

FLUORIDE CONTENT OF CLAY MINERALS AND ARGILLACEOUS EARTH MATERIALS

JOSEPHUS THOMAS, JR., H. D. GLASS, W. A. WHITE and R. M. TRANDEL

Illinois State Geological Survey, Urbana, IL 61801, U.S.A.

(Received 10 March 1977)

Abstract—A reliable method, utilizing a fluoride ion-selective electrode, is described for the determination of fluoride in clays and shales. Interference by aluminum and iron is minimal. The reproducibility of the method is about $\pm 5\%$ at different levels of fluoride concentration.

Data are presented for various clay minerals and for the $<2\text{-}\mu\text{m}$ fractions of marine and nonmarine clays and shales. Fluoride values range from 44 ppm (0.0044%) for nontronite from Colfax, WA, to 51,800 ppm (5.18%) for hectorite from Hector, CA. In general, clays formed under hydrothermal conditions are relatively high in fluoride content, provided the hydrothermal waters are high in fluoride content. Besides hectorite, dickite from Ouray, CO, was found to contain more than 50 times as much fluoride (6700 ppm) as highly crystalline geode kaolinite (125 ppm). The clay stratum immediately overlying a fluorite mineralized zone in southern Illinois was found to have a higher fluoride content than the same stratum in a nonmineralized zone approximately 1 mile away. Nonmarine shales in contact with Australian coals were found to be lower in fluoride content than were marine shales in contact with Illinois coals.

It is believed that, in certain instances, peak shifts on DTA curves of similar clay minerals are the result of significant differences in their fluoride content.

INTRODUCTION

In the study of the chemistry of the clay minerals, the emphasis over the years has been on cation content, or on cationic substitution. Although it is generally recognized that anionic substitution also occurs, particularly with the fluoride ion which readily proxies for the hydroxyl ion in crystal structures, there have been very few analytical data reported for anionic species. The few fluoride values that have been reported range from 180 ppm for an halloysite from Lawrence County, IN (Koritnig, 1951) to 47,500 ppm (4.75%) for a bentonite (hectorite) of hydrothermal origin from a location near Hector, CA (Ames *et al.*, 1958). This broad range of fluoride content warrants more study than has been allotted it to date, because fluorine may be a potentially important geochemical indicator of the origin and depositional environment of clays and shales.

The lack of reported fluoride data no doubt reflects the laborious and oftentimes inexact methods that, until relatively recent times, have characterized the determinations of fluoride. The accuracy of different methods involving the distillation of the fluoride has been suspect, in particular, for earth materials of high aluminum content, because aluminum cations form very strong complexes with fluoride in acid solution (Fox and Jackson, 1959). The introduction of the fluoride ion-selective electrode (Frant and Ross, 1966) has made the determination of fluoride much simpler and more reliable, and has been responsible for the recent dramatic increase in the output of fluoride values for all types of samples.

Fluorine is not rare. It is widely dispersed in nature, averaging 700 ppm in the crust of the Earth; Mason

(1965) ranks fluorine as the 13th most abundant element. The dissolved fluoride content of seawater is only 1.2–1.4 ppm (Carpenter, 1969), but this value is still ten times greater than the average dissolved fluoride content (0.1–0.2 ppm) of the major rivers of the world (Livingstone, 1963).

Being the most electronegative of the elements, fluorine forms the strongest bonds possible with other elements. Once in a structure, fluorine is extremely difficult to displace, or exchange. For example, Ekstrom (1973), in a recent study, tried to exchange the fluoride in fluorapatite with chloride in aqueous solutions; he found that no exchange took place in 2 weeks at temperatures up to 600°C, even in 4 M calcium chloride solutions.

From the geochemical standpoint, it is uncertain as to how much of the original fluoride is retained in detrital sediments during weathering and transport. From his investigation of weathering profiles, Koritnig (1963) concludes that in the course of weathering, fluoride is easily being leached and carried off. Carpenter (1969), however, pointed out that it would seem likely from the low fluoride content of rivers that the $<2\text{-}\mu\text{m}$ fraction of the suspended load of rivers retains the greater part of its fluoride content. If the latter is true, then a source rock, which may be either relatively high or low in fluoride content, provides most of the initial fluoride content of the detrital sediment. An increase in the fluoride content could occur through diffusion of fluoride ions from the water environment into the structure, followed by exchange with hydroxyl ions. If such a process occurs, then the nature of the structure, the fluoride content of the water environment, and the time

of contact of the sediment with the water environment would all contribute to the final fluoride content.

If authigenic deposits (deposits originating with nucleation from saturated solutions followed by precipitation and crystal growth) are assumed to have formed in ancient seas and rivers that contained about the same concentration of fluoride as the waters of today, then higher fluoride contents should be manifested by clays formed under marine conditions than by those formed in a nonmarine environment. Koritnig (1963), however, was of the opinion that, owing to overlapping factors, the fluoride content was not useful in indicating marine or nonmarine origin.

Clays formed under hydrothermal conditions can be unusually high in fluoride content, reflecting the higher fluoride content of the environment. However, as will be pointed out later, all hydrothermal environments are not necessarily high in fluoride content. Some saline lakes also are known to contain appreciable fluoride concentrations (Arad and Morton, 1969).

The purposes of the present work are two-fold: (1) to describe a reliable analytical procedure for determining fluoride in earth materials of high aluminum content, and (2) from the analytical data generated for clay materials, to determine if any trends are apparent, or to determine if general statements can be made regarding their fluoride contents.

EXPERIMENTAL

Materials

Most of the clays and clay minerals studied were from the collection of the Illinois State Geological Survey. Among these samples are clay minerals from the current Source Clay Minerals Project and from the earlier American Petroleum Institute (API) Project 49. A few samples were supplied by individuals listed in the Acknowledgements section of this report. Several U.S. Geological Survey rock standards and two National Bureau of Standards clay samples were used in the evaluation of the method.

Method for determination of fluoride

The method used to determine fluoride in clay materials was similar to that described by Ingram (1970) for silicate rocks, but with modifications. Samples are fused with granular sodium hydroxide (rather than with sodium carbonate) and then acidified. A citrate-citric acid buffer that also complexes aluminum and iron is added. The fluoride potential is determined with a fluoride ion-selective electrode. An aliquot of a standard fluoride solution is added to the original solution and the potential is again measured. The fluoride concentration is determined from the change of potential (ΔE). The standard addition method employed here virtually eliminates solution matrix variations. We found, as did Ingram (1970), that if the aluminum concentration is kept

below about 100 ppm in the acidified solution, its interference is minimal.

Apparatus. A fluoride ion-selective electrode and calomel reference electrode were used in conjunction with a Digital 112 research pH meter (all from Corning Scientific Instruments, Medfield, MA). Plastic beakers, volumetric flasks, and Teflon-coated magnetic stirring bars were used for fluoride-containing solutions. Nickel crucibles were used in the fusion of samples.

Reagents. All solutions were prepared with water that had passed through a mixed anion-cation exchange resin. The water contained less than 0.01 ppm fluoride. With the exception of the granular sodium hydroxide used in the fusion of samples, all chemicals were reagent grade.

Standard fluoride solutions were prepared as required from a 1-l. stock solution containing 4.199 g (1900 ppm, or 0.1000 M F^-) ultrapure sodium fluoride (Alfa Inorganics, Inc., Ventron Corp., Beverly, MA). The sodium fluoride had been dried at 120°C for 2 hr.

A concentrated citrate ionic-strength-adjustment buffer was prepared by dissolving 294 g sodium citrate dihydrate and 20.2 g potassium nitrate in 1 l. of water and adjusting the pH to 6.0–6.1 by addition of citric acid.

Two different sulfuric acid solutions, approximately 3 and 0.5 N, were used for adjustment of pH, the former for the initial neutralization step, and the latter for the final pH adjustment prior to buffering.

Procedure. All samples were dried overnight at 110°C. The <2- μm fractions of clays and shales were used, but samples from the Source Clay Minerals Project and from the API 49 Project were not fractionated.

In a typical determination, a 100-mg sample is mixed with 3.0–3.5 g of sodium hydroxide in a nickel crucible. The mixture is fused over a low flame for 15 min. Some experience is required to develop the proper technique for these fusions. Initially, the flame can be quite hot in order to quickly melt the fusion mixture; subsequently, the flame should be lowered to a point which will just maintain the melt. Severe creeping of the NaOH up the sides of the crucible will occur, if the flame is kept at too high a level.

Sodium hydroxide fusions are preferred to sodium carbonate because the former are much more easily removed by hot water extraction. However, the granular sodium hydroxide used contains about 5 ppm fluoride, and a blank must be run to correct for the amount of fluoride introduced into the system other than that coming from the sample.

The melt is permitted to cool for a few minutes. Deionized water (20–30 ml) is added to the crystallized melt in the crucible, which is then heated gently over an open flame. The mass is brought into solution (suspension) rather easily. The contents are transferred to a 300-ml plastic beaker. The crucible is

rinsed with small portions of deionized water and the rinsings are added to the beaker.

The pH of this solution is decreased to about 5.0 with sulfuric acid, which removes carbonate and bicarbonate via CO₂ formation. Continuous stirring removes most of the CO₂; a final adjustment of the pH with a few drops of 0.5 N H₂SO₄ may be necessary since the pH rises as the CO₂ is removed. The stronger acid solution (3 N) is used initially to bring the pH down to about 6.5, and then the 0.5 N H₂SO₄ is used to reduce the pH further. Aluminum becomes a problem if the pH is reduced too far (3.5–4.0). Because aluminum is amphoteric, the hydroxide formed redissolves at this low pH and the free aluminum cations form a strong complex with fluoride.

One M sodium citrate–0.2 M potassium nitrate (20 ml) is added to the beaker contents. This buffer solution also complexes aluminum and iron. As these cations are complexed away from their suspended hydroxides the solution clears. The contents of the beaker are then transferred to a plastic volumetric flask (200 ml) and the solution is made to volume with deionized water. The flask contents are transferred back to the beaker and are stirred while the potential (*E*) is determined with the fluoride ion-selective electrode. After equilibrium is reached and a stable *E* value is read, 5 ml of a standard fluoride solution (190 ppm) are added and *E* is again determined. If the fluoride content of the initial solution is sufficiently high, a stronger concentration (1900 ppm) of the standard fluoride solution is used to provide a large enough ΔE .

The fluoride concentration is calculated from the following equation (Orion Research, Inc., Cambridge, MA, 1970):

$$C_x = \frac{C_s}{10^{\Delta E/\text{slope}} \left(1 + \frac{V_x}{V_s}\right) - \frac{V_x}{V_s}}$$

where C_x is the fluoride concentration (molar) of unknown solution, C_s is the concentration (molar) of standard solution added, ΔE is the difference in *E* readings (mV), slope = $2.303 RT/nF$ = characteristic of a particular electrode (established with standard solutions over a 3- or 4-decade concentration range; generally in the range of 58.6–59.6), V_x is the volume of solution, V_s is the volume of standard solution added.

Evaluation of the method. Fluoride values for several U.S. Geological Survey rock standards are summarized in Table 1. The two NBS clay reference standards are included even though we were unable to find other reported fluoride data for these samples for comparison purposes. The values shown for the present study are mean values from at least four determinations for each sample. The average deviation is about $\pm 5\%$ at each level of fluoride content. The values in Table 1 for this method are in excellent agreement with values reported by Ingram (1970), and in good agreement with the consensus values reported

Table 1. Fluoride data for selected silicate standards of high alumina content

Sample	F, ppm		
	This method	Ingram (1970)	Others
W-1 Diabase	230	240	250*
G-1 Granite	685	724	700*
G-2 Granite	1400	1480	1200, 1200, 1205, 1300, 1400, 1400, 1600, 2000†
BCR-1 Basalt	520	--	500, 500, 500, 500, 700, 700†
AGV-1 Andesite	430	--	400, 400, 400, 500, 600, 600†
GSP-1 Granodiorite	3810	3870, 3856	1940, 3700, 3700, 3800, 3800, 3900, 4000, 4800†
NBS-97a Flint clay	295, 302 318, 328	--	--
NBS-98a Plastic clay	418, 439 442, 454	--	--

* Reported as the accepted value by Fleischer (1969).

† Values compiled by Flanagan (1969).

by other investigators. Owing to the necessarily small sample size, the high dilution, and the relatively large blank, the lower limit of detection of this method for fluoride in clay materials is about 10 ppm.

RESULTS AND DISCUSSION

Kaolin group

Among the clay minerals, the kaolin group contains the greatest number of hydroxyls per unit cell for possible substitution. However, as shown in Table 2, with two exceptions, the fluoride contents are relatively low for the two dozen kaolinites we have examined. Specific well-recognized samples included in Table 2 are the highly crystalline geode kaolinite from near Hamilton, IL, the well-crystallized Georgia kaolinite (Source Clay Minerals Project), and the poorly crystalline kaolinite from Anna, IL. Another 20 kaolinites from various locations in the U.S. were found to range in fluoride content from 125 to 630 ppm.

From these relatively low fluoride values it would appear that the kaolinite structure, once formed, does not permit significant penetration, diffusion and exchange of fluoride ions that are present in the water environment. (A slight amount of exchange, of course, would be expected during the formation of the kaolinite structure.) This lack of fluoride exchange in kaolinite has been reported in laboratory studies by Hofmann *et al.* (1956). They found that the exchange of fluoride (<1 N solution) for hydroxyl in kaolinite is reversible, and appears to be limited to the hydroxyl ions at the edges of the silicate layers and to those hydroxyl ions on the basal surfaces. In contrast is the degree of substitution that can and does occur in the hydroxyapatite structure (bone and teeth). It has long been recognized with the latter that all the hydroxyls can be exchanged irreversibly, in time, with the fluoride ions contained in ground water or seawater, thus forming fluorapatite (containing 3.77% fluorine, by weight). More recently, studies by Rao *et al.* (1975) show that the minerals of the serpentine group (chrysotile, antigorite and lizardite) will take up appreciable fluoride from aqueous solution.

Table 2. Fluoride content of samples from the kaolin group

Sample	F, ppm
Kaolinite	
Geode kaolinite (Hamilton, IL)	125
Georgia kaolinite (SCMP)	140
Kaolinite (Anna, IL)	400
Kaolinite (Cornwall, Eng.)	4310
Kaolinite (20 different locations)	125-630
Kaolin (Ciudad Hidalgo, Mex.)	210
Kaolin (San Luis Potosi, Mex.)	5500
Halloysite	
Halloysite (API 59 - Spruce Pine, NC)	85
Halloysite (Lawrence Co., IN)	135
Halloysite (API 13 - Eureka, UT)	800
Halloysite (Pope Co., IL)	2010
Dickite	
Dickite (API 15c - San Juanito, Mex.)	3700
Dickite (API 16b - St. George, UT)	5900
Dickite (API "Prime" - Ouray, CO)	6700
Dickite (Kansas)	575

It is not to be construed from this discussion that all kaolinites should be low in fluoride content. If the formation and precipitation of kaolinite were to occur in a water environment that is significantly higher in fluoride content than ordinary seawater, such as occurs in some hydrothermal waters, it would be expected that more fluoride would be incorporated in the kaolinite structure. This appears to be the case with the one Mexican kaolin (Table 2) containing 5500 ppm fluoride.

Both of the Mexican samples are of hydrothermal origin and have been described by Keller (1968, 1971). The sample from Ciudad Hidalgo came from a 'pocket' in the side of a hot-water spring area. The low fluoride content (210 ppm) of this sample is indicative of a low fluoride concentration in the water at this particular location. It is possible that the water, if magmatic initially had a high fluoride content but that the fluoride was removed by reaction with the country rock during the percolation of the water to the surface. Again, the water may have been surface water initially, then was heated at depth and later returned to the surface. The water thus may have never contained much fluoride. At San Luis Potosi, on the other hand, a sample of high-purity clay from the General Zaragoza mine is quite high in fluoride content, indicating that the water in which it was formed contained appreciable fluoride.

Some care must be taken in interpreting whether substitution of fluoride for hydroxyl has actually occurred in clay mineral structures, or whether fluoride-containing impurities (fluorspar, fluorapatite, tourmaline, etc.) are present in the clay. The sample from Cornwall, England, is such an example. This

Table 3. Fluoride content of different size fractions of Cornwall kaolinite

Size fraction	Sericite/kaolinite	F, ppm
Crude	--	7500
< 2 μm	1/4	4310
< 0.75 μm	1/9	2465
< 0.1 μm	1/2	6520
Coarse (sand)	--	12,000

clay presumably is a product of hydrothermal alteration of the St. Austell granite. The clay contains an appreciable quantity of sericite (Table 3) which is responsible for most of the fluoride content of the clay. X-ray powder diffraction provided estimates of the sericite/kaolinite ratios in the different size fractions. The wide variation in the fluoride content is readily apparent. The coarse sand-like material, highest in fluoride content of the fractions studied, was found to contain tourmaline and mica.

The fluoride content of the two halloysite samples from the classic deposits at Spruce Pine, NC and Lawrence County, IN, are seen to be low (Table 2). The halloysite from Eureka, UT, which is thought to be of hydrothermal origin, is somewhat higher in fluoride content; and the halloysite from Pope County, IL, which is almost certainly of hydrothermal origin, contains significantly more fluoride. The latter sample came from a shaft sunk for the production of fluorspar from a mineralized zone in extreme southern Illinois (Lamar, 1942).

In Table 2, the first three samples of dickite are of hydrothermal origin and contain 25-50 times the fluoride content of the well-crystallized geode kaolinite. From this, one might hypothesize that a certain minimal amount of fluoride substitution is responsible for the subtle differences that exist between the dickite and kaolinite structures. However, a Kansas dickite (Hayes, 1967), obtained through the Kansas Geological Survey, contained only 575 ppm fluoride. Because this value is in the range of values found for kaolinites, this hypothesis is not borne out.

Smectite group

Fluoride data for the smectite group are shown in Table 4. Mixed-layer Ordovician metabentonites are included in the discussion for convenience.

It has been mentioned that the lowest and highest fluoride values found have been for samples from the smectite group. The three nontronite samples from Washington are extremely low in fluoride; this indicates that the environment of formation was low in fluoride. Conversely, it follows that the environment

Table 4. Fluoride content of samples from the smectite group

Sample	F, ppm
Smectite	
Nontronite (API - Colfax, WA)	44
Nontronite (API - Excelsior, WA)	50
Nontronite (API 33a - Garfield, WA)	62
Hectorite (API 34a - Hector, CA)	50,640
Hectorite (API 34b - Hector, CA)	15,510
Hectorite (API "Best grade" - Hector, CA)	51,800
Hectorite (SCMP - Hector, CA)	27,500
Na-montmorillonite (SCMP - WY)	1110
Ca-montmorillonite (SCMP - TX)	845
Ca-montmorillonite (SCMP - AZ)	2875
Montmorillonite (API 11 - Santa Rita, NM)	3750
Montmorillonite (API 30 - Santa Rita, NM)	2230
Montmorillonite (API 21 - Burns, MS)	2955
Montmorillonite (API 22 - Amory, MS)	1630
Montmorillonite (API 23 - Chambers, AZ)	7100
Montmorillonite (API 25a - Upton, WY)	920
Montmorillonite (API 25b - Upton, WY)	870
Montmorillonite (API 27 - Belle Fourche, SD)	870
Montmorillonite (API 28 - Little Rock, AR)	1360
Bentonites (WY and SD - 5 samples)	900-1100
Ordovician metabentonites (eastern U.S. - 10 samples)	2000-7140
Pearlette Volcanic Ash	3000

Table 5. Fluoride content of attapulgite and sepiolite

Sample	F, ppm
Attapulgite (Georgia, FL - 4 samples)	4500-5450
Sepiolite (New Mexico)	4520
Sepiolite (Vallecas, Spain)	9440

of formation for the four hectorite samples, which are of hydrothermal origin, was very high in fluoride content. In the sample containing the most (5.18%) fluoride, approximately 50% of the hydroxyl ions in the structure have been substituted by fluoride ions.

Fluoride in another dozen smectites from various localities ranges from 850 to 7100 ppm. Thus, nontronite from Washington is unique in this group because it contains so little fluoride. It should be enlightening to examine nontronite from other localities.

Apparently originating from the same ash fall, five bentonite samples from Wyoming and South Dakota averaged about 1000 ppm fluoride. Ten mixed-layer Ordovician metabentonites from different localities in the eastern half of the U.S. were found to contain significantly more fluoride, ranging from 2000 to 7140 ppm. The variations are very likely to be due to differences in the fluoride content of the volcanic ashes from which they were derived. A sample of unaltered Pearllette Volcanic Ash from Texas was found to contain 3000 ppm fluoride.

Attapulgite and sepiolite

The few samples of attapulgite and sepiolite (Table 5) that we have examined are relatively high in fluoride content. Four attapulgite samples from the Georgia-Florida area averaged about 0.5% fluoride, as did a sepiolite from New Mexico. A sepiolite from Vallecas, Spain, contained nearly 1% fluoride.

Mica, chlorite and illite

Data for a few mica and chlorite samples are shown in Table 6. The mean fluoride values may not be representative for this sample type. It is obvious, however, that a wide range of fluoride content can be expected in magmatic rocks, which are possible source materials for illite. The halogen contents of magmatic rocks have been investigated in some detail. Studies by several workers have been summarized by Correns (1956), and the reader is referred to this excellent summary for a more thorough evaluation of magmatic rocks.

Table 6. Fluoride content of mica, chlorite and illite

Sample	F, ppm
Muscovite ("white mica" - location unknown)	1000
Biotite (location unknown)	11,820
Talc (North Carolina)	2665
Clinochlore (Tilley Foster mine - NY)	56
Ripidolite (Tilley Foster mine - NY)	23,850
Vermiculite (Montana)	2700
Illite (Fithian, IL)	1035
Illite (API 36 - Morris, IL)	1671
Illite (Pennel, MT - hydrothermal area)	5640
Illite (Hardin County, IL - 17 samples)	2315-8185
Glauconite (various locations - 12 samples)	470-4320

The biotite sample contains 10 times more fluoride than the muscovite. This is in line with the data reported by Correns (1956). Seraphim (1951) is of the opinion that the hydroxyl ion in biotite is less strongly polarized than in muscovite and can therefore be more easily replaced by the less polarizable fluoride ion.

The two chlorites in the study are from the same mine and have closely similar structures, but whereas the clinochlore sample contains very little fluoride, the ripidolite sample contains nearly 2.4% fluoride. The reason for such a marked difference in their fluoride contents is unknown. It is known, however, that clinochlore has appreciable aluminum in the octahedral layer, whereas nearly all the aluminum in ripidolite is in the tetrahedral layer (Campbell, 1972). This difference conceivably could account for a greater attraction for fluoride in the ripidolite structure.

The clay minerals illite and glauconite have mica structures. Most illites and many glauconites are dioctahedral, as is muscovite. Their fluoride contents, as shown in Table 6, range from 450 to 8185 ppm. The illites from Pennel, MT, and Hardin County, IL, are from known hydrothermal areas of high fluoride concentrations. The other illites and glauconites are marine or freshwater detrital deposits.

Argillaceous earth materials

The fluoride contents of clay or shale samples should be composites of the fluoride contents of the clay minerals present, together with any fluoride-containing impurities.

We have analyzed some 200 underclays and roof shales, mostly from the Pennsylvanian in Illinois. We have also analyzed samples from a shale stratum (Mississippian) in southern Illinois where the shale is in contact with a fluorite mineralized zone and, a short distance away (about a mile), where the shale is in contact with a nonmineralized zone. In addition, inasmuch as there is uncertainty concerning the depositional environment (marine or nonmarine) of some of the clays and shales in Illinois, we also have analyzed six nonmarine shales (Permian and Triassic) from Australia. These data are summarized in Table 7.

The fluoride contents of the roof shales and underclays of the Pennsylvanian in Illinois range from 450 to 2940 ppm. From X-ray powder diffraction studies of the clay minerals present, in general it appears that as the kaolinite content increases the fluoride content

Table 7. Fluoride content of argillaceous earth materials (<2- μ m fraction)

Sample	F, ppm
Clay and shale (Pennsylvanian, Illinois - 178 samples)	450-2940
Nonmarine shale (Permian and Triassic, Australia - 6 samples)	210-470
Yankeetown shale (Mississippian, Illinois)	
Mineralized zone (contact to 2 feet above contact - 7 samples)	6255-8185
Nonmineralized zone (1 foot intervals from contact - 10 samples)	2315-2800

decreases. This correlation is not unexpected in light of the fluoride values we have obtained for kaolinite samples from various localities.

The nonmarine shales from Australia are low in fluoride content, ranging from 210 to 470 ppm. Thus, these analyses give some indication that nonmarine shales and clays are slightly lower in fluoride content than marine shales and clays. Again, hydrothermal activity by high fluoride-bearing waters can introduce appreciable fluoride into clays and shales. For example, in the fluor spar area of extreme southern Illinois (Table 7), shale of the Yankeetown formation (Mississippian), which immediately overlies a mineralized limestone zone, was found to contain fluoride ranging from 6255 to 8185 ppm for samples taken within 2 ft of the contact. This same stratum in a nonmineralized zone approximately 1 mile away showed appreciably lower fluoride values, ranging from 2315 to 2800 ppm over a 10-ft interval, beginning at the contact. Daniel and Hood (1975) reported similar data, showing that the fluoride content of an illitic shale increases in the direction of a fault in the same geographical region. From these differences, and the data of Hofmann *et al.* (1956), we could conclude that post-depositional fluoride substitution occurs more readily in illite than in kaolinite.

Influence of fluoride substitution on thermal behavior

Apart from the geochemical implications of these data, it is of interest to know how the thermal behavior of a clay might be influenced by fluoride substitution in the clay mineral structure. In addition to all the recognized variables (crystallite size, heating rate, and sample size) in differential thermal analysis (DTA) work that influence both the position and intensity of endotherms and exotherms, it seems likely that because of stronger chemical bonding, sufficient fluoride substitution also can bring about some changes. One can speculate that with a more stabilized structure from increased fluoride substitution, the position of the dehydroxylation (defluorination) peak might be shifted to a higher temperature. In addition, if the fluoride is retained in the structure at the higher temperatures through chemical recombination, it could behave as a flux, thereby altering the nature of the higher temperature endotherms and exotherms.

Ross and Hendricks (1945), who published dehydration curves of montmorillonites, suggested that the greater stability they found for hectorite was due to the large amount of fluoride substitution. The break in the dehydration curve for hectorite is 150–200°C higher than that for any other montmorillonite they studied.

We have examined a number of published DTA curves of clay minerals from the API 49 Project (Grim, 1962; Kerr *et al.*, 1949). Of the materials from the API 49 Project for which we have fluoride analysis data, we believe that some of the differences apparent in the profiles can be attributed to higher fluoride

content, particularly with attapulgite and sepiolite. The delayed loss of hydroxyl water for these clay minerals is similar to that occurring with hectorite. In addition, for the sepiolite from Vallecas, Spain, the exotherm that occurs at the relatively low temperature of 830–850°C following structural breakdown, quite possibly is due to fluoride fluxing action. We have found that after 2 hr in a muffle furnace at 800°C, the sepiolite from Vallecas contained 1.31% fluoride. The increase in fluoride content over that (about 1%) in the sample dried overnight at 110°C indicates that the fluoride is retained for the most part in the structure, after appreciable weight loss from dehydroxylation. It would be desirable to re-examine clay minerals which vary significantly in their fluoride contents with some of the more modern supersensitive DTA apparatus.

Acknowledgements—The authors wish to thank Dr. W. D. Keller for the hydrothermal kaolin samples from Mexico, Dr. S. Patterson for the Cornwall kaolinite, Dr. D. A. Grisafe for the Kansas dickite, Dr. I. E. Odom for several glauconite samples, and Dr. C. Ward for the Australian nonmarine shale samples.

REFERENCES

- Ames, L. L., Jr., Sand, L. B. and Goldich, S. S. (1958) A contribution on the Hector, California bentonite deposit: *Econ. Geol.* **53**, 22–37.
- Arad, A. and Morton, W. H. (1969) Mineral springs and saline lakes of the Western Rift Valley, Uganda: *Geochim. Cosmochim. Acta* **33**, 1169–1181.
- Campbell, I. (1972) *Foreword in Glossary of Geology* (Edited by Gary, M., McAfee, R., Jr. and Wolf, C. L.), 857 pp.: American Geological Institute, Washington, D.C.
- Carpenter, R. (1969) Factors controlling the marine geochemistry of fluorine: *Geochim. Cosmochim. Acta* **33**, 1153–1167.
- Correns, C. W. (1956) The geochemistry of the halogens: *In Physics and Chemistry of the Earth* (Edited by Ahrens, L. H., Rankama, K. and Runcorn, S. K.), pp. 181–233. McGraw-Hill, New York.
- Daniel, M. E. and Hood, W. C. (1975) Alteration of shale adjacent to the Knight orebody, Rosiclare, Illinois: *Econ. Geol.* **70**, 1062–1069.
- Ekstrom, T. K. (1973) Synthetic and natural chlorine-bearing apatites: *Contrib. Mineral. Petrol.* **38**, 329–338.
- Flanagan, F. J. (1969) U.S. Geological Survey standards—II. First compilation of data for the new U.S.G.S. rocks: *Geochim. Cosmochim. Acta* **33**, 81–120.
- Fleischer, M. (1969) U.S. Geological Survey standards—I. Additional data on rocks G-1 and W-1, 1965–1967: *Geochim. Cosmochim. Acta* **33**, 65–79.
- Fox, E. J. and Jackson, W. A. (1959) Steam distillation of fluorine from perchloric acid solutions of aluminiferous ores: *Anal. Chem.* **31**, 1657–1662.
- Frant, M. S. and Ross, J. W., Jr. (1966) Electrode for sensing fluoride ion activity in solution: *Science* **154**, 1553–1555.
- Grim, R. E. (1962) *Applied Clay Mineralogy*: McGraw-Hill, New York.
- Hayes, J. B. (1967) Dickite in Lansing Group (Pennsylvanian) limestones, Wilson and Montgomery counties, Kansas: *Am. Miner.* **52**, 890–896.

- Hofmann, U., Weiss, A., Koch, G., Mehler, A. and Scholz, A. (1956) Intracrystalline swelling, cation exchange, and anion exchange of minerals of the montmorillonite group and of kaolinite: In *Proceedings of the Fourth National Conference on Clays and Clay Minerals* (Edited by Swineford, A.), Pub. 456, pp. 273–287. National Academy of Sciences–National Research Council, Washington, DC.
- Ingram, B. L. (1970) Determination of fluoride in silicate rocks without separation of aluminum using a specific ion electrode: *Anal. Chem.* **42**, 1825–1827.
- Keller, W. D. and Hanson, R. F. (1968) Hydrothermal alteration of a rhyolite flow breccia near San Luis Potosi, Mexico, to refractory kaolin: *Clays and Clay Minerals* **16**, 223–229.
- Keller, W. D., Hanson, R. F., Huang, W. H. and Cervantes, A. (1971) Sequential active alteration of rhyolitic volcanic rock to endellite and a precursor phase of it at a spring in Michoacan, Mexico: *Clays and Clay Minerals* **19**, 121–127.
- Kerr, P. F., Kulp, J. L. and Hamilton, P. K. (1949) Differential thermal analyses of reference clay mineral specimens: American Petroleum Inst. Project 49, Preliminary Report No. 3, 48 pp.
- Koritnig, S. (1951) Ein Beitrag zur Geochemie des Fluor: *Geochim. Cosmochim. Acta* **1**, 89–116.
- Koritnig, S. (1963) Zur Geochemie des Fluors in den Sedimenten: In *Unterscheidungsmöglichkeiten mariner und nichtmariner Sedimente* (Symposium held at Geologisches Landesamt Nordrhein-Westfalen, Krefeld, Germany), pp. 231–238. Thomas-Druckerei, Kempen-Niederrhein.
- Lamar, J. E. (1942) Halloysite clay in Illinois: *Illinois State Geol. Survey Circ. No.* **83**, 4 pp.
- Livingstone, D. A. (1963) Chemical composition of rivers and lakes: *U.S. Geol. Survey Prof. Paper* **440-G**, 64 pp.
- Mason, B. (1965) *Principles of Geochemistry*, 2nd edition: John Wiley, New York.
- Orion Research Inc. (1970) Added know-how on known addition: *Newsletter* **2**, Orion Research Inc., Cambridge, MA.
- Rao, K. V., Purushottam, D. and Vaidyanadham, D. (1975) Uptake of fluoride by serpentine: *Geochim. Cosmochim. Acta* **39**, 1403–1411.
- Ross, C. S. and Hendricks, S. B. (1945) Minerals of the montmorillonite group: *U.S. Geol. Survey Prof. Paper* **205B**, 23–80.
- Seraphim, R. H. (1951) Some aspects of the geochemistry of fluorine: thesis, Massachusetts Institute of Technology.