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THE FLUORAPATITE SYSTEM OF EQUILIBRIA IN THE CONDITIONS OF FORMATION OF SEDIMENTARY ROCKS

By A. V. Kazakov

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TRANSLATOR'S ABSTRACT

As part of unified research on the behavior of the fluoride ion in sedimentary rocks, the present study deals with the system $CaO-P_2O_5-HF-H_2O$ at 25° C. under conditions of sea sedimentation. The precipitated phases, their fields of crystallization and stability, the fluorine-phosphorus coefficient, and the isomorphism of fluorhydroxyl ions in the apatite lattice are considered and illustrated by orthogonal projections. The results lead to conclusions on fluorapatite sedimentation on phosphate shelves, with its consequent fixation of fluorine, expressed in the form of an average annual balance sheet for the processes involved.

V.L.S.

THE FLUORAPATITE SYSTEM OF EQUILIBRIA IN THE CONDITIONS OF FORMATION OF SEDIMENTARY ROCKS 1/

By

A. V. Kazakov

INTRODUCTION

The fluorine (F) of sedimentary rocks and natural waters has recently attracted increasing attention. There is a growing interest in its chemistry and geochemistry. The causes are both practical and theoretical. Workers in sanitation and hygiene consider as one of their problems the purification of drinking water from an excess of fluor-ion, dangerous to the human organism.2/ In zootechnics a method is gaining application for using a fluorless phosphate of calcium ("feed precipitate") in the feeding of animals.

The phosphate industry has begun to employ a thermal process for removing fluorine from phosphorites by replacing the fluor-ion in the apatite lattice by a hydroxyl group. This gives hydroxylapatite which is well assimilated by plants.

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

2/ It has been proved very recently that there is danger to the human body not only in an excess of fluorine in drinking water (a content of more than 2 mg/lt. of fluorine produces tooth decay, a spottiness of the enamel), but also in an insufficiency of it. Evidence establishes that the optimal content of fluorine in drinking water must be about 1.1 mg./lt. To obtain this content, the practice was started beginning with 1945 to introduce into drinking water deficient in fluorine (e.g. Lake Michigan and other sources) some fluorine in the form of sodium fluoride (the towns Newberry, Ottawa, etc.) sufficient to bring the content to 1.1 mg./lt. F.*

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* Such a content seems too high - Translator.

In very recent years a process has come into use of fluorining organic compounds with a view to obtaining plastics non-inflammable and non-soluble in ordinary solutions, especially resistant dyes, and so forth.

In soil-science and agricultural economics fluorine may be useful in combating pests. In the lithology of sedimentary rocks fluorine has proved an interesting index of phosphatic and non-phosphatic facies. Finally, fluorine is an important element forming minerals in the realm of metamorphic rocks (hypotherms, pneumatolysis, etc.) and relatively easily replaces isomorphically the hydroxyl groups.

All these considerations have prompted us to conduct a series of experimental investigations, which have made it possible to gain a more precise knowledge on the behavior of fluor-ion in sedimentary rocks, namely, the ways of its migration, dispersion, concentration, and formation of minerals.

Our experimental research on the balanced fluorapatite system and on the isomorphism of the hydroxylfluoride ion was carried out in close association with G. A. Markova, who directed the analytical work.

The experiments on the fluorite systems were done with the direct participation of E. I. Sokolova and A. Z. Vainshteim, of the Laboratory for synthesis of minerals of sedimentary rocks, Institute of Geological Sciences (IGN), Academy of Sciences of the U.S.S.R.

The general direction of the work, analysis of experimental data, and preparation of the present paper were made by A. V. Kazakov.

I. GEOCHEMISTRY OF FLUORINE

1. Data on fluorine and phosphorus

The history of the fluorine which reaches the sea basins is connected on the one hand with the flow of surface waters and on the other hand with the expulsion of fluorine compounds from the interior of the earth by volcanic eruptions.3/ The migration of the fluor-ion carried by water flow is most intimately related to phosphorus (phosphate-ion); therefore we give in Table 1 some data on phosphorus and fluorine, of interest to us.4/

Conclusions

Biological entities (plants, animals), being usually concentrators of phosphorus, avoid the accumulation of fluorine in their organs. This observation applies particularly to some seaweeds (lithothamnia), which can be called in this respect fluor-filters. Such avoidance also explains the fact that the mineral part of a living bony substance consists mainly of hydroxylapatite. The bony skeleton of an animal is subject to fluoridation only after the animal's death.

3/ This applies also to the fluorine compounds of volcanic origin which reach the sea basins one way or another.

4/ The content of fluorine in cores from a drill hole near the town of Kazan' (sediments C_3, P_1, and P_2), when calculated in percentages of weight, was on the average as follows:

	Percent	Average for	
Dolomites	0.025	10 samples	V. V. Danilova, 1949
Limestones	0.023	9	
Anhydrides	0.014	7	
Gypsum	0.012	5	
Clay shales	0.010	-	Shepherd, 1941

Table 1.--Data on phosphorus and fluorine

Sample no.	Substance	% P	% F	$100 \times \frac{\% F}{\% P_2O_5}$	Author, year
	I. BIOLOGICAL ENTITIES				
1	Seaweeds (Lithothamnia)	to $2.0 \cdot 10^{-1}$	$x \cdot 10^{-8}$	approx. 0.0000 x	
	Mustard family				
2	Turnip	$8 \cdot 10^{-1}$	$1 \cdot 10^{-4}$	0.027	% of living weight; Vinogradov, 1932
3	Cabbage	$7 \cdot 10^{-1}$	$1.0 \cdot 10^{-4}$	0.032	
	Leguminous plants				
4	Lentil	$5 \cdot 10^{-1}$	$1 \cdot 10^{-3}$	0.320	
5	Beans	$x \cdot 10^{-1}$	$2 \cdot 10^{-3}$	0.904	
6	Bone, keratin (of living organisms)	--	--	from 2.202 to 0.904	
	II. SOILS 1/				
7	Soils	$8.0 \cdot 10^{-2}$	fr. $1 \cdot 10^{-2}$ to $3 \cdot 10^{-2}$	from 5.5 to 16.4	Fersman, 1933, 253 Vinogradov, 1945
	III. EARTH CRUST				
8	Earth's crust (atmosphere, hydrosphere, lithosphere to a depth of 16 km.)	$1.2 \cdot 10^{-1}$	$2.7 \cdot 10^{-2}$ $2.6 \cdot 10^{-2}$ $8.0 \cdot 10^{-2}$ $1.0 \cdot 10^{-1}$	9.64	Clarke, 1920 Fersman, 1932 Vernadskii, 1925-1930
	IV. CRYSTALLINE ROCKS				
9	Basalts	$2.0 \cdot 10^{-1}$	--	--	Clarke, 1920
10	Granites	$1.0 \cdot 10^{-1}$	--	--	
11	Peridotites	$6.1 \cdot 10^{-2}$	--	--	
12	Cryst. rocks as a whole	$1.3 \cdot 10^{-1}$	--	--	Fersman, 1933, 282
13	Granitic pegmatites	$5.0 \cdot 10^{-2}$	$9 \cdot 10^{-2}$	79.0	

1/ The average content of fluorine in the soils of U.S.S.R. (average from 46 samples) is: 2×10^{-2} percent (according to Vinogradov, Danilova, 1948).

(TABLE 1 continued on next page)

Table 1.--Data on phosphorus and fluorine (continued)

Sample No.	Substance	% P	% F	$100 \times \frac{\% F}{\% P_2O_5}$	Author, year
			V. SEDIMENTARY ROCKS		
14	Clays, slates	$7.4 \cdot 10^{-2}$	--	--	Clarke, 1920
15	Sandstones	$3.5 \cdot 10^{-2}$	--	--	
16	Limestones	$1.7 \cdot 10^{-2}$	--	--	
17	Sedim. rocks as a whole	$6.5 \cdot 10^{-2}$	--	--	
			VI. WATERS 2/		
18	River waters	$x \cdot 16^{-6}$	approx. $2.0 \cdot 10^{-5}$	approx. 200	Vinogradov, 1938
19	Sea waters of normal salinity	$5.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-4}$	870	
20	Relict basins	--	--	to 3300	

2/ An increase of concentration of fluor-ion in the waters of drying ("relict") basins and a related increase in the total content of fluorine in the bottom sediments occur, naturally, also in sweet-water continental basins. Thus, E. S. Zalmanson determined in 1947 the content of fluorine in the bottom sediments of the western half of Lake Balkhash as being of the order of 4.2×10^{-2} percent, and in the saliferous eastern part of this lake as 9.8×10^{-2} percent.

Of considerable interest from the standpoint of lithologic facies and geochemistry is the so-called "fluorine-phosphorus coefficient" of rocks and natural waters: $\% F/\% P_2O_5$. According to Clarke (1920) and Berg (1932), this coefficient for the earth's crust in general is on the average:

$$\frac{2.65 \times 10^{-2} \% F}{1.2 \times 10^{-2} \% P \times 2.29} = 0.096.$$

Namely, it almost corresponds to the fluorine-phosphorus coefficient for fluorapatite (0.0893).

The fluorine-phosphorus coefficient for soils (averaging from 0.055 to 0.11) is also close to these figures. With the small value of the fluorine-phosphorus coefficient for soils, the situation appears at first glance paradoxical. But it can be explained by the known hydrolysis of fluorapatite in soils, brought about by the drainage of atmospheric waters. In this process, according to our experimental findings (see below), the fluorapatite disseminated in soils partly pushes the fluor-ion out into the drainage waters and replaces it by a hydroxyl-ion; meanwhile fluorine is carried away by the water flow.

For granitic pegmatites, usually enriched by fluorite and other minerals containing fluorine, the fluorine-phosphorus coefficient is considerably higher, increasing up to 0.79 according to E. A. Fersman (1933).

For fresh surface-waters the fluorine-phosphorus coefficient rises still further, reaching about 2.0 or more, on the average.

For ocean water the fluorine-phosphorus coefficient attains values of the order of:

$$\frac{1.0 \times 10^{-4} \% \text{ F}}{5.0 \times 10^{-6} \% \text{ P} \times 2.29} = 8.70$$

In ancient or "relict" sea basins the coefficient reaches still higher values.

2. Minerals containing fluorine

Table 2 gives data on 34 known minerals containing fluorine. Its examination leads to the following conclusions:

(a) The predominant majority (26) of the minerals containing fluorine are related to processes of the type of pneumatolysis and hypotherms, in which the fluor-ion is replaced isomorphically by the hydroxyl ion.

(b) Only 6 minerals are genetically related to magma.

(c) Four minerals are directly connected with vulcanogenic processes.

(d) Only two minerals--fluorite and fluorapatite--are genetically related to sea sediments of normal salinity at an early stage of salinification, and three minerals--fluoborite, schairerite, and sulfohalite--to processes of advanced halogenesis (salt lakes and drying "relict" basins).

We shall concern ourselves in the present paper principally with the migration of fluor-ions in sea sediments.

Table 2.—Natural minerals containing fluorine

Sample no.	Mineral and its formula	System	Optical index	Specific gravity	Conditions of formation
	I. ALUMINO-SILICATES				
	a) Group of lithium micas				
1	Lepidolite $KLiAl_2Si_3O_9(OH,F)_2$	Monoclinic	Nm = 1.553	2.8 - 3.3	Magmas, pneumatolysis (pegmatitic veins, metamorphic rocks)
	b) Group of micas Mg - Fe				
2	Phlogopite $KMg_3AlSi_3O_{10}(OH,F)_2$		--	2.75 - 2.97	
3	Biotite $K(Mg,Fe^{\cdot\cdot})_3AlSi_3O_{10}(OH,F)_2$		Ng from 1.630 to 1.677 Np from 1.580 to 1.623		
4	Lepidomelane $KFe^{\cdot\cdot}{}_3Fe^{\cdot\cdot\cdot}Si_3O_{10}(OH,F)_2$	Monoclinic	Ng 1.733 Np 1.615		Granite, gneiss
5	Tsinnval'dite $K_2Li_2(Mg,Fe^{\cdot\cdot})_2(Al,Fe^{\cdot\cdot\cdot})_4Si_6O_{20}(OH,F)_4$	Monoclinic	--	2.9 - 3.1	
	c) Group of topaz and garnet				
6	Topaz $Al_2SiO_4(OH,F)_2$	Orthorhombic	--		Depth pneumatolysis 375-575°C
7	Vesuvianite $(SiO_4)_5Al_2Al(OH,F)(Ca,Mg,Fe)_6$		--		

Table 2.--Natural minerals containing fluorine (continued)

Sample no.	Mineral and its formula	System	Optical index	Specific gravity	Conditions of formation
	II. MAGNESIUM FLUOR-ORTHOSILICATES OF THE CHONDRODITE GROUP				
8	Norbergite $Mg_2SiO_4Mg(F,OH)_2$	Orthorhombic	Ng = 1.590 Np = 1.563	3.1 - 3.2	Pneumatolysis in dolomitic limestones and lavas
9	Chondrodite $2Mg_2SiO_4Mg(F,OH)_2$	Monoclinic	Ng = 1.62-1.64 Np = 1.59-1.60	3.1 - 3.2	
10	Humite $3Mg_2SiO_4Mg(F,OH)_2$	Orthorhombic	Nm = 1.57-1.63	3.1 - 3.2	
11	Clinohumite $4Mg_2SiO_4Mg(F,OH)_2$	Monoclinic	Nm = 1.64-1.67	3.1 - 3.2	
	III. PHOSPHATES				
	a) Group of apatites				
12	Apatite $Ca_5(PO_4)_3(F,OH)$	Hexagonal	E = 1.630 W = 1.633	3.2	Magmas, pneumatolysis, therms; sedim. rocks
	b) Group of wagnerite				
13	Wagnerite $Mg_3P_2O_8Mg(OH,F)_2$	Monoclinic	Ng = 1.582 Np = 1.569	3.07 - 3.14	Metamorphic rocks, veins
14	Triplite $R''_3P_2O_8R(OH,F)_2$, where R = Fe, Mn, Ca, Mg	Monoclinic	1.65-1.68	3.44 - 3.8	
	c) Group of aluminophosphates - Group of amblygonite				
15	Amblygonite $AlPO_4(Li,Na)F$	Triclinic	--	3.05 - 3.11	In granites together with lepidolite
16	Herderite $(Ca,Be)_2PO_4(F,OH)$	Orthorhombic or monoclinic	--	3	Pneumatolysis (with topaz, beryl)
17	Wavellite $Al_3(PO_4)_2(OH,F)_35H_2O$	Orthorhombic	--	2.3 - 2.5	

Table 2.--Natural minerals containing fluorine (continued)

Sample no.	Mineral and its formula	System	Optical index	Specific gravity	Conditions of formation
		IV. SIMPLE FLUORIDES			
		a) Group of fluorite and sellaite			
18	Fluorite CaF_2	Cubic	1.434	3.01 - 3.25	Hydrotherms, volcanogenic, sedimentary
19	Sellaite MgF_2	Tetragonal	W = 1.378	2.97 - 3.15	Inclusion in fluorspars, Colorado
20	Tizonite $(Ce, La, Di)F_3$	Tetragonal	--	6.10	
		b) Group of oxifluorides			
21	Nocerite $2(Ca, Mg)F_2(Ca, Mg)0$	Hexagonal	W = 1.509 E = 1.485	2.96	Volcanic tuff near Napoli
22	Fluocerite $(Ce, La, Di, V)_2OF_4$	Hexagonal	--	5.7 - 5.9	Pegmatites
		c) Hydrates			
23	Fluellite $AlF_3 \cdot H_20$	Orthorhombic	1.490	2.17	Pneumatolysis, together with $Sn0_2$
		V. COMPLEX FLUORIDES			
		Group of cryolite (waterless)			
24	Cryolite $3NaF \cdot AlF_3$	Monoclinic	Ng = 1.340 NP = 1.338	2.95 - 3.00	Pneumatolysis, veins in gneisses and granites
25	Chiolite $2NaF \cdot AlF_3$(or $5NaF \cdot 3AlF_3$)	Tetragonal	W = 1.349 E = 1.342	2.84 - 2.90	
26	Prosopite $Ca(F, OH)_2 \cdot 2Al(F, OH)_3$	Monoclinic	Ng = 1.510 Np = 1.501	2.88	
27	Gearksutite $CaF_2 \cdot Al(F, OH)_3 \cdot H_20$	Monoclinic	1.454	2.75	Together with cryolite
28	Pachnolite $NaF \cdot CaF_2 \cdot AlF_3 \cdot H_20$	Monoclinic	1.413	2.98	Weathering of cryolite

Table 2. --Natural minerals containing fluorine (continued)

Sample no.	Mineral and its formula	System	Optical index	Specific gravity	Conditions of formation
29	Ralstonite $(Na_2Mg)F_2 \cdot 3Al(F, OH)_3 \cdot 2H_2O$	Cubic	1.43	2.55	Together with cryolite
30	Creedite $2CaF_2 \cdot 2Al(F, OH)_3 \cdot CaSO_4 \cdot 2H_2O$	Monoclinic	1.46 - 1.49	2.71	
		VI. FLUOSILICATES			
31	Hieratite $2KF \cdot SiF_4$	Cubic	--	--	Pneumatolysis, fumaroles
		VII. FLUOHALOGENIDES			
32	Fluoborite $3MgO \cdot B_2O_3 \cdot 3Mg(F, OH)_2$	Hexagonal	--	2.89	
33	Schairerite $Na_2SO_4 \cdot Na(F, Cl)$	Trigonal	--	2.612	
34	Sulfohalite $2Na_2SO_4 \cdot NaCl \cdot NaF$	Cubic	--	2.69	Lake salts, California

II. CONDITIONS OF THE FORMATION OF FLUORAPATITE IN SEDIMENTARY ROCKS

3. The system $CaO-P_2O_5-HF-H_2O$

Introductory remarks

The present investigation of the four-component system $CaO-P_2O_5-HF-H_2O$ is a natural continuation and expansion of our previous work on the tri-component system $CaO-P_2O_5-H_2O$ (Kazakov, 1937), carried out by introducing an additional component, the fluor-ion. As should have been expected theoretically, three new precipitated phases are obtained in this more complex system:

Fluorite . . . . CaF_2

Fluorapatite . . . . $Ca_5(PO_4)_3F$

Fluor-hydroxylapatite. . . . . $Ca_5(PO_4)_3(F,OH)$

Naturally, each of these new phases has its own fields of crystallization and stability.

From the methodological standpoint this investigation proved to be more complicated than the study of the tri-component system $CaO-P_2O_5-H_2O$. First of all, attention must be called to a number of analytical difficulties due to the small amounts of P_2O_5 and partly of F.

In the extreme alkaline fields of the system the equilibrated concentration of P_2O_5 declines to an infinitesimal value of the order of 0.005-0.001 mg./lt. P_2O_5. To obtain reliable results in such cases it is necessary to employ 5 to 6 liters of equilibrated solution even when applying the good colorimetric method of Tsinsadze with the use of an electrophotocolorimeter. This quantity requires in turn using large containers (5 to 10 liters in capacity and treated with paraffin) for the reactions;

conducting the work with oil or mercury locks on the mixers, under conditions of all possible sterilization and of double distillation, for the prevention of pollution; treating the dry residue, obtained by evaporation, with hydrogen peroxide before the determination of P_2O_5; and so forth.

The fluorine was determined according to Penfield (by elimination), with a subsequent titration with thorium nitrate. In the case of small concentrations of CaO (less than 5 mg./lt.), controlling determinations were made by the nephelometric method.

To obtain more crystallized sediments and a balanced state of the system, the first phase of the process (mixing the reagents) was made to last from 30 to 50 hours. The second phase of the process--decrease of residual oversaturation ("a seasoning" period in each experiment)--lasted from 1 to 2 months, with a systematic control of the liquid phase with respect to pH and P_2O_5. Moreover, the experiments themselves were conducted by two methods, which allowed studying the onset of equilibrium in two ways, with respect to dissolution and with respect to crystallization. It is proper to mention here that the second method is more reliable because the process of dissolution not infrequently ceases long before the onset of equilibrium in the case of exceedingly dilute solutions. We employed principally the method of slow crystallization, mostly at a rate of about 5 mg./lt. P_2O_5 per hour. The reagents were:

(a) lime water $Ca(OH)_2$;

(b) orthophosphoric acid $H_3PO_4 \cdot aq$;

(c) the source of fluorine was mostly NaF.

Method of mixing reagents

In most cases the solutions $Ca(OH)_2$ and H_3PO_4 were poured simultaneously at a definite given speed from burets (or automatic-dosage instruments) into a container with a mixer. For a good formation (crystallization) of precipitated phases, we ordinarily used slow crystallization at a rate of the order of 5 mg./lt. P_2O_5 per hour. Fluorine (as NaF or HF) was mostly introduced together with H_3PO_4.

The mixing of reagents (the first phase of the reaction) usually continued from 24 to 100 hours; the second phase of the reaction (holding off the system until equilibrium) lasted mostly about one month.

The precipitated phases were controlled by ordinary methods of chemical analysis and of crystal optics; in a number of cases the sediments were studied by techniques of X-ray structural analysis and of thermal analysis.

The system CaO-P_2O_5-HF-H_2O investigated by us has significance not only in interpreting the geochemistry of fluorine in sedimentary rocks and the origin of sedimentary fluorapatite and fluorite, but also in questions of agrochemistry, the physiology of phosphate feeding of plants, and the chemistry of soils. Enthusiasm over the theory of the "absorbing complex" in soil sciences has in a number of cases obscured the problem and unfortunately has retarded the application of the theory of phase equilibria within the ranges of low concentrations for the study of soil processes.

The results of our experiments are summarized in table 3 (59 experiments) and table 4 (27 experiments). In both tables the data are arranged in an order from the weakly acid to the extremely alkaline fields.

Table 3.--System $CaO-P_2O_5-HF-H_2O$ at 25°C.

Table 3.--System $CaO-P_2O_5-HF-H_2O$ at 25°C.

Serial no.	Reagents: Concentrations, Mg/1: CaO	Reagents: Concentrations, Mg/1: P_2O_5	Reagents: Concentrations, Mg/1: F	Reagents: Pulp, solid:liquid: 1	Reagents: Pulp, solid:liquid: gr/1	Given ratios: CaO: :P_2O_5	Given ratios: mg/1	Rapidity of crystallization mg/1 P_2O_5 per/hr	"Seasoning" expressed in days	Equilibrated liquid phase, mg/1: CaO	Equilibrated liquid phase, mg/1: P_2O_5	Equilibrated liquid phase, mg/1: F	Equilibrated liquid phase, mg/1: pH	PRECIPITATED PHASES: Chemical composition: % CaO	% P_2O_5	% F	% undissolved sediments	p.p.p.2/ 900°/100°C.	Σ	ΣΣ	%CaO/%P_2O_5	%F/%P_2O_5 x 100	Formulas
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
107	--	--	0	--	--	1.06:1	--	6.9	16	50.4	103.0	0	6.37	47.30	40.95	0	0.58	10.95	99.80	99.80	1.154	0	$Ca_3P_2O_8 \cdot H_2O$ + + $CaHPO_4 \cdot 2H_2O$
49/II	548	1437	0	10	--	1:1	--	2	36	39.3	81.5	0	6.58	45.0	47.63	0	0	8.35	100.98	100.98	0.945	0	Same
48/II	548	1437	0	10	--	1:1	--	28	22	31.4	69.8	0	6.54	49.69	43.58	0	0	6.05	99.32	99.32	1.140	0	$Ca_3P_2O_8 \cdot H_2O$
227/II	548	1437	0	--	--	1:1	--	4	17	32.0	56.0	0	6.58	49.18	43.23	0	0	7.31	--	100.48	1.138	0	"
28/II	548	1437	0	--	--	1:1	--	quick mixing	58	32.0	48	0	6.35	--	--	--	--	--	--	--	--	0	"
51/II	548	1437	0	--	--	1.2:1	--	0.4	68	31.4	43.4	0	6.86	46.67	42.53	0	--	10.59	99.79	99.72	1.097	0	"
134	--	2000	20	10	--	--	--	8	30	20	9.0	0.14	7.08	51.17	41.77	0.56	0.08	6.32	99.90	99.67	1.204	1.34	
76	1294	1443	43	10	0-2.34	1.04:1	10	5.7	32	16	9.4	0.62	7.10	51.51	39.23	1.31	0.07	8.01	100.18	99.63	1.265	3.34	$Ca_3P_2O_8 \cdot H_2O + CaF_2$
108	--	--	--	--	--	0.97:1	--	6.1	15	12	5.0	0	7.20	49.72	44.52	0	0.52	6.05	100.81	100.81	1.117	0	$Ca_3P_2O_8 \cdot H_2O$
135	--	2000	10	--	--	--	--	8	7	13.4	3.70	0.10	7.30	52.39	39.62	0.25	0.16	7.74	99.96	99.86	1.314	0.63	$Ca_5(PO_4)_3 \cdot (F,OH)$
132	--	2000	100	--	--	--	--	--	75	14.0	3.35	0.94	7.15	51.34	39.29	1.92	0	7.39	99.92	99.12	1.235	4.89	"
133	--	2000	50	--	--	--	--	8	60	11.5	3.15	0.25	7.10	51.30	40.65	0.95	0	6.48	99.38	--	--	2.33	"
42/II	--	--	--	5	--	1.40:1	--	4	18	11.2	3.7	0	6.97	52.94	40.52	0	0	5.82	99.28	--	1.306	0	$Ca_5(PO_4)_3OH$
109	--	--	--	--	--	0.93:1	--	6	12	9.6	3.0	0	7.30	51.40	41.06	0	0.31	7.10	99.87	100.17	1.254	0	"
131	--	2000	1000	--	--	--	--	50	--	9.0	0.82	15.4	7.40	50.23	33.92	10.61	0	8.98	103.74	99.29	--	32.5	$Ca_5(PO_4)_3F + CaF_2$
137	--	2000	1	--	--	--	--	8	30	7.0	0.30	0.04	7.5	52.51	39.63	0.05	0	7.48	99.67	--	--	0.13	$Ca_5(PO_4)_3(F,OH)$
74	1165	1374	52	10	0-1.55	1.34:1	10	5.5	44	8.0	0.050	0.45	7.90	52.15	38.16	1.20	0.08	8.25	99.84	--	--	3.14	"
77	1165	1374	52	10	0-1.62	1.20:1	10	5.5	33	6.6	0.080	0.60	8.00	51.82	36.01	1.64	0.16	10.28	99.91	--	--	4.55	"
80	914	1258	2000	9	0-0.23	--	10	3.1	18	14.1	0.090	6.0	8.11	49.81	33.92	3.00	0	14.07	100.80	--	--	8.85	Close to $Ca_5(PO_4)_3F$
147	--	2000	300	--	--	--	--	--	8	15.6	0.10	15.7	7.85	50.03	36.08	4.50	0	10.69	101.30	99.41	--	12.5	$Ca_5(PO_4)_3F + CaF_2$
148	--	2000	350	--	--	--	--	--	8	17.4	0.10	14.6	8.05	50.57	37.21	5.50	0	8.36	101.64	99.25	--	14.8	"
120	1200	2000	286	2	--	1:1	--	--	12	17.9	0.04	8.7	7.80	50.35	37.52	3.51	0	9.15	100.53	--	--	9.30	$Ca_5(PO_4)_3F$
136	--	2000	5	--	--	--	--	8	20	20.0	0.20	0.08	7.6	53.54	39.24	0.15	0.12	7.13	100.17	--	--	0.39	$Ca_5(PO_4)_3(F,OH)$
103	641	1416	2000	9	--	1.51:1	10	3.13	18	20.0	0.08	6.50	8.5	53.31	32.87	3.00	0.47	11.13	100.78	99.52	--	9.12	$Ca_5(PO_4)_3F$
153	--	2000	250	--	--	--	--	--	30	22.3	0.072	15.0	8.1	51.35	37.16	5.85	0.02	7.98	102.36	99.90	--	15.7	$Ca_5(PO_4)_3F + CaF_2$
152	--	2000	500	--	--	--	--	--	20	24.0	0.07	16.6	8.60	49.28	29.33	9.52	0	14.57	102.70	98.69	--	32.5	"
150	--	2000	300	--	--	--	--	--	20	25.5	0.06	16.1	8.15	50.30	35.77	5.98	0	9.74	101.79	99.79	--	16.7	"
106	640	1416	2000	9	0-0.168	1.52:1	20	3.15	32	27.0	0.080	6.8	8.30	50.85	35.89	3.10	0.36	10.73	100.93	99.86	1.275	8.60	Close to $Ca_5(PO_4)_3F$
149	--	2000	500	--	--	--	--	--	30	30.0	0.08	14.8	8.20	50.83	33.57	8.10	0	10.03	102.53	99.13	--	24.1	$Ca_5(PO_4)_3F + CaF_2$
151	--	2000	350	--	--	--	--	--	30	35.6	--	16.0	8.30	50.47	32.01	5.88	0	13.10	101.46	98.00	--	18.4	"
161	--	2000	200	--	--	--	--	--	20	39.2	0.036	7.5	8.20	52.43	34.59	3.24	0	9.01	99.27	98.89	--	9.36	}
102	906	1657	2000	9	0-0.087	2.24:1	10	0.74	18	43.6	0.050	6.8	9.00	51.00	29.88	2.70	0.06	17.27	100.91	99.78	--	9.03	}$Ca_5(PO_4)_3F$
101	727	1258	2000	9	0-0.034	3.88:1	10	0.27	24	44.4	0.040	7.3	9.16	48.84	28.58	--	0.51	19.68	--	--	--	--	$Ca_5(PO_4)_3F + CaF_2$
43/II	--	--	--	10	--	1.80:1	--	4.0	27	44.8	0.015	0	9.24	58.06	40.20	0	--	5.78	99.04	99.04	--	--	$Ca_5(PO_4)_3OH$
154	--	2000	250	--	--	--	--	--	30	49.0	0.040	15.4	8.71	51.36	33.22	5.88	0.03	11.38	101.87	99.40	--	17.7	$Ca_5(PO_4)_3F + CaF_2$
155	--	2000	400	--	--	--	--	--	40	50.0	--	13.61	8.67	55.40	28.40	10.60	0.05	10.54	103.99	99.53	--	37.3	"
143 1/	--	--	--	4	--	--	--	--	9	51.2	0.030	16.5	8.5	--	--	--	--	--	--	--	--	--	"
144	--	--	--	2	--	--	--	--	18	--	--	14.7	8.12	--	--	--	--	--	--	--	--	--	"
141	--	--	--	--	--	--	--	--	--	62.4	0.015	14.5	8.75	--	--	--	--	--	--	--	--	--	"
130	1200	2000	400	4	--	--	--	8	30	66.7	0.020	15.0	8.62	52.05	35.33	6.68	--	7.83	101.89	99.09	--	--	"
52/II	--	--	--	--	--	1.40:1	--	--	37	73.1	0.031	--	9.02	54.07	40.07	0	--	5.54	99.68	99.68	--	--	$Ca_5(PO_4)_3OH$
156	2000	1000		--	--	--	--	--	30	73.6	0.052	13.5	8.80	52.20	23.06	15.0	0.03	10.51	105.80	99.59	--	65.0	$Ca_5(PO_4)_3F + CaF_2$
105	906	1657	--	--	0-0.304	2.24:1	20	0.73	7	83	0.045	12.1	9.50	53.69	30.83	4.03	0.44	12.73	101.72	100.03	1.549	13.1	"
118	--	--	--	--	--	5:1	40	--	12	106.4	0.040	13.0	9.58	52.68	25.96	4.38	0.11	18.65	101.78	99.94	--	16.8	"
104	727	1258	2000	9	0-0.055	3.92:1	20	0.28	7	107	0.013	13.4	9.60	51.74	25.83	5.25	0.53	18.69	102.04	99.83	--	20.3	"
110	1000	2000	2000	10	0-0.170	5:1	10	4	16	118	0.020	12.0	9.7	53.28	27.24	4.73	0	14.72	--	--	--	17.3	"
45/II	--	--	--	10	--	2.20:1	--	4	38	139.7	0.011	--	10.5	53.23	40.08	0	--	5.98	99.29	99.29	--	0	$Ca_5(PO_4)_3OH$
113	1000	2000	2000	9	0-0.173	5:1	20	4.4	22	347	0.010	6.3	--	53.44	29.15	2.87	0.61	14.69	100.76	99.56	--	9.86	$Ca_5(PO_4)_3F + CaF_2$
183	--	5000	750	10	--	2.2:1	--	50	10	591	--	6.0	--	53.14	32.38	3.28	0.01	12.12	100.93	99.55	--	10.13	"
185	--	5000	1250	--	--	--	--	50	10	566	0.040	5.80	--	52.85	28.32	3.70	1.07	14.50	100.44	99.89	--	13.07	"
182	--	5000	625	--	--	--	--	50	7	553	0.045	6.1	--	52.44	28.27	2.42	0.71	16.07	99.91	98.75	--	8.55	$Ca_5(PO_4)_3(F,OH)$
184	--	5000	875	--	--	--	--	50	10	644	--	6.0	--	52.66	27.90	3.27	1.00	15.37	100.20	98.83	--	11.72	$Ca_5(PO_4)_3F + CaF_2$
181	--	5000	500	--	--	--	--	50	7	662	--	6.2	--	52.83	32.03	3.70	0.36	12.12	101.04	99.49	--	11.6	"
112	1000	2000	2000	8	0-0.024	100:1	10	1	117	720	0.010	4.7	--	--	--	--	--	--	--	--	--	--	"
116	--	--	--	--	--	--	--	5	20	1210	<0.05	0	>11.0	--	--	--	--	--	--	--	--	--	$Ca_5(PO_4)_3OH + Ca(OH)_2$
111 1/	--	--	--	10	--	--	--	--	--	1212	0.005	--	--	--	--	--	--	--	--	--	--	--	}Triple ~~dot~~ point
115 1/}	--	--	--	10	0.55	--	--	--	7	1244	0.002	2.5	--	--	--	--	--	--	--	--	--	--	}$Ca_5(PO_4)_3F$ +
119 }	--	--	--	10	--	--	--	--	25	1199	0.001	2.4	>11.0	--	--	--	--	--	--	--	--	--	}+ $CaF_2 + Ca(OH)_2$
										1210	0	0											$Ca(OH)_2$

1/ Taken from the literature for 25°C. and verified.

2/ Loss on ignition

Table 4. --System $CaO-HF-H_2O$ at 25°C.

Serial no.	Reagents: Concentration gr. /lt. CaO	Reagents: Concentration gr. /lt. F	Reagents: Method of mixing	Given stoichiometric norm in % CaO	Rapidity of cryst., mg. /lt. CaF_2 per hour	"Seasoning" in days	Equilibrated liquid phase, mg. /lt CaO	Equilibrated liquid phase, mg. /lt F	Equilibrated liquid phase pH	Solid: Liquid phase gr. /lt.	Precipitated phase %CaO	Precipitated phase %F	Precipitated phase Sum
1	2	3	4	5	6	7	8	9	10	11	12	13	14
86	527	1143	Ca(OH) HF	7.4	433-32	30	0.30	718.8	2.26	0.316	51.45	48.82	100.27
85	1054	1000	"	17.8	14.6	37	0.30	522.2	2.34	0.224	--	--	--
87	527	889	"	21.2	43-32	30	0.30	458.4	2.34	0.233	--	--	--
88	527	691	"	36.5	--	30	0.40	310.8	2.45	--	--	--	--
89	527	538	"	56.2	--	30	2.0	170.2	2.61	--	--	--	--
90	527	418	"	83.4	--	30	4.8	58.4	2.91	--	--	--	--
96	--	1000	HF $Ca(OH)_2$	100	Quick mixing	30	5.4	42.0	3.21	--	--	--	--
83	1054	1000	$Ca(OH)_2$-HF	100	939-420	39	10.7	20.0	5.57	--	--	--	--
98	1294	1000	HF-$Ca(OH)_2$	105	79-36	30	28.0	18.4	8.70	There is a Debye picture			
84	1054	1000	"	100	2000-880	37	31.4	15.0	8.51	--	--	--	--
142 1/		(CaF_2)				17	31.3	17.4	8.60	0.315	--	--	--
129 1/	20	5.0	$Ca(OH)_2$+HF+CaF_2	--	--	1	32.2	16.0	8.27	--	--	--	--
99	914	1000	$Ca(OH)_2$-HF	125	--	25	41.6	16.3	9.05	0.122	--	--	--
128 1/	43	3.1	$Ca(OH)_2$+HF+CaF_2	--		3	53.2	14.5	8.86	1.261	--	--	--
138	1200			147	80	22	71.2	15.4	8.87	0.106	--	--	--
124	1258	5183	HF-$Ca(OH)_2$	--	12	9	102	14.0	--	0.066	--	--	--
127 1/	100	2	$Ca(OH)_2$+HF+CaF_2	--	--	3	109	11.0	--	--	--	--	--
126 1/	170	1.3	"	--	--	2	178	9.0	--	0.489	--	--	--
100	1294	1000	$Ca(OH)_2$-HF	>100	--	24	190	9.5	--	--	--	--	--
123	1258	5183	HF-$Ca(OH)_2$	--		9	206	11.5	--	--	51.19	48.50	99.69
94	527	153	$Ca(OH)_2$-HF	280	--	30	238	11.0	9.99	0.426	--	--	--
95	527	119	"	370	--	30	267	10.7	--	0.264	--	--	--
122	1258	5183	HF-$Ca(OH)_2$	--	--	11	456	7.8	--	--	--	--	--
121	1258	5183	"	--	--	12	711	5.3	--	1.0	Double point $Ca(OH)_2$ + CaF_2		
186 1/			CaF_2	--	--	--	1038	4.0	--	--	--	--	--
114 1/	$(Ca(OH)_2) + (CaF_2)$					14	1212	2.6	>11	--	--	--	--
117	$(Ca(OH)_2) + (CaF_2+HF)$.				160	30	1213	3.0	>11	--	$Ca(OH)_2$ 1/	--	--
The average of nos. 114 and 117 is taken as.							1213	2.8	>11	--	--	--	--

1/ The solubility of $Ca(OH)_2$ at 25°C. is taken to be 1200 mg. /lt. CaO.

In all, we conducted and analyzed 86 lengthy experiments covering fields within a broad range of values of pH (from 6 to 12) and of equiponderant concentrations (from 103 to 0.001 mg./lt. P_2O_5, and from 0 to 790 mg./lt. F).

After the equilibrated systems used in these experiments were filtered, we conducted 231 quantitative determinations of CaO, P_2O_5, and F in the liquid phases and 349 quantitative analytical determinations in the solid phases, not counting control determinations within the procedures of the experiments themselves.

Figure 1 shows the orthogonal projection of a three-dimensional model of the given system, made upon the vertical plane of coordinates CaO and P_2O_5. Figure 2 gives the same projection upon the horizontal plane of the coordinates CaO and F. Figure 3 presents the system in the plane of the coordinates pH and P_2O_5.

4. Characterization of the solid phases of the system and of the fields of their stability

The system $CaO-P_2O_5-HF-H_2O$ (isotherm 25°C.) was found to have in the fields of low concentrations of P_2O_5 seven precipitated phases, among which fluor-hydroxylapatite is a phase of variable composition. (See table 5).

5. Isomorphism of fluor-hydroxyl ions in the apatite lattice

The introduction of the fluor-ion component into the system $CaO-P_2O_5-H_2O$ considerably changes its appearance in the alkaline fields as well as the composition of bottom sediments because the fluor-ion enters into the crystal lattice of hydroxylapatite, forming first of all a wide

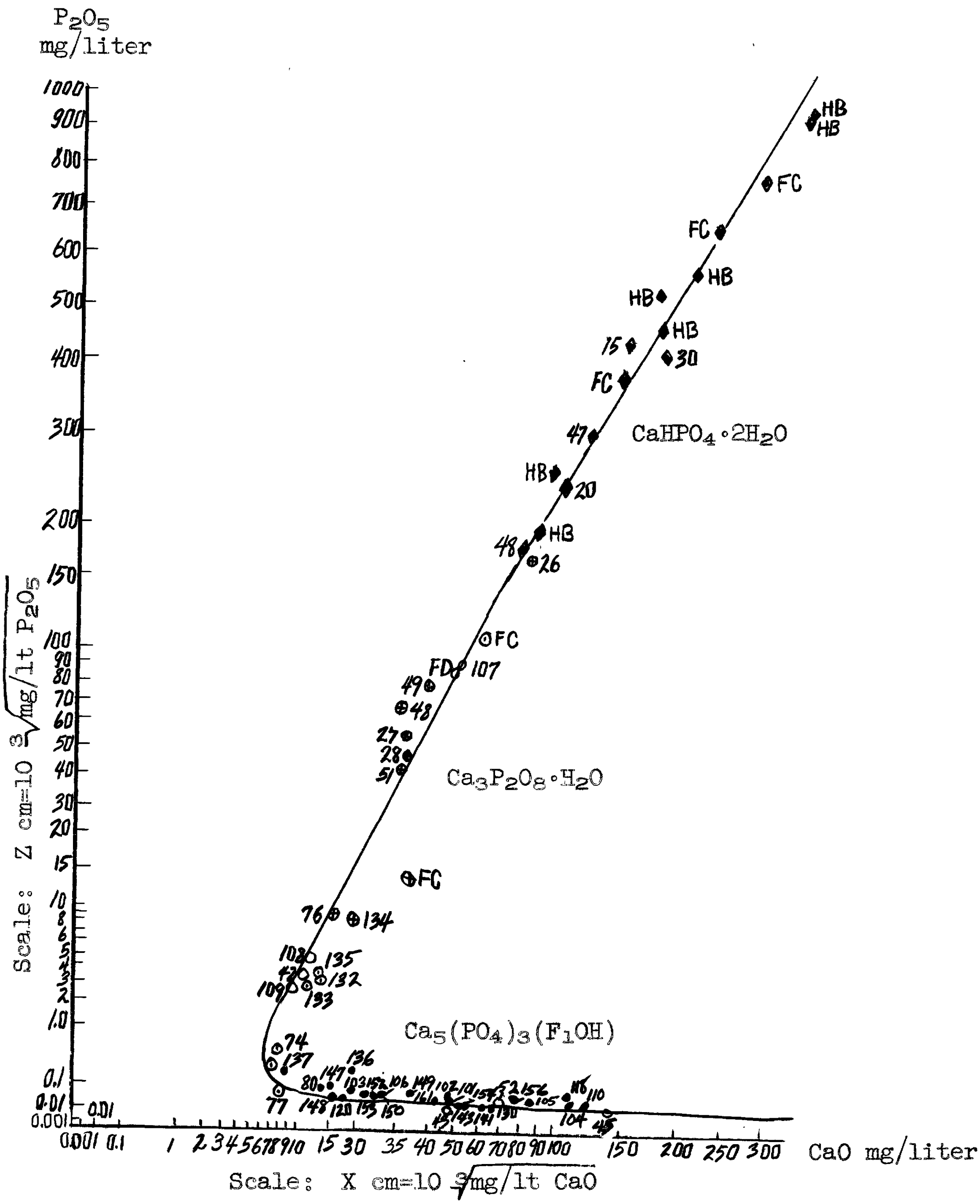


Figure 1.--System of the equilibria of CaO-P_2O_5-HF-H_2O at 25°C in the neutral and alkaline fields. Orthogonal projection upon the coordinate plane CaO-P_2O_5 mg/liter. Symbols are the same for figure 2.

Precipitated phases:

1. ● $CaHPO_4 \cdot 2H_2O$ (monetite)
2. ⊕ $Ca_3P_2O_8 \cdot H_2O$ (tricalcium-phosphate)
3. ○ $Ca_5(PO_4)_3OH$ (hydroxylapatite)
4. ◎ $Ca_5(PO_4)_3(F,OH)$ (fluorhydroxylapatite)
5. ● $Ca_5(PO_4)_3F$ (fluorapatite)
6. ◆ $Ca_5(PO_4)_3F + CaF_2$ (fluorapatite + fluorite)
7. • CaF_3 (fluorite)
8. ∘ $Ca(OH)_3$ (calcium hydroxide)

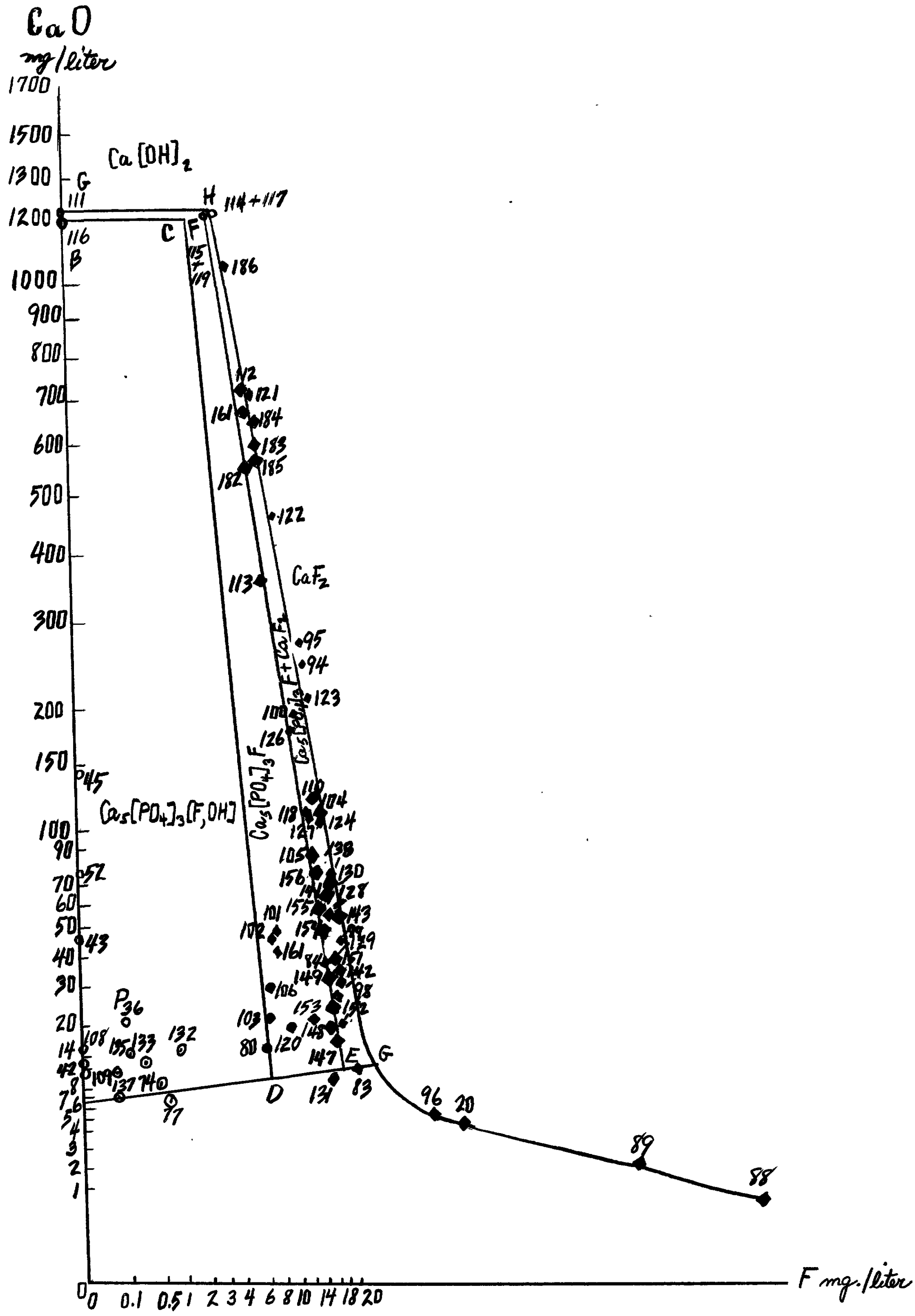


Figure 2.--System CaO-P_2O_5-HF-H_2O at 25°C. Projection upon the coordinate plane CaO-F mg./liter.

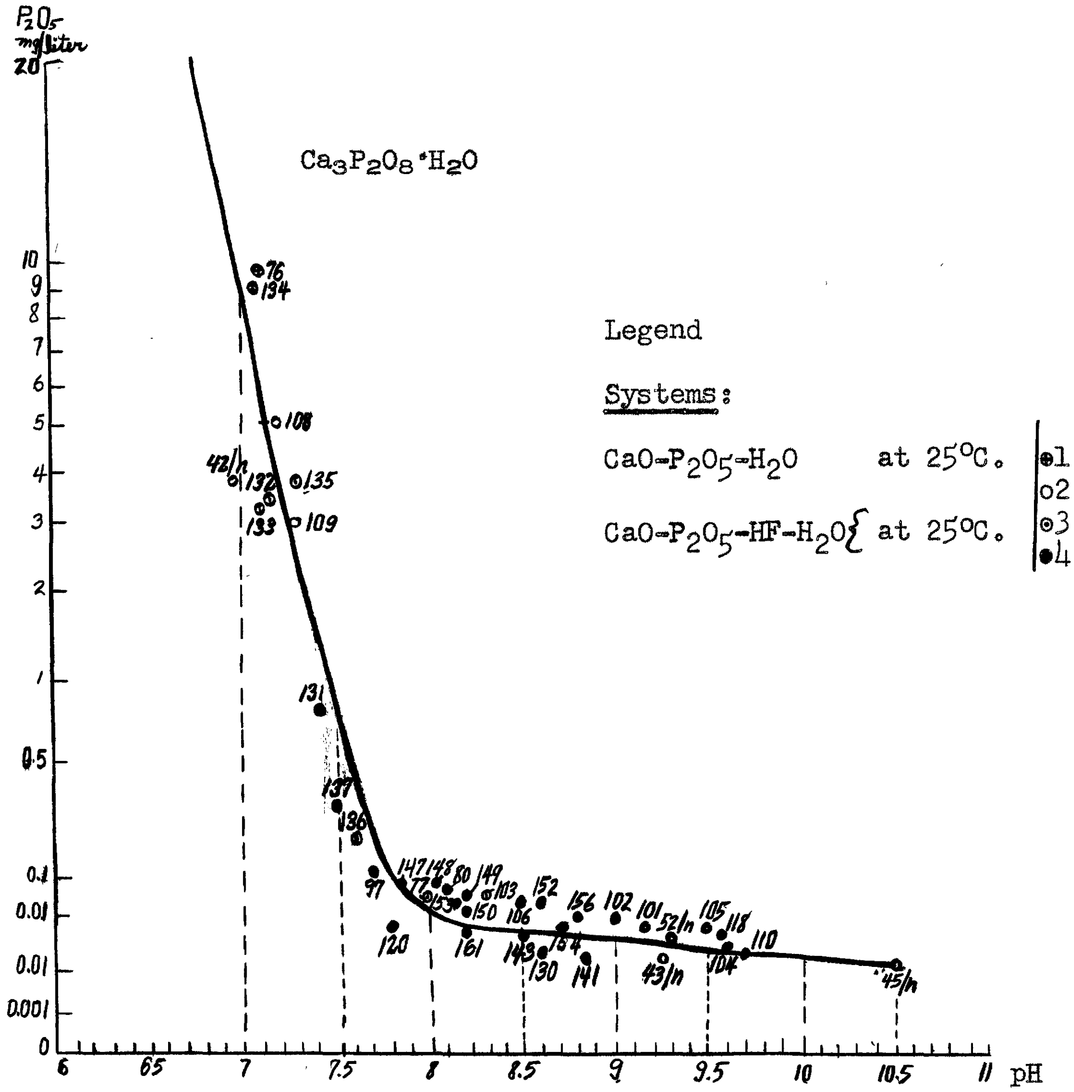


Figure 3.--System $CaO-P_2O_5-HF-H_2O$ in the coordinates pH-P_2O_5 at 25°C.

1. tricalcium-phosphate
2. hydroxylapatite
3. fluor-hydroxylapatite
4. fluorapatite

Table 5. --Precipitated phases of the system $CaO-P_2O_5-HF-H_2O$ (isotherm 25°C.) and the fields of their stability

Serial nos.	Precipitated phases	Points on the diagram	FIELDS OF STABILITY Composition of the equilibria of the liquid phase, mg./lt.			
			CaO	P_2O_5	F	pH
1	Diphosphate, hydrous (brushite) $CaHPO_4 \cdot 2H_2O$	--	$\geqslant 40$	$\geqslant 82$	--	$\leqslant 6.5$
2	Tri-calcium phosphate $Ca_3P_2O_8 \cdot H_2O$	--	from 40 to 12	from 82 to 5	--	from 6.5 to 7.1
3	Hydroxylapatite $Ca_5(PO_4)_3OH$	from 108 to 137 (Fig. 3)	12-6 6-1200	from 5 to 0.30 from 0.30 to 0.001	-- --	$\geqslant 7.1$
4	Fluor-hydroxylapatite $Ca_5(PO_4)_3(F,OH)$	from AD to BC (Fig. 2)	12-6 6-1200	same	from 0 to 9 (Point D)	$\geqslant 7.1$
5	Normal fluorapatite $Ca_5(PO_4)_3F$	from DE to CF	from 9 (point D) to 1210	"	from 1.5 (point C) to 17 (point E)	$\geqslant 7.1$
6	Fluorite CaF_2	from G to H	same	"	from 2.5 (Point F) to 16-18	
7	Calcium hydroxide $Ca(OH)_2$	111	1212	0	0	
	TRANSITION POINTS					
8	$Ca_3P_2O_8 \cdot H_2O + Ca_5(PO_4)_3(F,OH)$ point of experiment	108	12	5		7.1
9	$Ca_5(PO_4)_3OH + Ca(OH)_2$	Point B (exp. 116)	1210	0.005	0	--
10	$Ca_5(PO_4)_3F + CaF_2 + Ca(OH)_2$	Point F (exp. 115-119)	1200	0.001	2.5	--
11	$CaF_2 + Ca(OH)_2$	Point H (exp. 114-117)	1213	0	2.8-3.0	--

field of isomorphic mixtures (fluor-hydroxylapatite), as shown on Figure 2, field ABCD.

With a greater increase of the concentration of fluorine in the balanced liquid phases, up to a content of 1 to 7 mg./lt. (namely 1 mg./lt. F in the extreme right alkaline fields, and 7 mg./lt. F in the almost neutral, left fields on Fig. 2), the content of fluorine in the bottom sediments also increases and reaches the content of the normal sediments of fluorapatite, with a ratio (% F : % P_2O_5) x 100 = 8.93 (Fig. 2, field CDEF).

A further increase of the content of fluorine in the system at first does not result in the formation of new precipitated phases, until the balanced liquid phase has reached concentrations up to 2.5 mg./lt. of fluor-ion in the extreme alkaline fields and concentrations up to 17 mg./lt. F in the extreme left neutral fields (Fig. 2, line EF). From this moment, however, fluorite begins to settle upon the precipitated phases, together with fluorapatite, forming the field EFHG of the double sediments $Ca_5(PO_4)_3F + CaF_2$.

Finally, with a further increase of fluor-ion content in the liquidus and a decrease of P_2O_5, a narrow field is formed by the sediments of fluorite alone (Fig. 2, line GH).

For a fuller clarification of the regularities governing the process of fluoridation of hydroxylapatite, we have summarized in Table 6 and Figure 4 experimental data on the coefficients of fluoridation, the interphase distribution of fluorine, and the double points $Ca_5(PO_4)_3F + CaF_2$. These data are taken from experiments made within the fields having values pH = 8.0 ± 0.5, 9.5 ±, and 10, corresponding concentrations 40, 50 to 100, and 600 mg./lt. of CaO, and variable quantities of fluorine in the liquidus.

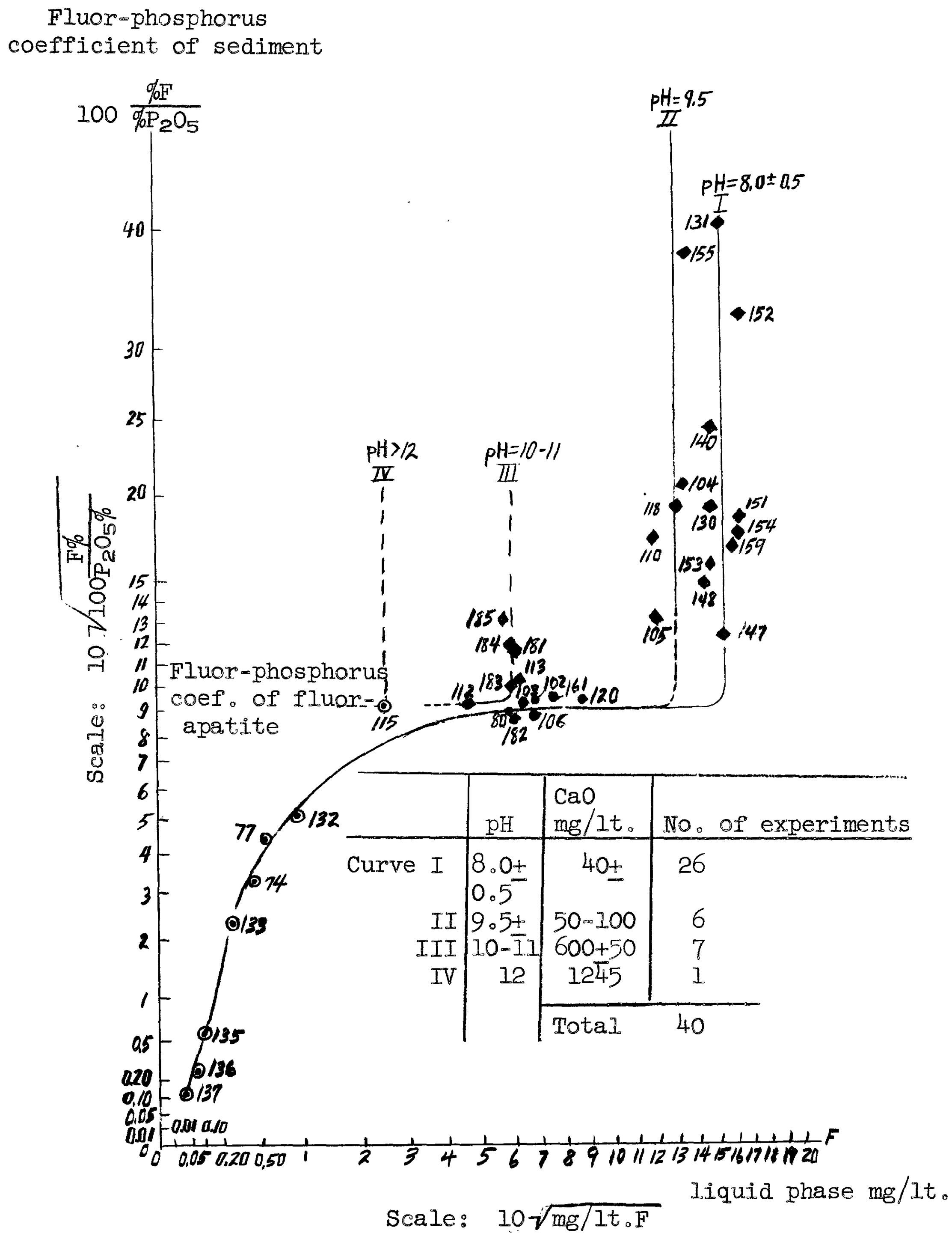
Table 6.--The extent of fluoridation of hydroxylapatite in its dependence upon the concentrations F and CaO in equilibrated solutions ($t = 25^{o}C.$)

(Curve I on fig. 4, for pH = 8.0 ± 0.5)

Serial no.	LIQUID PHASE mg./lt				SOLID PHASE					
	pH	CaO	P_2O_5	F	% F	$\%P_2O_5$	$\frac{\%F}{\%P_2O_5} \cdot 100$ 1/	% of fluoridation $\frac{100.k}{8.93}$	Coefficient of inter-phase distribution: $\frac{\%F \text{ in solid phase}}{\%F \text{ in liquid phase}}$	
137	7.50	7.0	0.30	0.04	0.05	39.63	0.13	0.56	12500	Sediments $Ca_5(PO_4)_2(F,OH)$ of hydroxyl-fluorapatite
136	7.60	20.0	0.20	0.08	0.15	39.24	0.39	4.37	18750	
135	7.30	13.4	3.70	0.10	0.25	39.62	0.63	7.05	25000	
133	7.10	11.5	3.15	0.25	0.95	40.65	2.33	26.1	38000	
74	7.90	8.0	0.050	0.45	1.20	38.16	3.14	35.2	26680	
77	8.00	6.6	0.080	0.60	1.64	36.01	4.55	51.0	27330	
132	7.15	14.0	3.35	0.94	1.92	39.29	4.89	54.7	20430	
80	8.11	14.1	0.090	6.0	3.00	33.92	8.85	99.1	5000	Sediments close to normal $Ca_5(PO_4)_3F$ fluorapatite
103	8.5	20.0	0.080	6.5	3.00	32.87	9.12	102.1	4616	
120	7.80	17.9	0.040	8.7	3.51	37.52	9.30	104.1	4035	
106	8.30	27.0	0.080	6.8	3.10	35.89	8.60	96.3	4559	
161	8.20	39.2	0.036	7.5	3.24	34.59	9.36	101.8	4320	
101	9.16	44.4	0.040	7.3	--	28.58	--	--	--	
147	7.85	15.6	0.10	15.7	4.50	36.08	12.5	--	--	2-phase sediments $Ca_5(PO_4)_3F+CaF_2$
148	8.05	17.4	0.10	14.6	5.50	37.21	14.8	--	--	
153	--	22.3	0.072	15.0	5.85	37.16	15.7	--	--	

etc. (No. 150, 154, 130, 149, 152, 131)

1/ The quantity $\frac{\%F}{\%P_2O_5}$ we will further call the "fluorphosphorus coefficient."



	pH	CaO mg/lt.	No. of experiments
Curve I	8.0± 0.5	40±	26
II	9.5±	50-100	6
III	10-11	600±50	7
IV	12	1245	1
		Total	40

Figure 4.--Diagram of the isomorphism of hydroxyl-fluor-ions in the lattice of apatite (isotherm of 25° C.).

Figure 4 was plotted as follows: On the abscissa we measured the equilibrated content of fluor-ion in the solution in units of mg. of fluorine per liter; the scale of the abscissa is 10 $\sqrt{\text{mg./lt. F.}}$ On the ordinate we plotted the corresponding percentage content of fluorine in the precipitated phases, expressed in units of the coefficient (% F: % P_2O_5) relative to % P_2O_5. This coefficient k for normal fluorapatite is (3.77 %F):(42.22 % P_2O_5) = 0.0893. The scale for values on the ordinate in Figure 4 is $10\sqrt{100.k}$ or $10\sqrt{100(\%F : \%P_2O_5)}$.

An analysis of the curve of inter-phase distribution of fluorine in the system $CaO-P_2O_5-HF-H_2O$ shows that an augmentation of the content of fluor-ion in the solutions of the system is accompanied by a very rapid increase of its content in the precipitated phase. The curve of the isomorphic replacement of the hydroxyl-ion by fluorine has the shape of a hyperbola (curve I, Fig. 4).

When a 100-percent fluoridation is reached, the curve of sediments of normal fluorapatite becomes a segment of a straight line disposed parallel to the abscissa axis, until the content of fluorine in the solution attains a certain limit-value which marks the start of the precipitation of fluorite CaF_2. Beginning with the latter moment a further addition of fluor-ion to the system ceases to increase the balanced concentration of fluorine in the solution, and the entire fluorine residue settles in the form of CaF_2, producing a two-phase sediment $Ca_5(PO_4)_3F + CaF_2$. This moment of transition appears on the diagram as a sharp break in the curve of fluorine distribution and its change into a straight vertical line.

It is relevant here to cite some data from the papers of Professor D. P. Grigor'ev (1935 and others) on the synthesis of magnesial-ferric micas, whose hydroxyl group can be fully replaced by fluorine. We give the isomorphic end-series of the micas of this type, studied synthetically.

Phlogopite.................... $\begin{cases} \text{from } KMg_3AlSi_3O_{10}(OH)_2 \\ \text{to } KMg_3AlSi_3O_{10}F_2 \end{cases}$

Biotite (according to Morozevich........... $\begin{cases} \text{from } K(Mg, Fe^{\cdot\cdot})_3AlSi_3O_{10}(OH)_2 \\ \text{to } K(Mg, Fe^{\cdot\cdot})_3AlSi_3O_{10}F_2 \end{cases}$

Lepidomelane.................. $KFe_3^{\cdot\cdot}Fe^{\cdot\cdot\cdot}Si_3O_{10}(OH,F)_2$.

D. P. Grigor'ev (1935) notes correctly: "in artificial micas the fluorine must take the places of the hydroxyl group, as is actually confirmed by X-ray investigations...." (p. 350).

6. Geologic-genetic interpretation of the fluorapatite system

In sea basins of normal salinity there is a widespread process of fluorine fixation, consisting in the deposition of fluorapatite in areas of phosphatic shelves; it is examined in detail in the paper of A. V. Kazakov (1939). This process of phosphorite formation is the first stage of the separation of fluorine in the cycle of development of sea-bottom lithogenesis.

The average content of phosphorus and fluorine in natural waters is given in Table 7.

It is interesting to express the process of fluorapatite sedimentation, with its fixation of fluorine, in the concrete form of an average annual balance-sheet, based on the tonnage and salt mass of world-wide yearly river-water discharge. We give average figures.

Annual evaporation from the entire hydrosphere: 428,000 km^3. (according to Knipovich, 1938)

Average annual quantity of precipitation over dry land: 106,822 km^3.

Annual discharge of river waters into seas and oceans: 26,700 km^3.

Annual emission, in solution, by river waters into the world ocean: P_2O_5...............about 1 million tons
F..................about 5.3 million tons.

Table 7.--Average content of phosphorus and fluorine in natural waters (Vinogradov, 1938)

	P_2O_5		F	
	Clark %P	mg./lt. P_2O_5	Clark %F	mg./lt. F
	A. SEA WATERS (WORLD OCEANS)			
World oceans	$5.0 \cdot 10^{-6}$	0.114	$1.0 \cdot 10^{-4}$	1.0
	B. RIVER WATERS			
Volga	--	--	--	0.10-0.12
Dnepr	--	--	--	0.16-0.17
Don	--	--	--	0.30
Average	--	0.04	--	0.20

If we take for the basis of calculations the readjustable equilibrium of salt composition and salt mass in the world's oceans, established during geologic time, as set forth by V. I. Vernadskii and others, we can consider that, on the average, all this mass of phosphorus, namely, about 4 million tons of phosphorites (taking provisionally their content to be 25 percent P_2O_5), is sedimented annually from the water mass of the world-oceans upon respective "phosphate shelves" in one or another degree of concentration and dispersion.

With the given chemosedimentation of phosphorites, these minerals capture (for saturating with fluorine the apatite lattice of the phosphate substance of phosphorites) about 90 thousand tons of fluorine, which constitutes, however, only about 1.7 percent of its annual discharge by river waters.

Thus, the larger part of fluorine excess is concentrated in the world's oceans up to an average content of 1 mg./lt. A further increase in the concentration of fluorine is limited by the removal of fluorine from the world's oceans under conditions of "relict" basins, mainly in the form of fluorite, which reminds us of the fate of the other haloids, chlorine and bromine.