxides	
		Salts	mg./lt.
NaCl	27.021	MgO	2183
NaBr	0.085	CaO	587
KCl	0.739		
MgCl ₂	2.493		
CaCl ₂	1.163	CO ₂	108
NaHCO ₃	0.206	Cl	19241
MgSO ₄	3.368	SO ₃	2240
Average specific gravity	1.028		

The salts NaCl, NaBr, KCl, and NaHCO₃ were weighted and introduced in a dry form. The salts MgCl and CaCl₂, which are hygroscopic, and the salt MgSO₄.xH₂O, which has the tendency to become dehydrated in dry air, were introduced as solutions based on calculations.

In order to prevent the precipitation of gypsum, the salts were placed in a receptacle in the order indicated in Table 15.

The results of the experiments on the solubility of CaF_2 in sea water of normal salinity are summarized in Tables 16 and 17.

TABLE 16

Solubility of crystalline CaF_2 in sea water of normal salinity (1 "Sea Water") at $t^\circ = 0^\circ\text{C}$.

(An average equiponderant 7.0 adopted)

Duration of experiment, in days	Solid:Liquid	pH	Analysis of liquid phase, in mg./lt.F
1	1:20	7.94	4.5
22	1:20	-	6.0
28	1:20	-	6.0
34	1:20	-	6.5
37	1:20	-	7.5
47	1:20	-	7.0

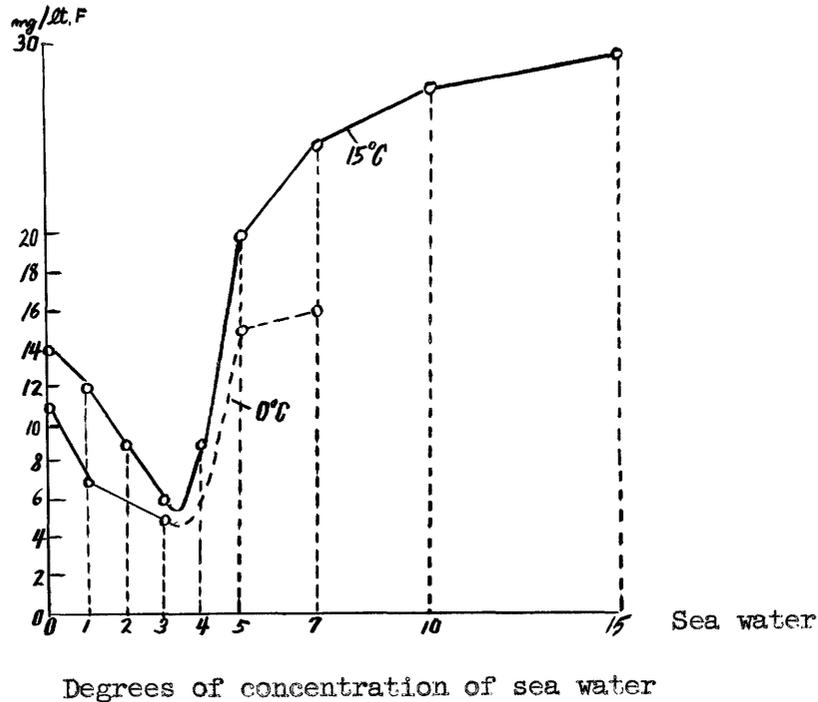
TABLE 17

Solubility of crystalline CaF_2 in sea water of normal salinity at $t^\circ = 15^\circ\text{C}$.

Solid:Liquid = 1:20 (an average equiponderant 12 adopted)

Duration of experiment, in days	F in mg./lt.	pH
10	6	-
30	7	8.30
40	6	8.08
50	14	-
60	12	-
68	11	7.94
78	11	-
100	11	7.94
110	13	8.08
125	12	-

Figure 10.--Solubility of fluorite in sea water of varying salinity.



On the basis of these experiments the solubility of CaF_2 in the sea water of normal salinity should be taken as:

for $t^\circ = 0^\circ\text{C}$7 mg./lt. F,
 for $t^\circ = 15^\circ\text{C}$12 mg./lt. F.

Though this solubility is thus markedly smaller than that in chemically pure water, nevertheless it is from 7 to 12 times greater than the actual content of fluorine in the water of the world's oceans (about 1 mg./lt. F).

Consequently, the water of the world's oceans is still far from saturated with fluorite, and deposition of fluorite from pure continental waters and from waters in sea basins of a normal salinity is not possible.

IX. FLUORITE IN THE SYSTEM OF SEA WATER OF HIGH SALINITY

A. Evaporation in closed basins (type of "closed systems;" principle of "solar diagram")

In the natural systems of over-saline sea basins the problem of fluorite equilibrium becomes much more complicated. It is convenient to

distinguish first of all between closed systems (without influx of pure water) and open systems (with influx of pure water), and between systems with elimination of the salt deposits (in nature - by coverage with silt) and systems without elimination of precipitated phases, namely, such that do not exclude their eventual metamorphism. From the thermal standpoint systems can be isothermal and polythermal (with a variable temperature of evaporation in the basin), and so forth.

Let us consider the simple case of closed evaporating basins. This type of evaporation of sea water with a corresponding separation of salts is well studied in the classical papers of Usiglio (1849) for the water of the Mediterranean Sea, Van-Goff (1897-1905), and N. S. Kurnakov and V. I. Nikolaev (1932).

The results of our experiments show that the principal factors influencing the extent of CaF_2 solubility in saline solutions of sea water are as follows:

(a) The concentration of the cation Ca (as common ion with fluorite) markedly diminishes the solubility of fluorite. Here belong gypsum, bicarbonate of calcium, and calcium chloride. Therefore, we should be interested in the sum of all the cations of calcium in solutions of evaporating sea water, expressed in mg./lt. Ca (Fig. 4).

(b) The concentration of MgSO_4 (in gr./lt.) diminishes the solubility of fluorite at small concentrations and markedly increases it at concentrations greater than 2 gr./lt. MgSO_4 (Fig. 7).

(c) A marked increase in the solubility of fluorite is produced by NaCl, up to a concentration of 100 gr./lt. NaCl (Fig. 6).

(d) Sodium sulfate behaves indifferently (Fig. 6).

(e) The solubility of fluorite is decreased by low temperature and increased by high temperature.

The experiments of Usiglio showed that the maximum equponderant concentration of calcium salts during the evaporation ($40^{\circ}\text{C}.$) of water in the Mediterranean Sea occurs at a 4-fold evaporation (2.448 gr./lt. Ca). Thereupon, beginning with a 5-fold condensation of water volume, there is a precipitation of gypsum and an intensive sedimentation of calcite, marking a transition of the system into a condition less favorable for the separation of fluorite.

A somewhat different picture is indicated by the experiments of Van Goff (1897-1905), who dealt with the isothermal evaporation of sea water at a lower temperature, $25^{\circ}\text{C}.$ In this case the beginning of the precipitation of gypsum and of NaCl is moved further in the direction of more concentrated solutions.

In our experiments with concentrated sea water the beginning of the precipitation of a small amount of gypsum and calcite corresponded to a 7-fold evaporation by volume. A considerable precipitation of gypsum mixed with calcite began only in solutions with a 10-fold, and particularly a 15-fold, evaporation by volume. Our experimental results on the solubility of fluorite in sea waters of various degrees of evaporation are summarized in Tables 18-28 and in Figure 10.

The above-indicated series of our experiments on the solubility of fluorite in sea water was supplemented by a group of tests at $10^{\circ}\text{C}.$, in which powdered gypsum was added to the sea water. As should have been expected, the addition of gypsum reduces still further the solubility of fluorite in sea water during the first stages of the water's evaporation, up to a 5-fold condensation of volume inclusive (see Table 26.)

Thus, as the concentration (evaporation) of sea water progresses, factors with opposite effects make their appearance. The increase in the cations of calcium (mainly of gypsum) reduces the solubility of fluorite, whereas the increase in the concentration of NaCl (up to a definite limit) and principally of $MgSO_4$ increases this solubility. The residual effect of these opposing influences creates for closed basins a condition in which the minimum solubility of fluorite corresponds to the stage of a 3- to 4-fold condensation of sea water by volume, marking the limit of saturation with fluorite at low temperatures.

After the beginning of gypsum precipitation and a decrease in the concentration of the cations of calcium (common to fluorite) in the solution, the solubility of fluorite begins to increase rapidly (see Fig. 10), and the separation of fluorite ceases.

TABLE 18

Solubility of crystalline fluorite in sea water of a 2-fold condensation by volume (2 "Sea Water"). Condition of experiment: Solid:Liquid = 1:20; $t^{\circ} = 15^{\circ} C.$

Duration of experiment, in days	mg./lt. F	pH
Shaking 3 times daily		
10	8	-
20	9	-
30	9	8.41
40	9	8.08
50	9	-
60	12	-
100	12	8.08
110	12	8.08
155	10	8.30
170	8	8.20
210	10	8.20
240	10	8.10
Average:	9	8.10 \pm 0.10
Experiment with continuous mechanical shaking		
3	10	-
10	10	-

TABLE 19

Solubility of crystalline fluorite in sea water
of a 3-fold condensation by volume (3 "Sea Water").
Solid:Liquid = 1:20; $t^{\circ} = 15^{\circ} \text{C}$.

Duration of experiment, in days	mg./lt.F	pH
Shaking 3 times daily		
10	5	8.20
20	7	-
30	5	8.20
40	7	-
57	7	8.20
77	7	8.08
110	5	-
125	6	8.10
155	7	-
260	7	8.10
Average:	6	-
Experiment with continuous shaking		
3	5	-
30	6	-
Experiment at $t^{\circ} = 0^{\circ} \text{C}$; daily shaking		
6	5	8.1
21	6	8.1

TABLE 20

Solubility of crystalline fluorite in sea water
of a 4-fold condensation by volume (4 "Sea Water").
Solid:Liquid = 1:20; $t^{\circ} = 15^{\circ} \text{C}$.

Duration of experiment, in days	mg./lt.F	pH
Shaking 3 times daily		
23	8	8.20
37	10	8.08
62	10	8.15
92	10	8.10
122	10	8.10
165	8	8.20
230	9	-
Experiment with continuous shaking		
3	13	-
10	11	-

TABLE 21

Solubility of fluorite in sea water of a 5-fold
condensation by volume (5 "Sea Water").
Solid:Liquid = 1:20; $t^{\circ} = 15^{\circ} \text{C.}$

Duration of experiment, in days	mg./lt. F	pH	Duration of experiment, in days	mg./lt. F	pH
Continuous shaking			Shaking 3 times daily		
32	14	8.00	12	17	8.0
42	16	8.00	20	16	-
78	16	-	96	16	-
93	18	8.10	Experiment at 0°C.		
135	18	-	32	15	8.0
195	16	-	43	15	8.0
			Control experiment with elimination of fluorine and a continuous shaking in a thermostat (15°C.)		
			-	20	-
			-	18	-

TABLE 22

Solubility of fluorite in sea water of a
7-fold condensation by volume (7 "Sea Water").
Solid:Liquid = 1:20; $t^{\circ} = 15^{\circ} \text{C.}$

Duration of experiment, in days	mg./lt. F	pH
Continuous shaking		
25	20	8.14
76	30	-
92	25	-
Average:	25	-
Same at 0°C.		
25	11	8.0
36	15	-
50	16	-

TABLE 23

Solubility of fluorite in sea water
of a 10-fold condensation
by volume (10 "Sea Water").
Solid:Liquid = 1:20; $t^{\circ} = 15^{\circ}\text{C}$.

Duration of experiment, in days	mg./lt.F	pH
Shaking 2 times daily		
16	30	-
26	30	-
43	25	-
65	24	-
Average:	28	-

TABLE 24

Solubility of fluorite in sea water
of a 15-fold condensation
by volume (15 "Sea Water").
Solid:Liquid = 1:20; $t^{\circ} = 15^{\circ}\text{C}$.

Duration of experiment, in days	mg./lt.F	pH
16	30	8.10
26	30	8.10
43	36	8.10
65	30	8.10
Average:	30	-

TABLE 25

Solubility of fluorite in sea water of various concentration

Degree of condensation of sea water by volume	pH	Equiponderant concentration, in mg./lt. F	
		$t^{\circ} = 0^{\circ}\text{C}$	15°C
0 (chemically pure H_2O)	7.0	11	14
1 "SW"	8.0	7	12
2 "	8.10	-	9
3 "	8.10	5	5-6
4 "	8.10	-	9
5 "	8.0	15	20
6 "	-	-	24
7 "	-	16	25
10 "	7.90	-	28
15 "	8.0	-	30

TABLE 26

Influence of gypsum on the solubility of CaF_2 in sea water, of various concentration.
Solid:Liquid = 1:20; $t^{\circ} = 10^{\circ}\text{C}$.; pH = 8.10 ± 0.10 .

Duration of experiment, in days	Concentration of sea water	Equiponderant concentration, in mg./lt.F
Continuous shaking		
41	1 "SW"	9
41	2 "	8
41	3 "	6-7
41	5 "	7

TABLE 27

Average principal saline composition of river waters and sea waters

Serial No. of experiment	Cl	SO ₄	HCO ₃ CO ₃	Ca	Mg	K	Na	Fe ₂ O ₃ & Al ₂ O ₃	SiO ₂	Br	Sum	Dry residue 110°C	Author and year
1	5.68	12.14	35.15	20.39	3.61	2.12	5.79	2.75	11.67	-	100.0		Clarke 1920
2	35.29	7.69	0.21	1.20	3.72	1.11	30.59	-	-	0.188			
In percentages of the sum of ions													
Same in mg./lt. (selected examples)													
3	2.5	5.0	113.5	39.7	9.6	-	-	0.18 Fe	-	-		1.59.4	Drachev, 1941
4	1.6	18	188	40	14	10							
5	12	104	178	52	16	27.5							Clarke
6	20737	2887	138	425	1367	141	5902	-	-	42.3			
	11.3	24.3	70.3	40.8	6.8	4.2	11.6						
Same in percent equivalents													
7	5.01	7.90	36.64	32.22	8.77	9.01					99.55		Recalculated by V. Sulin, 1935
8	45.22	4.62	0.16	1.77	8.92	39.31					100.0		

TABLE 28

Modification of the average chemical composition of river water by boiling (in mg./lt.)

Degree of condensation, by volume	Cl	SO ₄	CO ₃	Ca	Mg	K	Na	F	Notes
1	11.3	24.3	70.3	40.8	6.8	4.2	11.6	0.2	Dry residue at 110° = 200 (condit.)*
10	113	243	703	408	68	42	116	2	
100	1130	2430	-	4080	680	420	1160	20	Settling of CaSO ₄ , CaCO ₃
200	2260	-	-	-	1380	840	2320	40	
800	9040	-	-	-	5520	3350	9280	160	

* The average dry residue is taken in its entirety to be 200 mg./lt.; the figures of Clarke are recomputed accordingly.

B. Evaporation in relict basins

It is left to us now to consider briefly the regularities governing the equilibrium of fluorite in open evaporating basins with an influx of pure (river) waters. Generally speaking, such conditions in the evolution of relict basins are the most frequent in nature because completely closed basins are exceptions.

Obviously, the new factor which is introduced here into the process of the concentration of sea water, developing according to the classic type of the "solar diagram", is the additional evaporation of incoming pure (river) waters. These waters have to be examined briefly.

The saline content of river waters is somewhat varied because it depends, first of all, upon the conditions of soil and climate in the river

basin and upon the rocks eroded by the river. However, average annual figures can be deduced, as has been done by Clarke and other investigators (see Table 27).

Table 27 shows clearly that river waters must undergo a very considerable condensation by volume in order to attain an ionic concentration equal to that of oceanic water.

	Cl	Na	Mg	SO ₄	K	Ca
Coef. condensation: ocean w./river w.	1835	509	198	119	34	10.4

It is necessary to note, however, that the cations of K and Mg are strongly absorbed by hydrous aluminosilicates during their chemosedimentation and processes of diagenesis of bottom silts (principally during the formation of hydrous micas), so that they drop out from the salinity equilibrium. This applies also to calcium, the main mass of which (brought into the ocean by river waters in the basic form of bicarbonate) precipitates from ocean water as calcite.

In a considerable measure this is also true of SO₄²⁻, which precipitates in sea basins in the form of gypsum and anhydrite during the early stages of the "solar diagram" of evaporation.

From this standpoint, greater dependence can be placed on the coefficients of condensation for the ions showing a relatively "inert" behavior toward mineral formation and biogenic fixation, such as Na, Cl, and apparently Br.

If we follow up the change in the average chemical composition of river waters during their evaporation we will see that, in order to achieve a concentration of Mg-ion equal to its concentration in sea water of normal salinity, it is necessary to have at least a 200-fold condensation of river waters by volume. In such case the concentration

of fluorine would be $200 \times 0.2 = 40$ mg./lt. F. If, however, we take a sea water of a 4-fold condensation (4 "SW"), for which the solubility of fluorite is the smallest according to Fig. 10, then the respective coefficient of concentration for river waters would have to equal to 800, and the content of fluorine would rise to $800 \times 0.2 = 160$ mg./lt. F; that is, it would exceed by far its limits of solubility under these conditions (4 - 6 mg./lt. F). In these calculations, we do not take into consideration, as indicated above, the fixation of magnesium during the chemo-sedimentation of hydrous micas, so that the real coefficients of concentration of river waters must be still higher, apparently approaching the chloride coefficient.

Thus, in open drying relict basins and lagoons with an inflow of pure waters, the conditions are still more favorable for the sedimentation of fluorite. Under these conditions fluorite must precipitate together with calcite within a range close to the sedimentation of gypsum.

X. GENERAL CONCLUSIONS OF A GEOLOGIC-GENETIC NATURE

1. Among the 34 known minerals containing fluorine, only 6 minerals occur in the thermodynamic conditions of sedimentary rocks; of these, 4 are referable to saline lake deposits of a late stage of halogenesis, being rare minerals, and only the remaining 2 may be referred to marine sediments.

The majority of the other minerals containing fluorine are formed under the thermodynamic conditions of high temperature and pressure (hydrotherms, pneumatolysis, magmas, volcanogenic processes, etc.)

2. The 2 above-indicated minerals containing fluorine and referable to marine sediments are fluorapatite (seldom fluorhydroxylapatite)

and fluorite; the range of their formation extends to the thermodynamic conditions of high temperatures and pressures (magmas, hypotherms, vein-deposits, etc.), which characterize their crystal lattice as very stable.

The experimental data, presented above on the fluorapatite-fluorite systems of equilibria, content of fluorine in natural waters, and geologic-lithologic analysis of occurrences of sedimentary fluorite and fluorapatite, make it possible to increase considerably the precision of our knowledge on the conditions of formation and stability of apatite and fluorite in sedimentary basins of different types.

A. Pure-water basins

3. In pure-water basins the usual content of fluorine in the water is, on the average, about 0.2 to 0.5 mg./lt., and the extent of fluorite solubility is correspondingly:

11 mg./lt. for F at 0°C.,
15 mg./lt. for F at 20°C.

Under these conditions any possibility of the precipitation of fluorite naturally is excluded.

4. The possibility of the precipitation of hydroxylapatite, with the usual attendant fixations of fluoride-ion from the water, is also excluded because of the negligible concentration of phosphate-ion in pure waters and of the comparatively small pH.

5. However, a partial extraction of fluoride ion from pure waters by the fluoridation of the bony substance (hydroxylapatite) of animal carcasses is still possible under these conditions. We have demonstrated experimentally that the coefficient of the fluoridation of hydroxylapatite of bony substance (substitution of OH' for F) reaches

from 55 to 60 percent. For hard waters (high content of Ca) the coefficient of the fluoridation of hydroxylapatite is still higher.

B. Sea basins of normal salinity

6. The salts of sea water exert a varying influence on the solubility of fluorite. This problem was clarified by a study of the solubility of CaF_2 in the aqueous solutions of a number of pure salts.

(a) The salts of calcium (sulfates, chlorides, and others), which have a common cation Ca with fluorite, decrease the solubility of fluorite. In a saturated aqueous solution of gypsum the solubility of fluorite decreases to 6 mg./lt. F. In aqueous solutions of CaCl_2 the decrease is still greater, down to 2.6 mg./lt. F.

(b) The salts of magnesium, on the contrary, sharply increase the solubility of fluorite. Thus, for example, with a content of 10 gr./lt. MgSO_4 the solubility of fluorite (15° C.) increases to 50 mg./lt. F; with a content of 100 gr./lt. MgSO_4 it increases to 110 mg./lt. F; and with a content of 260 gr./lt. MgSO_4 it increases to 300 mg./lt. F.

(c) The salt NaCl , when dissolved in neutral solutions to a concentration of 100 gr./lt., increases the solubility of fluorite (to 18 mg./lt. F); but with more concentrated solutions the curve of the solubility of fluorite declines sharply (to 8 mg./lt. F).

(d) Aqueous solutions of Na_2SO_4 have no effect on the solubility of fluorite.

7. The direct experiments conducted by us on the solubility of fluorite in ocean water of normal salinity showed a solubility of 12 mg./lt. F at 15° C., and of 7 mg./lt. F at 0° C.; namely, 10 times

higher than the actual content of F in the ocean water (4 mg./lt. F, on the average). Thus, the possibility of the deposition of fluorite in sea basins of normal salinity is completely excluded.

8. In sea basins of normal salinity there is another widespread process of fixation of fluorine, namely, the sedimentation of fluorapatite in areas of phosphate shelves. This process has been considered in detail by us in another paper.

9. The content of F in ocean water is several tens of times higher than the content of phosphorus:

P_2O_5 in a zone of photosynthesis 0.01-0.05 mg./lt.

P_2O_5 in a zone at depths of 300-400 m. .. up to 0.30 " "

F in all zones of the ocean, on the average.. 1.0-1.2 " "

Such ratios can occur only in the case of insufficient amounts of the chemosedimenting mass of calcium phosphate (apatite lattice), and from this standpoint the above-indicated quantities of fluorine in ocean water must be considered as residuals (excesses) left over after a full saturation of the settling phosphate sediments (phosphorites) with fluorine to the extent of the formation of normal fluorapatite.

C. Relict sea-basins of high salinity

1. Closed basins (principle of "solar diagram")

10. As the concentration (evaporation) of sea water progresses, there appear, together with the increase of the absolute concentration of F in the water mass, a whole series of new factors having opposite effects on the solubility of fluorite (compare with paragraph 6).

11. Beginning with the moment at which a 3- to 4-fold evaporation of sea water is reached by volume, the solubility of fluorite decreases

down to 4-5 mg./lt. F, and the curve of the solution crosses the line of the concentration of fluorine of sea water; that is, the medium becomes saturated with fluorite.

12. However, this first period of a possible precipitation of fluorite in relict and closed sea basins is short, because the concentration of the cation Ca^{++} decreases beginning with the onset of gypsum sedimentation whereas the dissolving effect of $NaCl$ and $MgSO_4$ upon fluorite increases. As a result, the water system of the drying salinified basin again ceases to be saturated with fluorite. Under natural conditions the deposition of holopelites usually prevents the dissolving of the previously precipitated fluorite.

2. Open drying relict basins with an influx of pure waters

13. The sea basins of the open, drying, relict type with an influx of pure waters offer much greater possibilities of the deposition of fluorite in the course of the basin's evaporation, first of all because of the sharply higher content of fluorine in river waters relative to the total mass of salts, in comparison to ocean water. The salt composition of river waters is 280 times richer in fluorine than the salt composition of sea water:

$$\begin{array}{l} \text{river waters} \dots\dots\dots \frac{0.2 \text{ mg./lt. F}}{200 \text{ mg./lt.}} = 1, \times 10^{-3} \\ \text{ocean waters} \dots\dots\dots \frac{1.0 \text{ mg./lt. F}}{35,000 \text{ mg./lt.}} = 2.8 \times 10^{-5} \end{array}$$

For example, in order to achieve, by means of evaporation of river waters of average composition, a concentration of Mg-ion equal to its concentration in sea water of normal salinity, it is necessary to have at least a

200-fold condensation of river water by volume. This would result in a content of fluoride ion equal to $200 \times 0.2 \text{ mg./lt. F} = 40 \text{ mg./lt. F}$, which exceeds by far the solubility of fluorite.

3. Basins in the last phase of halogenesis
(stages of the deposition of potassium salts and borates)

14. With a further drying of sea basins and their transition to the phase of deposition of potassium salts (and primary borates), there begins the last stage of precipitation of fluorite from eutonic (sic) brine. All in all then, the possible processes of deposition of fluorides in a zone of cumulative sedimentation are reducible to those listed in Table 29.

Table 29

Facies conditions of deposition of fluorapatite and fluorite,
and of fluoridation of bony substance

Serial No.	Basins	Processes		
		Fluoridation of bony substance	Sedimentation of phosphorites (fluorapatite)	Sedimentation of fluorite CaF_2
1	Pure-water basins	+	None	None
2	Sea basins of normal salinity	++	+ sediments on the shelves of basins in phosphate formations	None
3	Relict sea basins in an early stage of salinification (closed and open types)	+	None	+ 1st early stage of the 3- to 4-fold concentration of sea water, continuing up to the beginning of the sedimentation of gypsum
4	Same, in the stage of sedimentation of anhydrite and halite	+	None	None
5	Eutonic brine of drying sea basins	?	None	+ 2d stage, occurring within the range of sedimentation of potassium salts and borates (from eutonic brine)

D. The fluorine-phosphorus coefficient as a facies index

15. The geologic-genetic conclusions advanced above indicate that sedimentary fluorite can be a sensitive index of the facies of sea basins at an early stage of their salinification (up to the time of the sedimentation of gypsum and anhydrite).

Its use for such purposes may be accomplished by means of the "fluorine-phosphorus coefficient", $\% F : \% P_2O_5$, which equals 0.0893 for normal fluorapatite. The actual values of the fluorine-phosphorus coefficient for the phosphorites of the plateau of the USSR usually vary within the range of 0.10 to 0.12; that is, the phosphorites contain somewhat more fluorine than is required by the formula for normal fluorapatite $Ca_5(PO_4)_3F$ and always include a free highly dispersed $CaCO_3$. This feature is apparently connected with the wide-spread property of poorly soluble sediments to capture during their crystallogenesis small quantities of other poorly soluble neighbouring compounds; it may be also related to the as yet little-studied physico-chemical phenomena of "joint sedimentation" and formation of anomalous, mixed crystals. Taking this circumstance into consideration, we propose that the 0.15 to 0.20 value of the fluorine-phosphorus coefficient for a sedimentary rock be considered as an already reliable indication of the presence of fluorite deposition therein and that such a sedimentary rock be referred to the early (pre-gypsum) salinification period of a salinified sedimentary basin.

From this standpoint sedimentary fluorite is a typical mineral index of halogenic facies. In a number of questionable cases of fluorite determination, gross analyses for F and P_2O_5 can also give objective indications on the facies conditions of the investigated sedimentary rocks.

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