

## STUDIES OF THE SUBSTITUTION OF OH<sup>-</sup> BY F<sup>-</sup> IN VARIOUS HYDROXYLIC MINERALS\*

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### ABSTRACT

The extent of replacement of the hydroxyl ions by fluorine in the type clay minerals and alumina hydrates has been studied by four separate methods: back-titration of developed alkalinity, wet analysis for fluorine, quantitative infra-red absorption spectroscopy of the OH band, and powder x-ray diffraction techniques. It has been found that relatively large amounts of fluorine (up to 50% of the total hydroxyl ions) are taken up by these minerals, the amount increasing with temperature. The magnitude of the exchange is similar in the type clay minerals, but in minerals such as diaspore, hydrogen bonding appears to strongly inhibit exchange. The question as to whether the fluorine replaces the hydroxyl in the lattice or decomposes the clay cannot be unequivocally answered. Positive evidence is found for the latter in the presence of cryolite in the highly fluorinated products, but in general, stoichiometric exchange may be the predominant reaction.

### INTRODUCTION

Fluorine is the twelfth most abundant element in igneous rocks and what is perhaps more significant is that it ranks third among the most abundant anions (after O<sup>2-</sup> and OH<sup>-</sup>). Considerable experimental work has been done to determine the distribution of the most abundant cations among various crystalline phases as a function of composition, temperature and pressure with oxygen as the common anion. Recently such work has been extended to include hydroxyl as a component anion in the crystalline phases which were being studied. In contrast with this, very little experimental work is at hand which concerns the relationships among these phases in the presence of fluorine. Fluorine is a good example of a dispersed element occurring in a variety of the most common minerals (Barth, 1947) and forming only one fairly common "ore"—fluorite, CaF<sub>2</sub>. In its dispersion it substitutes for (OH)<sup>-</sup> and only rarely for O<sup>2-</sup> with corresponding loss of cation valence. Thus, one might expect that fluorine should be considerably more abundant in sedimentary rocks than in igneous or metamorphic rocks. This however, does not appear to be the case from the scanty data which are available. Rankama and Sahama (1950) give 140 gm. of CaF<sub>2</sub> per ton as the content in soils, although some bentonites have been reported with as much as 7,400 gm. F per ton.

In the clay minerals themselves which permit such a wide variety of cation substitution, one would expect that the chances for anion replacement of (OH)<sup>-</sup> by F<sup>-</sup> would be particularly favorable. The experimental

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work to date on anion replacement is limited. Dickman and Bray (1941) in an earlier study demonstrated that large amounts of OH are released into solution when kaolinite is equilibrated with  $\text{NH}_4\text{F}$  solutions even at room temperature. Romo (1954) confirmed this finding by the use of infra-red spectra, and attributed this OH release to exchange of lattice hydroxyl by  $\text{F}^-$ . After this study had been initiated, Samson (1952) reported similar results but attributed his "adsorption" of fluorine to initial bonding to the aluminum of the lattice followed by breakup of the lattice by splitting off of  $(\text{AlF}_6)^{-3}$  groups. No attempt was made to explain the nature of the fluorinated clay phase nor was mention made of the disposition of the  $(\text{AlF}_6)^{-3}$  radicals. There were two quite different (though not mutually exclusive) explanations of the "adsorption" of F and the release of OH from clays. The first is the simpler one: stoichiometric anion exchange of fluorine for hydroxyl. In the second, solutions of neutral fluorides are presumed to react with and "decompose" the clay minerals with a resultant formation of various solid complex fluoride phases and the release of OH ions into the solution. In support of the former view, it should be mentioned that fluorine and hydroxyl appear to be in the proper relationship to each other as far as ionic size, charge and polarizability are concerned to make for efficient exchange. Moreover, in micas and amphiboles this substitution is well-known. In fact the more recent analyses show that fluorine is perhaps more abundant in these hydroxylated phases than the earlier analyses had suspected. However, this exchange may not take place to any great extent at low temperatures. Evidence for the second alternative of "decomposition" would be found in the formation of new phases or the presence of the clay cations in solution. Samson (1952) showed that small amounts of  $\text{Al}^{3+}$  were detectable in solution showing that this decomposition had taken place to some extent. In the present study a variety of analytical methods was employed in an attempt to arrive at more definite and quantitative data describing the exchange or decomposition of hydroxyl clays in neutral fluoride solutions. The effect on the fluorine absorption of the structure of the clay phase of its cation content and of the nature of the contained hydroxyl was also examined.

## EXPERIMENTAL

### 1. *Materials Used*

Specimens of kaolinite, chrysotile, muscovite, boehmite, and diasporite were selected from well-established sources and their purity was checked by examination under the petrographic microscope and by x-ray diffraction. Each sample was fractionated by sedimentation to give  $<1\mu$  *e.s.d.* particles. As supplementary information, it was also established

by means of infra-red spectroscopy that each one of them gave an easily distinguishable  $(\text{OH})^-$  band. In selecting these minerals, representatives of several different major structural groups were thereby investigated: two- and three-layer silicates, dioctahedral and trioctahedral minerals, minerals with and without hydrogen bonding. The samples used were as follows: kaolinite, API No. 4 from Macon, Georgia; muscovite from Spruce Pine, North Carolina (well-formed single crystals); chrysotile from Thetford, Quebec; boehmite—synthetic (prepared hydrothermally at  $250^\circ\text{C}$ . and 10,000 psi pressure), and diaspore from Mexico, Missouri.

## 2. Methods of Investigation

In order to be able to arrive at some conclusions not only about the extent of exchange but also about the nature of the exchange process, the following different methods were used to follow the reaction:

### A. Titration of Excess Alkalinity

In previous work on this problem by Dickman and Bray (1941) and by Romo (1954), it was established that if hydroxyl ions are replaced by fluoride ions when a neutral fluoride salt is added in solution to a hydroxylic silicate, an excess alkalinity is developed which can be titrated with standard acid. Following their procedure, one gm. samples of  $<1\mu$  kaolinite, chrysotile, muscovite, boehmite, and diaspore were saturated with 0.4 N NaF and were washed with alcohol three times to eliminate the excess of salt. The pH of all the suspensions were  $7.0 \pm 0.2$ . These samples were then transferred to 400 ml. Erlenmeyer flasks to which there were added 50 ml. of standard solutions of NaF of varying molar strength. Then 10 drops of bromothymol blue indicator were added to each flask. The color indicated that the suspensions were at neutrality. It was noticed, however, that as time went on, the suspensions became alkaline as indicated by the appearance of a dark blue color. The excess alkalinity was titrated back to pH 7 with standardized 0.10 N HCl. From time to time small amounts of fluoride solution were added to each flask with the purpose of keeping the concentration of fluoride in the suspension constant. Three series of experiments were carried out:\* (1) at room temperature, (2) at  $60^\circ\text{C}$ ., and (3) by bringing the contents of flasks to boiling before each titration was performed. The titration data are presented in Figs. 1, 2, and 3 where m. eq. of  $(\text{OH})^-$  released per 1.00 gm. of solid phase are plotted as a function of time.

\* In addition several different types of blanks were run to check the effect of the beaker material, the effect of the NaCl formed on titration with HCl, et cetera. No significant alkalinity was found to be due to any of these causes considered.

In Fig. 1 the effect of concentration of  $F^-$  in the solution on fluorine absorption by kaolinite at one temperature ( $25^\circ C.$ ) is shown graphically, and in Fig. 2 the exchange in boehmite, kaolinite, and muscovite is compared in runs at  $60^\circ C.$  The titrations were carried out for a period of nearly three months at the end of which the reactions were proceeding very slowly. The marked influence on fluorine absorption of concentration of  $F^-$  in the solution and of the increase of temperature (i.e., kaolinite in 0.5 N solution) is noteworthy. The increase of OH release with con-

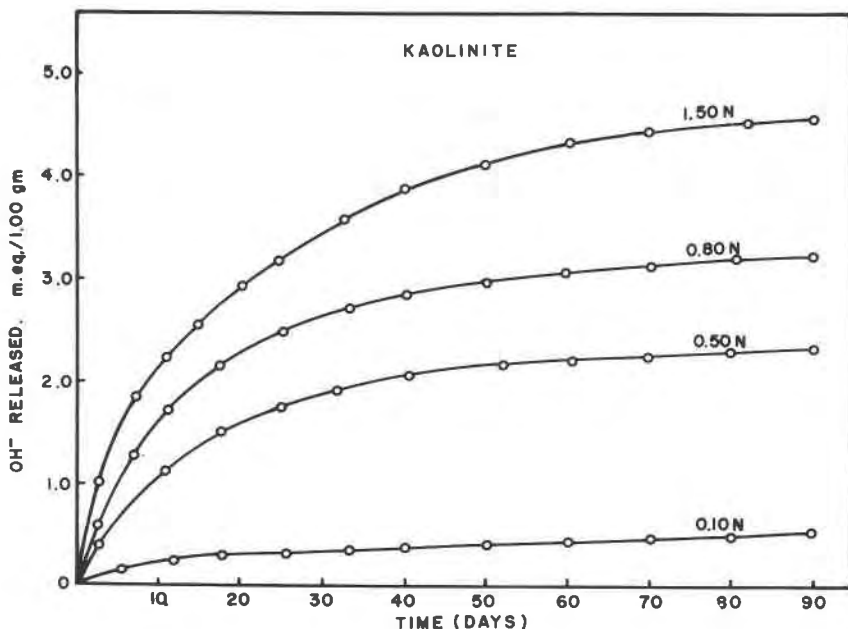


FIG. 1. Cumulative amount of  $(OH)^-$  (in milliequivalents/gms. of clay determined by direct titration) released into solution by reaction between kaolinite and dilute NaF solutions of varying concentration. This series was run at room temperature.

centration would appear to be against the "purely-exchange" phenomenon hypothesis since in that case at equilibrium, in the presence of an *excess* of fluoride ions the same final product should be attained at any one temperature. It may, of course, be contended that three months is not sufficient for the attainment of equilibrium and that in infinite time the curves would all meet.

In considering these titration data due regard must be had for the possible buffering action of the phases involved. However Romo (1952) has shown that the buffering capacity of the chief clay minerals at neu-

trality is only of the order 0.01 pH units and may therefore be neglected. The formation of complex ions and other side reactions producing  $(\text{OH})^-$  ions may also influence these data and these are discussed in a later section.

### B. Analysis for Fluorine

The second method chosen for a study of the extent of reaction was direct analysis for F in the final product. After the reaction rates had decreased considerably (usually after about three months) the solid

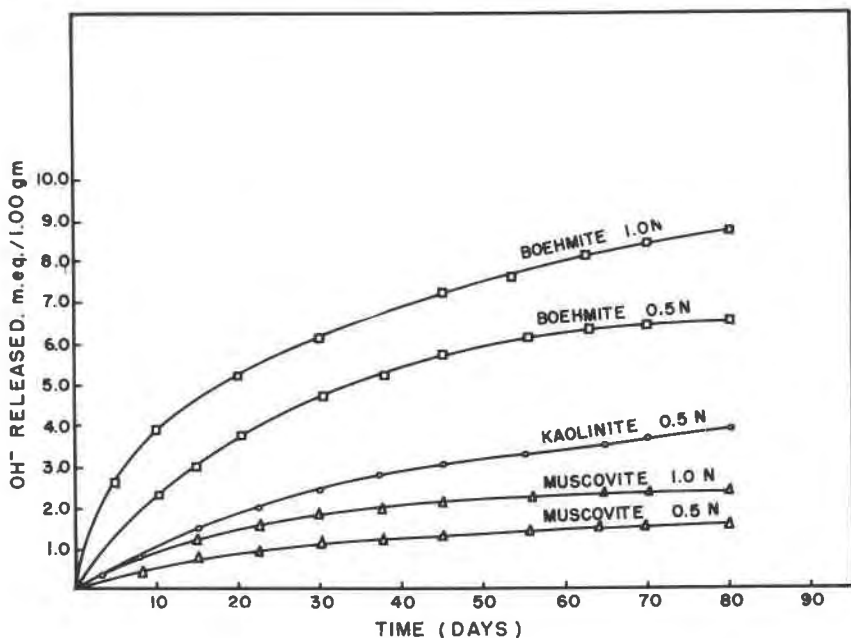


FIG. 2. Comparison of amounts of  $(\text{OH})^-$  released by different minerals in contact with NaF solutions of indicated concentration. This series was run at  $60^\circ \text{C}$ .

phase was separated from the fluoride solution by centrifuging. To achieve a complete removal of the fluoride the suspensions were centrifuged twice with distilled water and three times with 95 per cent ethyl alcohol. The fact that all the free fluoride has been removed was established on blanks as follows: Samples of 0.5 gm. of each of kaolinite and chrysotile were shaken with 50 ml. of 1 N NaF for ten minutes, then they were left standing for one hour. After this the solid phase was separated by centrifuging several times with water and 95 per cent ethyl alcohol. The analysis for  $\text{F}^-$  in the solid phase indicated that five wash-

ings as given above were enough to remove completely all the free fluorine.

In the analytical determination of fluorine use was made of Willard's reaction (1933) as modified by Armstrong (1933). The distillation of fluorine from a water-HClO<sub>4</sub> system in silicates was found to give unsatisfactory results. Invariably it was found that the recovery is incomplete. Therefore a series of extraction tests with HClO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> mixtures were made. It was found that use of 20 ml. of acid (2V) H<sub>2</sub>SO<sub>4</sub>- (8V) HClO<sub>4</sub> per 50 ml. of water gave the best results. The final procedure evolved is as follows:

#### *Reagents:*

*Thorium nitrate:* Dissolve 7.000 gm. of Th(NO<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O in one liter of water.

*Indicator:* Dissolve 0.100 gm. of sodium alizarin sulfonate in 100 ml. of water.

*Buffer:* Dissolve 10.00 gm. of CH<sub>2</sub>Cl-COOH and 2.20 gm. of NaOH in 100 ml. of water.

The pH of this buffer should be adjusted to 3.80, adding either acid or base as required.

*Standard NaF solution:* Dissolve enough oven-dried salt (c.p. grade) to give 1 mg. F/ml.

*Acid mixture:* Mix H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> in the proportions of 2:8 by volume.

#### *Procedure:*

Fuse sample of fluorine-containing silicate (0.10 to 0.20 gm.) with 0.5 to 1.0 gm. of Na<sub>2</sub>CO<sub>3</sub>. Extract by heating the crucible in water at 80° C. until the alkaline cake is dissolved. Transfer the solution to a distilling flask (total volume 500 ml.) provided with a dropping funnel containing water and a thermometer and distill at a temperature of 145° ± 3° C. As the distillation proceeds at the rate of 3 ml./min., water is added drop-wise to maintain the composition constant. A volume of 100 to 200 ml. is distilled depending on the concentration of F in the sample. The distillates in every case are made up to volume and aliquots withdrawn for analysis.

To aliquot in 50 ml. volumetric flasks, add 10 drops of indicator and NaOH drop-wise until a pink color appears. Such color should turn yellow upon the addition of one or two drops of 0.1 N H<sub>2</sub>SO<sub>4</sub> (pH 3.6). Then add three ml. of buffer and make up to volume with water. Transfer the contents to a 250 ml. beaker and titrate with standard Th(NO<sub>3</sub>)<sub>4</sub> solution until the pink color just appears. A blank is carried for any correction if needed. A standard curve was plotted by distilling the fluorine from fused kaolinate which contained known amounts of fluorine. An overall estimation of errors indicates that the accuracy of determinations is within ± 2.0% in the range of 0.1 mg. F to 5 mg. F.

The comparison of analytical results shown in Table 1 indicates that there is reasonable agreement between m. eq. of (OH)<sup>-</sup> released and m.

TABLE 1. RELATION OF M.E. OH<sup>-</sup> EXCHANGED BY F<sup>-</sup> IN VARIOUS MINERALS

Mineral	Treatment	m.e. OH/gr.	m.e. F/gr.	Presence of Other Phase
Kaolinite	0.10 N (RT)	0.48	0.54	
	0.50 (RT)	2.20	2.36	x
	0.80 (RT)	3.22	3.27	x
	1.50 (RT)	4.50	4.67	xx
	0.50 N 60° C.	3.90	4.06	x
	1.50 N 60° C.	7.50	7.67	xx
	1.0 N Boiled	2.65	2.77	
Muscovite	0.10 N (RT)	0.11	0.13	
	0.50 N (RT)	0.70	0.76	
	0.50 N 60° C.	1.50	1.58	
	1.00 N 60° C.	2.30	2.23	x
	1.00 N Boiled	3.10	2.88	x
Chrysotile	0.10 N (RT)	0.42	0.53	
	0.50 N (RT)	1.72	1.90	
	1.00 N Boiled	3.42	3.55	
Boehmite	0.10 N (RT)	0.12	0.16	
	0.50 N (RT)	0.31	0.50	
	0.50 N 60° C.	6.50	6.84	x
	1.00 N 60° C.	8.60	9.26	xx
Diaspore	0.10 N (RT)	negligible traces		
	0.50 N (RT)	0.75	0.84	xxx

eq. of F<sup>-</sup> found in the solid phases which may suggest that the substitution of (OH)<sup>-</sup> by F<sup>-</sup> is stoichiometric.

### C. Infra-red Spectroscopy

The use of infra-red spectroscopy in elucidating the molecular structure of organic compounds has proved to be very useful, especially in cases where the detection of functional groups becomes essential. In studies of anion exchange, such as that of the substitution of (OH)<sup>-</sup> by F<sup>-</sup> in layer silicate structures, infra-red spectroscopy provides a possible means of actually detecting changes in (OH)<sup>-</sup> concentration. Romo (1954) used this method to show that fluorine replaces lattice hydroxyls in kaolinite, and it was used here as one of the means of studying the variations of (OH)<sup>-</sup> content of the solid phase as a result of replacement by F<sup>-</sup> in various minerals. For quantitative work with powders the KBr pressed disc technique is satisfactory and this was used

throughout. The I.R. absorption spectra were recorded with a double-beam Perkin Elmer model 21 spectrometer using a slit opening of  $8.40\mu$  and slow scanning.

The variations in hydroxyl content were determined by the method of integration of areas. However some of the absorption bands recorded contained actually a band corresponding to hydroxyls ( $\lambda=2.75\mu$ ) and an overlapping weaker band at  $\lambda=2.95$ , which is often attributed to "free water." Thus, prior to integrating the areas, the contribution of the overlapped free water band has to be eliminated. This was done in an approximate but simple manner by symmetrical extrapolation of the band at  $\lambda=2.75\mu$ . An error limit of  $\pm 3\%$  was found between the dupli-

TABLE 2. COMPARISON OF ANALYTICAL RESULTS OF PERCENTAGES OF EXCHANGE OF  $(OH)^-$  BY  $F^-$  IN VARIOUS MINERALS

Mineral	Treatment	Titration	F <sup>-</sup> Kaolinite	I.R. Analysis
Kaolinite	0.1 N (RT)	3.27	3.68	4.0
	0.5 N (RT)	15.00	16.20	17.0
	0.5 N 60° C.	22.00	23.20	26.0
	1.5 N 60° C.	48.70	49.20	53.0
Muscovite	0.1 N (RT)	2.32	2.75	3.0
	1.0 N 60° C.	48.30	46.80	42.0
	1.0 N Boiled	64.50	61.00	59.0
Boehmite	0.5 N 60° C.	38.80	41.00	25.0*
	1.0 N 60° C.	51.50	61.00	34.0*

\* The anomalous values here must be due in part to the fact that the OH absorption in boehmite is spread out over several bands.

cate runs of the same sample which is not high if one considers the number of factors which can contribute to this error.

The results converted to percentages are shown in Table 2 and are also compared with the data obtained from the  $(OH)^-$  titration and fluorine analysis in Fig. 3 and Table 2. The agreement among the three methods is good, showing that amounts of  $F^-$  detected are equivalent to the amounts of  $(OH)^-$  released and also correspond to the amount of  $(OH)^-$  lost by the solid phase.

#### D. X-ray Diffraction

One of the limitations of each of the preceding three methods is that although each provides a measure of either the loss of  $(OH)^-$  or the presence of  $F^-$  in the "total solids" there is no prima facie evidence that the



fluorine is actually being exchanged for (OH)<sup>-</sup> in the lattice concerned. However the agreement among the data (see Fig. 3) is such that the exchange concept would appear reasonable. X-ray diffraction methods might provide such first-hand evidence by establishing both the absence or presence of extraneous phases and by showing the gradual and continuous shift of spacings characteristic of solid solutions. In this, of course, the close similarity in ionic radii of F<sup>-</sup> and (OH)<sup>-</sup> renders the method insensitive at best.

Powder x-ray diffraction patterns were therefore used to check the phase content of the product after exchange, every sample being so examined. A high angle Norelco or G.E. diffractometer with filtered CuK radiation was used for this purpose, with hollow aluminum slides, which were packed to avoid excessive orientation and eliminate errors of eccentricity. With respect to the determination of the presence of new phases in the solids left after saturation for three months, it was found that in most cases in which more than two m. eq. of (OH)<sup>-</sup> had been exchanged per gram of sample it was possible actually to detect the powder pattern lines of a new phase, cryolite. This same phase was found in all the samples which contained an extraneous phase. The minerals themselves showed no evidence of decomposition, even in those cases where half the hydroxyls had been replaced. This, of course, is a qualitative measure, but no evidence was found for the diminution or change of intensities nor for the formation of any other layer silicates. The quantitative estimation of the Na<sub>3</sub>AlF<sub>6</sub> formed presents a very difficult problem which cannot be solved directly except in a rough manner and under the limitations of several unverifiable assumptions.

The evaluation of the amounts of Na<sub>3</sub>AlF<sub>6</sub> formed was obtained by running a set of standard mixtures of kaolinite with varying concentrations of Na<sub>3</sub>AlF<sub>6</sub>. The variation in intensity of the peak at 2.76 Å was found to be related to concentration linearly. Thus the concentration of Na<sub>3</sub>AlF<sub>6</sub> in the various samples was estimated by measuring the intensities of this peak and referring that to the working curve. In this way it was found that the concentrations of Na<sub>3</sub>AlF<sub>6</sub> varies from traces up to 10 per cent. This estimate can only err on the low side. Some (if not much) of the Na<sub>3</sub>AlF<sub>6</sub> may be of too fine a size to contribute to the Bragg diffraction. The fine particle size of the cryolite which formed is not the same as that used in the standardizing runs, and this may also vitiate the results.

The second aspect of the x-ray data with which we were concerned was the possibility that the cell dimensions, and hence spacings in the pattern, would show a regular shift as a function of the F<sup>-</sup> content. Since precise data could most easily be obtained for the basal spacings,

these were measured carefully on the Norelco diffractometer at a scanning rate of  $1/8^\circ 2\theta$  per minute giving reproducibilities to within  $.01^\circ$ . No sufficiently significant shifts in spacing were found to enable any definite conclusions to be drawn. A very small increase in the  $d_{001}$  spacing of the most fluorinated muscovite was noticed amounting to  $0.04 \text{ \AA}$ , but the change was so small as to make quantitative statements meaningless. The failure to obtain such quantitative cell dimension changes which could be correlated with the amount of fluorine exchanged eliminated one of the only methods capable of yielding unequivocal proof for the "exchange" hypothesis.

#### DISCUSSION OF RESULTS

The most surprising feature of the results is the extent to which the reaction (either exchange or decomposition, or both) will proceed even

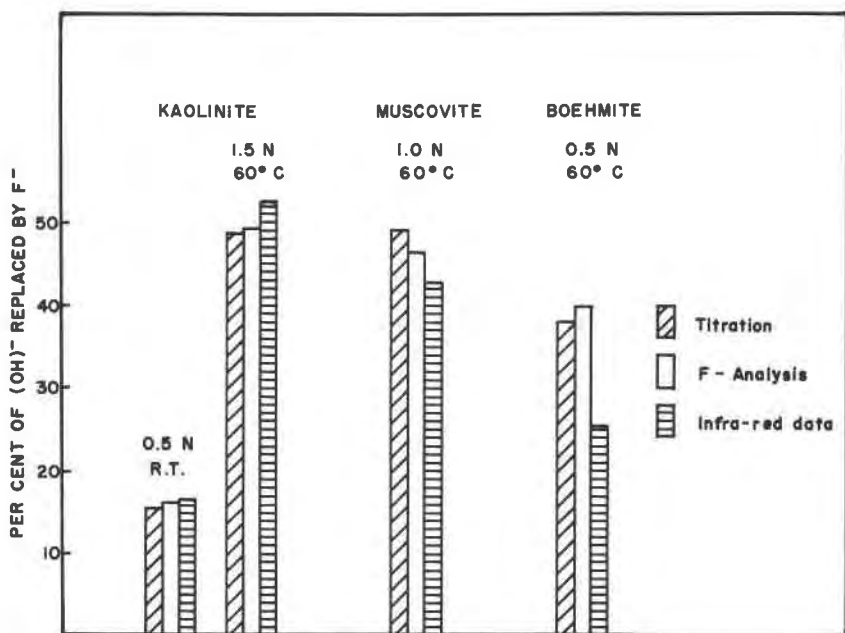


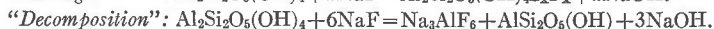
FIG. 3. Histogram comparing the extent of exchange as determined by the different methods used; the temperature and concentration of NaF is indicated for each of the cases selected.

at room temperature. The data obtained by titration of the excess alkalinity developed, which constitute a measure of the hydroxyl released, have been shown to be equivalent within reasonable experimental error

to the amount of fluoride ion taken up in the total solid phase. Moreover, the infra-red spectra have established that the hydroxyl ions left in the mineral when estimated quantitatively account for the rest of the total hydroxyl content of the original mineral. The results of the three methods have been compared in a histogram in Fig. 3, and it is seen that the infra-red data tend to give a somewhat low value for the amount of "replacement," i.e., the amount of (OH)<sup>-</sup> found in the residue tends to be slightly high, which may be expected since strong adsorption at "fresh" surfaces formed during the reaction will give rise to errors in this direction. The general correlation is considered good.

From these data, however, one cannot decide unequivocally between the two possibilities which are available to explain the mechanism of the fluorine "take-up." The failure of the x-ray data to confirm the exchange hypothesis does not of itself speak for the decomposition, since it may be very reasonably argued that (OH)<sup>-</sup> and F<sup>-</sup> are so similar in ionic properties that not much difference may be found in any case.\* On the other hand if it were possible to rely on the estimates of the amount of Na<sub>3</sub>AlF<sub>6</sub> formed, one would be led to conclude that the exchange reaction was the predominant one, since even in cases where half of the hydroxyls of the lattice have been released only about 5-10% of Na<sub>3</sub>AlF<sub>6</sub> are estimated to have been formed. Further in these same samples where the fluorine take-up is considerable, one would expect a more definite effect on the absolute and relative intensities within the powder pattern for the clay mineral itself. Here a quantitative measure is impossible but no major changes were found in any case.

The two types of explanation can be expressed in greatly simplified form as follows:



The former equation is a reasonable view of what may actually take place while the latter is a highly idealized summary of the second alternative and of course does not really represent the actual process. It does indicate the direction of reaction and possible products. The elimination of aluminum and the increase in the Si/Al ratio in the clay phase will tend to develop 2:1 layer silicates from the 1:1 minerals, and from the former if the extent of fluoride take-up is large, zeolites or silica will have to be formed, since no layer minerals richer than the montmorillonites-micas are known. In the case above, it is seen that a coincidence leads to the formula of the residue being identical with that

\* However, values published after completion of this study of 001 for F phlogopite and OH-phlogopite show a difference of the order of 0.17 Å.

for pyrophyllite (as representative of the 2:1 montmorillonites and micas). Pyrophyllite would not, however, appear in the residue because the necessary activation energy is not available.

Although the the actual process cannot be decided, some further information may be obtained from the time and temperature function of the extent of fluoride take-up. From the plots shown in Figs. 1, 2, and 3 it is possible to construct hypotheses regarding the possible rates of reaction. The titration curves presented therein show clearly that the release of  $(OH)^-$  is dependent upon the concentration of NaF in solution which was kept constant in every case. From a cursory examination of the structure of these minerals, it is obvious that in most of them there are two types of hydroxyl groups: those which are on the outer edges of the "brucite" or "gibbsite" layers and are readily accessible, and those which are "inside" the lattice and are less accessible. Therefore, it is conceivable that two simultaneous processes may be taking place independently of each other—one involving direct exchange with the solution, and the other a diffusion process of fluorine ions into the lattice.

The nature of the reactions and specific rate constants can be evaluated by the usual treatment of these data. Such a treatment of the data has been performed for the kaolinite case. However the extent of subjectivism involved in fitting the curves does not justify the presentation of the numerical data. By such a procedure, one can arrive at fair agreement assuming two first-order reactions taking place simultaneously. The faster reaction rate constant would correspond phenomenologically to the exchange of the exposed surface hydroxyls. The slower one, possibly corresponding to the diffusion process of the fluorine into the inner layers, gave a rate constant approximately ten times as small.

The data also provide some indications of answers to our original questions. Thus the influence of the cation in the clay is seen to be minor since chrysotile and kaolinite give total reaction values in the same range. Morphology, particle size and surface area must also play only minor roles for these are quite different for chrysotile and kaolinite. Between the 1:1 (kaolinite family) and 2:1 (mica-montmorillonite groups) there is likewise no striking difference although the total exchange seems to be distinctly lower in the latter. This may be only a reflection of the lower total  $(OH)^-$  content. Lastly with respect to the effect of hydrogen bonding in the hydroxyls, there does appear to be a definite difference between boehmite and diaspore. The diaspore samples showed the presence of large amounts of  $Na_3AlF_6$  even at very low concentrations and at room temperature, and in the lowest concentrations of NaF they showed hardly any  $F^-$  take-up. On the other hand, boehmite shows an "exchange" of about the same magnitude as the layer silicates. This could

be attributed to the marked hydrogen bonding in diaspore which, in effect, means that diaspore has no true hydroxyls that can be exchanged by fluorine.

In conclusion it may be stated therefore that there is extensive and fairly rapid transfer of F<sup>-</sup> ions from solution to the solid phase when brought in contact with most layer silicates, and that this does constitute "fixation" of fluorine. However the mechanism of this fixation is left in doubt. No positive evidence for the replacement of the OH<sup>-</sup> in the lattice by F<sup>-</sup> was obtained. On the other hand, some evidence—which appeared quantitatively insufficient to account for all the F-fixation—was obtained for "decomposition" of the clay minerals and the formation of non-clay insoluble fluorides.

#### ACKNOWLEDGMENT

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#### REFERENCES

- ARMSTRONG, W. D. (1933), Modification of the Willard-Winter method for fluorine determination: *J. Am. Chem. Soc.*, **55**, 1741-1742.
- BARTH, T. F. W. (1947), Geochemical cycling of fluorine: *J. Geology*, **55**, 420.
- DICKMAN, S. R., AND BRAY, R. H. (1941), Replacement of adsorbed phosphate from kaolinite by fluoride: *Soil Sci.*, **52**, 263.
- RANKAMA, K., AND SAHAMA, TH. (1950), *Geochemistry*. The Univ. of Chicago Press, Chicago. Chapter 44.
- ROMO, L. A. (1952), Ph.D dissertation. Chemistry Dept., Univ. of Wisconsin.
- ROMO, L. A. (1954), Role of lattice hydroxyls in phosphate fixation and their replacement of fluoride: *J. Coll. Sci.* (In Press).
- SAMSON, R. H. (1952), Fluoride absorption by clay minerals and hydrated alumina: *Clay Min. Bull.* **I**, N-8, 266-270.
- WILLARD, H. H., AND WINTER, O. B. (1933), Volumetric method for the determination of fluorine: *Anal. Chem.*, **5**, 7-10.

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