CONCENTRATION OF DIOCTAHEDRAL MICA AND VERMICULITE USING A FLUORIDE SOLUTION

by

C. I. Rich

Department of Agronomy
Virginia Polytechnic Institute, Blacksburg, Va.

ABSTRACT

A solution containing fluoride (0.4 N NH_4F, 0.1 N HCl, N NH_4Cl), permits the concentration of dioctahedral mica and dioctahedral vermiculite in mixed clay systems. Allophane, halloysite, kaolinite, and in particular, Mg-rich montmorillonite, biotite, and vermiculite of clay size, are destroyed in 24–48 hr at room temperature. A salt-free, NH_4-saturated sample, weighing 80 mg, is shaken in 80 ml of the fluoride solution. The residue is washed with water and X-ray diffraction patterns made.

The method has use in characterizing some of the 2:1 layer silicates in clays. Anatase, if present, is also concentrated and is more positively identified by X-ray diffraction.

INTRODUCTION

Some of the principal components of many soil clays are dioctahedral mica and expansible derivatives thereof. A method has been devised to concentrate these components by dissolution of other common major components of the clay fraction.

The technique has use in characterizing some of the 2:1 layer silicates in clays and in concentrating anatase as well as the dioctahedral mica and vermiculite. The distinguishing features of the proposed method are its specificity for concentrating dioctahedral mica and dioctahedral vermiculite and its simplicity.

Kiely and Jackson (1964, 1965) proposed a method for concentrating quartz and feldspar by the dissolution of the layer silicates. These authors also review other methods for the removal of layer silicates from quartz and feldspars.

Hashimoto and Jackson (1960) published a method for the stepwise removal of (1) allophane, gibbsite, and amorphous SiO_2 and Al_2O_3, (2) interlayer material, and (3) kaolinite and halloysite by initially heating successively at 110, 400, and 500°C, respectively, followed by a 2.5 min boiling in 0.5 N NaOH.

Brown (1953) and Rich and Obenshain (1955) employed neutral NH_4F to remove interlayer material from vermiculite. Rich and Cook (1963) used the

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fluoride solution proposed here for removing interlayer material and it also was employed by Cotton,* to prepare a dioctahedral mica-vermiculite from which K was subsequently removed. This dioctahedral vermiculite gave 12 orders of (00l) X-ray reflections, thus permitting a one-dimensional structural study of the mineral.

Black and Rich (1963, p. 19) studied the reaction rate and the reaction products when a Matapeake soil clay was shaken or leached with the fluoride solution. Distinct phases of reaction, apparently first order, were observed. Allophane and other amorphous components containing Al, Fe, and Si were removed first.

METHODS AND MATERIALS

The proposed fluoride extracting solution ("F solution") has the following composition: 0.4 N NH_4F, 0.1 N HCl, N NH_4Cl. To prepare the solution, 14.8 g of NH_4F, 53.5 g of NH_4Cl, and 100 ml of N HCl were added to about 500 ml of H_2O and the solid components dissolved. The solution was diluted to 1000 ml with H_2O, mixed, and stored in a polyethylene bottle.

The clay sample was made free of salts and was NH_4-saturated with NH_4Cl. (If salts are present, insoluble fluorides may precipitate. Excess NH_4Cl need not be removed, however.)

To a 100-ml polypropylene tube, 80 mg of the sample and 80 ml of the "F solution" were added. The mixture was shaken for 24 hr and then was washed with water three times in a centrifuge.

The residue was transferred to a glass slide in 1 ml of H_2O, and, after the slurry had dried, X-ray diffraction patterns were obtained. Nickel-filtered Cu $K\alpha$ X-radiation, generated at 40 kV and 20 mA, was employed; the patterns were recorded logarithmically.

The soil clays generally were from the Ap horizons of widely separated soils. The specimen minerals were obtained from Ward's Natural Science Establishment, Rochester, New York. The biotite came from Ontario, Canada; vermiculite from Libby, Montana; montmorillonite from Otay, California and Clay Spur, Wyoming; nontronite from Washington; chlorite from Chester, Vermont; and illite from Morris, Illinois. The "halloysite" came from a weathered pegmatite in a quarry at Piney River, Virginia.

The clay fractions were separated by the method of Jackson (1956). The 2–0.2 μ fraction of each soil was used in this study. In the case of specimen minerals, after light grinding, the samples were dispersed in water. Minerals not of clay size were reduced in particle size in a Waring Blendor. The 2–0.2 μ fraction was later separated. The X-ray patterns obtained for the untreated 2–0.2 μ specimens were typical for these minerals and are not shown here.

* Cotton, S. B. (1965), Hydrolysis of aluminum in synthetic cation exchange resins and dioctahedral vermiculite. Ph.D. thesis, Virginia Polytechnic Institute, Blacksburg.

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RESULTS

Soil Clays

The soil clays, whose diffraction patterns are shown in Fig. 1, gave sharp 10 Å and higher order (001) peaks after treatment. The dioctahedral nature of the residue was indicated by (060) reflections near 1.50 Å.

Even the Lloyd soil clay, which consists largely of kaolinite, showed a marked concentration of the 10 Å component. Some of the kaolinite and

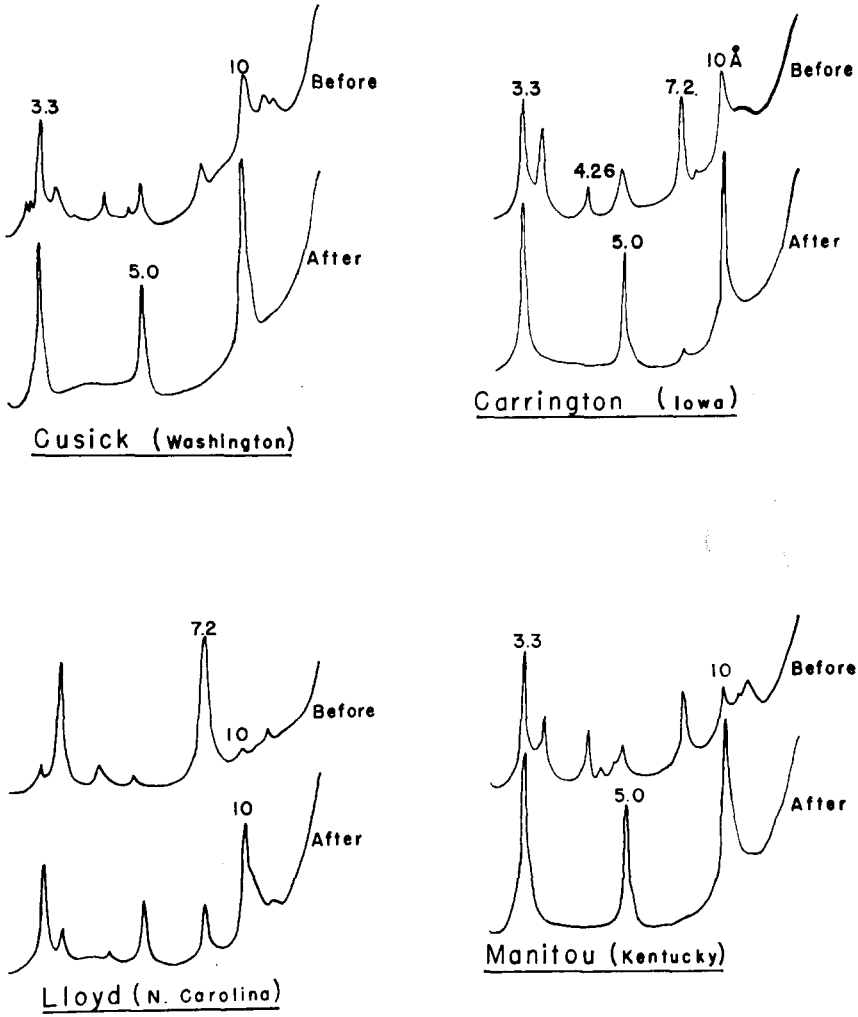


FIG. 1. Effect of the reaction of soil clays with the "F solution" for 24 hr as indicated by X-ray diffraction patterns of NH_4-saturated samples heated at 110°C.

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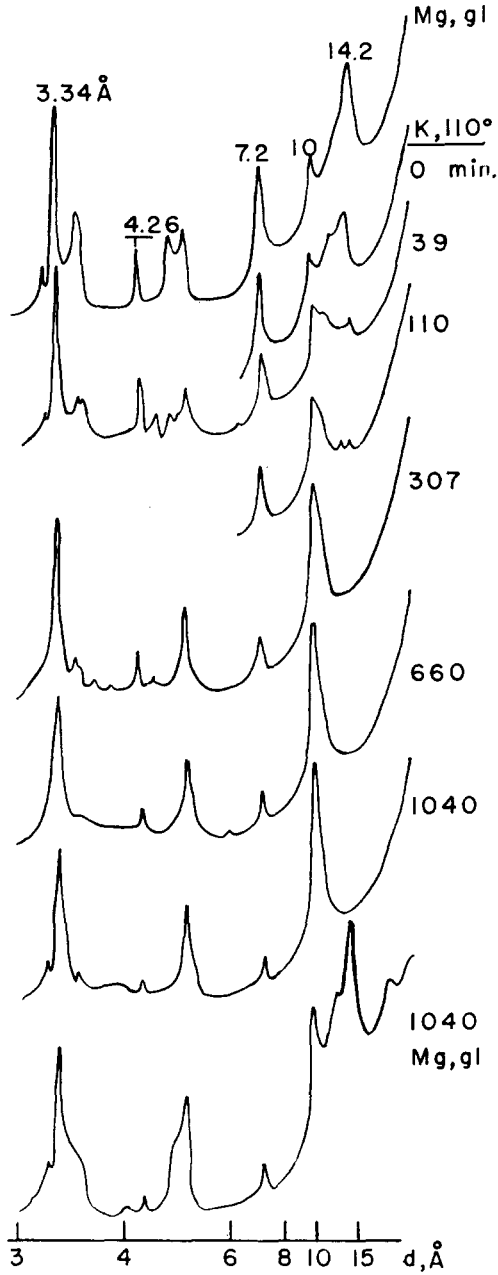


FIGURE 2.—Effect of reaction time of "F solution" on 2–0.2 μ fraction from a Matapeake B2 soil; also expansion of final product on Mg saturation.

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quartz remained in the sample but probably could be removed by shaking with the "F solution" for a longer period of time.

A portion of the 10 Å mineral, after treatment, is really NH_4-saturated dioctahedral vermiculite (or high-charge montmorillonite), derived by NH_4 saturation and collapse of the expansible layer silicate to 10 Å. A large part of the NH_4^+ ions in the clay can be removed by washing with N $MgCl_2$. The vermiculite portion then gives a 14.5 Å spacing.

Figure 2 gives the results of an experiment on reaction time of the "F solution" with a Matapeake clay from Virginia. The progressive increase in the intensity of the 10 Å peak, as well as expansion of the vermiculite portion of the final product, is evident.

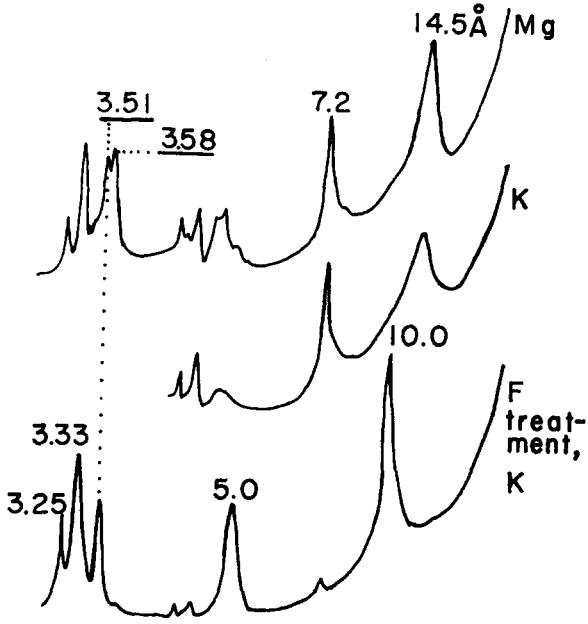


FIGURE 3.—Concentration of anatase in a Red Bay soil clay by a 24-hr reaction with the fluoride solution as indicated by X-ray diffraction patterns. The 3.51 Å peak is attributed to anatase.

A Red Bay soil clay from Mississippi (Glenn and Nash, 1964) gave a 3.51 Å peak near the 3.58 Å kaolinite peak (Fig. 3). After the fluoride treatment, the intensity of the 3.51 Å peak was reinforced,and because additional peaks at 2.38, 1.89, and 1.665 Å became evident, it is concluded that the 3.51 Å as well as the additional peaks are those for anatase. The sample contained 14.9% TiO_2 (Glenn and Nash, 1964). Thus, the fluoride treatment enabled a more positive identification of this mineral.

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Specimen Minerals

A large proportion (86%) of the Wyoming montmorillonite was dissolved by the "F solution" in 24 hr but the residue gave the typical pattern for the mineral (Fig. 4). Otay montmorillonite, a high-Mg and high-charge type, was dissolved. A mica impurity was residual and $MgNH_4AlF_6$ was precipitated. Eureka halloysite (not shown) was also dissolved completely in the "F solution" (80 mg in 80 ml) and $(NH_4)_3AlF_6$ was precipitated. The addition to this system of only 0.1 meq of $MgCl_2$ produced a distinct 5.75 Å peak and 1 meq of $MgCl_2$ converted all of the $(NH_4)_3AlF_6$ to $MgNH_4AlF_6$. Specimen kaolinite was also dissolved but much more slowly than specimen halloysite or kaolinite in soil clays. Nontronite was also dissolved. Vermiculite and nearly all of the biotite was dissolved and the $MgNH_4AlF_6$ compound was formed. In addition, a mineral with 9.3 and 8.4 Å peaks (amphibole?) also was residual in the vermiculite sample. The trioctahedral chlorite was more resistant, but such minerals are rarely found in association with dioctahedral mica in soils.

The Piney River "halloysite" contained muscovite and feldspar which were concentrated by reaction of the sample with the "F solution".

DISCUSSION

The fluoride solution as prepared is buffered at pH 5.0. Iron and aluminum are complexed by fluoride at this pH (Fife, 1959). Exposed OH^- groups of clay minerals are attacked even by neutral NH_4F (Huang and Jackson, 1964, p. 19) and according to these authors, no detectable mineral-bound fluoride develops in a neutral NH_4F solution. Hoffman *et al.* (1956), in contrast, interpret the initial reactions of NH_4F with clay minerals as an exchange of the F^- ion for OH^- groups.

The rapid dissolution of halloysite and kaolinite, particularly the former, can be attributed to attack on exposed OH^- groups and complexing of aluminum.

As interlayer material is removed, expansible 2:1 layer silicates become NH_4-saturated and the high-charge types tend to collapse. Thus, there is a tendency for surface attack to be limited to the edges and the outside planar surfaces of these minerals.

The reason for the rapid attack on trioctahedral mica and vermiculite is not clear. The insolubility of the reaction product, $MgNH_4AlF_6$, may be involved. MacEwan (1949), however, pointed out that trioctahedral montmorillonites are usually rather readily dissolved in dilute acid. Grim (1953, pp. 299–300) also cited work which showed that Mg-rich montmorillonites seem most susceptible to electrodialysis.

Hoffman *et al.* (1956) noted that grains, judged to be amorphous silicic acid, were formed when neutral NH_4F destroyed kaolinite. The work of Black and Rich (1963) suggests that, in the fluoride solution proposed here,

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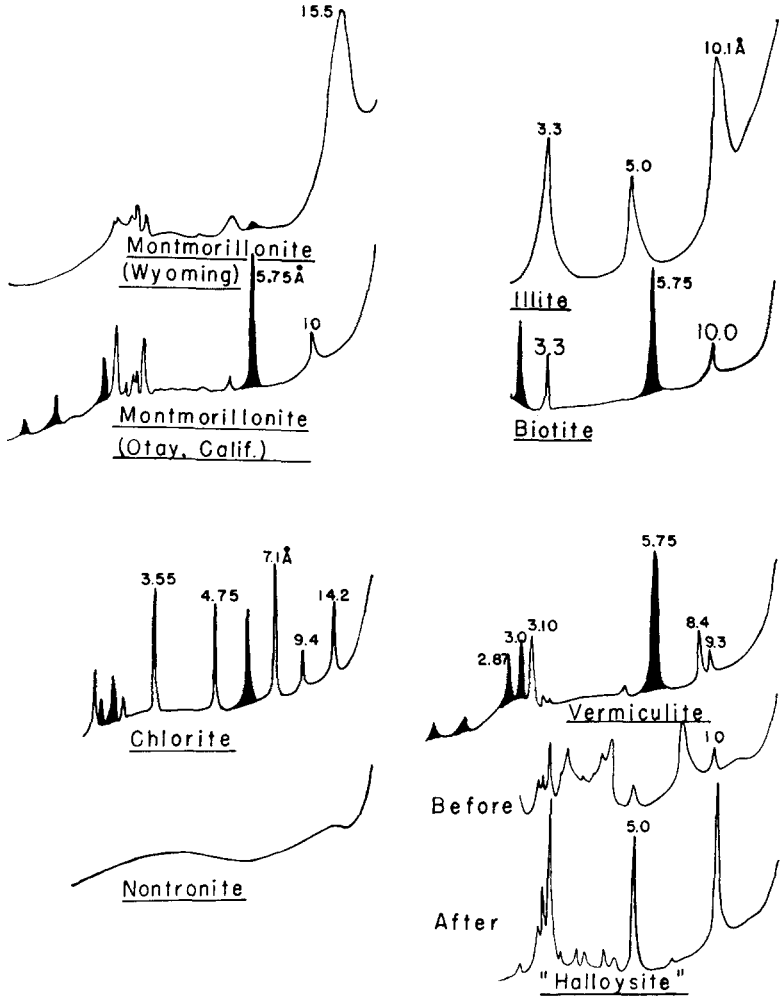


FIGURE 4.—Effect of the reaction of specimen minerals of clay size with the "F solution" for 24 hr as indicated by X-ray diffraction patterns of NH_4-saturated samples. The reaction product, $MgNH_4AlF_6$, is identified by "solid" peaks.

silica is removed in solution. The fact that quartz is destroyed also supports this conclusion.

During 1040 min, 55% of the sample weight but only 14% of the original potassium was dissolved from Matapeake clay (Black and Rich, 1963, p. 19). These results showed that even the mica is attacked but much less than other components. Quantitative separation of the mica component of soil clays by this method is thus not likely.

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