

## ANATASE AND RUTILE DETERMINATION IN KAOLINITE DEPOSITS

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**Abstract**—Hexafluorotitanic acid ( $\text{H}_2\text{TiF}_6$ ) selectively dissolves kaolinite and most other phyllosilicate minerals of soils and sediments, concentrating free crystalline  $(\text{Ti,Fe})\text{O}_2$  minerals (partially substituted anatase and rutile) in the residue. A series of  $\text{H}_2\text{TiF}_6$  reagents was standardized by analysis of the Ti content and by tests with pure anatase and commercial kaolinites. The Ti in the  $\text{H}_2\text{TiF}_6$  solution selected (made from 49% HF + reagent  $\text{TiO}_2$ ) was 16.5% by weight as analyzed by the Tiron method. Treatment of pure anatase with the reagent  $\text{H}_2\text{TiF}_6$  resulted in a 98% by weight recovery of  $\text{TiO}_2$  in the residue. The fraction of  $\text{TiO}_2$  recovered in the residue of commercial Georgia kaolinites was 88–101% after treatment with the selected  $\text{H}_2\text{TiF}_6$  reagent. Isolates from nine Georgia kaolinite samples with varying amounts of  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  were examined by X-ray powder diffraction, scanning electron microscopy and elemental analysis. The main constituent of the  $(\text{Ti,Fe})\text{O}_2$  isolates was anatase for all samples, with minor amounts of coarser rutile and mica from coarser kaolinite. The anatase and rutile isolates contained 74–93%  $(\text{Ti,Fe})\text{O}_2$  with 0.5–3.1% Fe. The other constituents of the isolates were muscovite of mica (0.3–7%), quartz (0–9%) and amorphous relics of vermiculite and/or kaolinite (6–19%). Rutile, muscovite and quartz appear to be detrital but the anatase and relics are probably authigenic. Fine anatase appears to stick on the muscovite flakes as revealed by scanning electron microscopy and heavy liquid data for separation of these two minerals. The  $(\text{Ti,Fe})\text{O}_2$  isolates from kaolinites which passed with the first magnetic concentrate of anatase were coarse, on the order of a few microns dia., as revealed by the scanning electron microscopy. Those passed with subsequent extensive magnetic concentrates from the same samples were finer. The anatase isolated from kaolinite purified by removal of as much of the impurities as possible by magnetic means was extremely fine, most of the particles being on the order of 0.1  $\mu\text{m}$  dia. More than one third of the total  $\text{Fe}_2\text{O}_3$  in kaolinites magnetically separated in the first pass was extracted by the citrate–bicarbonate–dithionite treatment after hot NaOH dissolution of 52–74% of the kaolinite, showing that the  $\text{Fe}_2\text{O}_3$  had been mainly associated within the kaolinite. Only 2–6% of the total  $\text{Fe}_2\text{O}_3$  was extracted from magnetically purified kaolinite after 40–50% of this kaolinite had been dissolved, indicating that most of the Fe is in the anatase and rutile fraction.

### INTRODUCTION

The purposes of this paper are (a) to report on the standardization of synthesis of a  $\text{H}_2\text{TiF}_6$  solution suitable for the selective dissolution method for isolating anatase and rutile from sedimentary kaolinites and soils and (b) to characterize the  $(\text{Ti,Fe})\text{O}_2$  minerals, isolated from commercial kaolinites, by X-ray powder diffraction, scanning electron microscopy, and chemical methods.

Titanium occurs in most soils and silicious igneous, metamorphic, and sedimentary rocks, as structural  $\text{Ti}^{4+}$  in silicates and as free oxides. The amount varies from less than 0.5% in little weathered soils of temperate regions to as much as 25% in the highly weathered ferruginous latosols of Hawaii (Sherman, 1952). Much of the Ti in the finer particles occurs in secondary minerals such as leucoxene ( $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ ) and anatase ( $\text{TiO}_2$ ). In coarse silt and very fine sand the Ti largely resides in primary minerals such as rutile and brookite ( $\text{TiO}_2$ ), sphene ( $\text{CaSiTiO}_5$ ) and ilmenite ( $\text{FeTiO}_3$ ). In the  $\text{H}_2\text{TiF}_6$  method F forms complexes with Al

and Si of aluminosilicate minerals. The examination of  $(\text{Ti,Fe})\text{O}_2$  mineral isolates by various techniques is expected to give a better understanding of these minerals in kaolinite deposits and soils with respect to weathering phenomena, including differentiation of detrital from authigenic Ti minerals.

In iron-containing titanium oxides in kaolinite from Georgia, the Ti was evenly distributed through the kaolinite "book" fraction, according to electron beam scanning (Weaver, 1968). Commercial kaolinites for paper coating have been cleaned of  $\text{TiO}_2$  by froth flotation (Greene and Duke, 1962) and differential flocculation–sedimentation (Maynard *et al.*, 1969). A separate anatase phase was observed in the heavy liquid separation of soil clays (Francis *et al.*, 1970). Isolation of  $\text{TiO}_2$  minerals was accomplished by HF–HCl treatment (Raman and Jackson, 1965), but this reagent is too aggressive (Campbell, 1973) unless much silicious material is dissolved (according to the X-ray diffractograms) and the  $\text{H}_2\text{SiF}_6$  generated does the isolation. An attempt has been made to differentiate Ti isomorphously substituted in minerals from that occurring as free  $\text{TiO}_2$  (Dolcater *et al.*, 1970), but the  $\text{H}_2\text{TiF}_6$  reagent was not quantitatively standardized

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and some precipitation of Ti from the reagent occurred in certain mafic (phlogopitic mica) and calcareous samples.

#### MATERIALS

Tests of different  $\text{H}_2\text{TiF}_6$  solutions were carried out with kaolinite from Twiggs County, central Georgia, U.S.A. (150-110-A) and its magnetic concentrate (Dolcater *et al.*, 1970). Isolates of  $(\text{Ti},\text{Fe})\text{O}_2$  were made from the kaolinite (separated into coarse and fine fractions by water washing) and one from the Wrens vicinity in eastern Georgia (furnished courtesy of the J. M. Huber Corporation). Each of these three samples was split by the J. M. Huber Corp. (courtesy W. F. Abercrombie) into three parts, (a) as kaolinite passed with the first magnetic concentrate of anatase, (b) as kaolinite passed with subsequent extensive magnetic separations of anatase and (c) as the remaining cleaned (low anatase) kaolinite. As controls, montmorillonitic soil from Brawley, CA, ferruginous Pauwela soil, HI and weathered phlogopite (Dolcater *et al.*, 1970) were used.

#### METHODS

Into a 1-l, wide-necked, polyethylene bottle, 400 ml of 49% HF ( $d = 1.2 \text{ g/ml}$ ) was introduced. About 10 g (a scoop from a weighed 180-g lot) of reagent grade  $\text{TiO}_2$  (Baker) was added to the HF in the bottle, with care that none stuck in the neck. The bottle was capped and swirled slowly in an ice-water bath, because the reaction is exothermic. A 10-g increment of  $\text{TiO}_2$  was added every 2 or 3 hr and the suspension swirled every half hour until 50 g of  $\text{TiO}_2$  had been added. The bottle was then tightly capped because no more heat was produced. The bottle was put on a slow moving shaker, shaken vigorously each hour, and more 10-g additions of  $\text{TiO}_2$  made until the entire 180 g of  $\text{TiO}_2$  had been added. After standing 10 ml of the suspension was filtered through a fine-porosity filter paper (Whatman 50), a 5-ml aliquot of the filtrate weighed and suitably diluted and the amount of Ti determined colorimetrically by Tiron (Jackson, 1958). Absorbance at 400 nm was taken after a half hour for complete development of the yellow color. Aliquots were pipetted immediately after approx. 1:160000 dilution; a  $\text{TiO}_2$  precipitate occurs in 3-4 days. Negative interference by fluoride ion on the Ti-Tiron complex occurs when F is 10 p.p.m. or more in the final solution (Yoe and Armstrong, 1947), but the concentration of F was far below this amount, in the diluted  $\text{H}_2\text{TiF}_6$  solution. If the concentration of Ti was less than 16.5% by weight,  $\text{TiO}_2$  was added in 10 g increments. Each time the bottle of  $\text{H}_2\text{TiF}_6$  solution was placed in a water bath at  $80^\circ\text{C}$  for 1 hr and stirred every 10 min to insure saturation of the solution with the most reactive (predominantly amorphous)  $\text{TiO}_2$  of the reagent. 210 g of  $\text{TiO}_2$  usually was required for a Ti concentration of 16.5% by

weight. The  $\text{H}_2\text{TiF}_6$  solution was cooled to room temperature, centrifuged in 100-ml plastic tubes and the supernatant liquid collected through fine porosity filter paper and stored at room temperature in a tightly closed polyethylene bottle.

To a 1-g kaolinite sample in a plastic centrifuge tube of 100-ml capacity, 30 ml of  $\text{H}_2\text{TiF}_6$  solution was added and the tube was capped tightly with a rubber stopper. The solid:solution ratio was maintained at 1:30 for various sizes of sample. During the first 3 hr, the stopper was periodically opened slightly (hood) to relieve the pressure from the formation of gaseous  $\text{SiF}_4$  and then replaced tightly, after which the tube was shaken vigorously. The tube was then placed in a water bath at  $45 \pm 2^\circ\text{C}$  for two days and shaken 7 times each day. Care was taken at each shaking that the material was suspended and none stuck at the bottom of the tube. Extreme care was taken against any evaporation of the  $\text{H}_2\text{TiF}_6$  reagent around the mouth of the tube to avoid  $\text{TiO}_2$  precipitation. The residue was washed three times with 30 ml of N HCl, twice with 0.1 N HCl, and finally five times with distilled water to avoid drying residual HCl. The residue was then dried at  $105^\circ\text{C}$  for 12 hr and weighed.

In one experiment, a 1 g kaolinite sample was boiled in each of three 300 ml lots of 0.5 N NaOH for 80 min (Hashimoto and Jackson, 1960) to dissolve kaolinite and thus preconcentrate the  $(\text{Ti},\text{Fe})\text{O}_2$  minerals before the  $\text{H}_2\text{TiF}_6$  isolation procedure. Thereafter, Fe released to citrate-bicarbonate-dithionite (CBD) extraction was determined colorimetrically by the orthophenanthroline method which uses a test solution of about pH 2 (Jackson, 1969).

Dried, powdered samples were put on glass slides wetted with acetone, spread, dried and X-rayed with Ni filtered Cu radiation with a  $3^\circ$  slit and  $2^\circ/\text{min}$  scanning speed.

For revealing the relative fineness or coarseness of the anatase and rutile, 50 mg of a  $\text{H}_2\text{TiF}_6$  isolate from the first magnetic concentrate of coarse Twiggs County kaolinite (1a), extensively treated with heavy liquid (tetrabromoethane), was shaken in distilled water. After 5 min, the finer fraction in suspension was pipetted from the coarser part, which had fallen to the bottom of the vial and both fractions were X-rayed.

For scanning electron microscopy, about 20 mg samples were washed first with 10 ml of 0.1 N HCl to remove any possible cementing agents and then 5 times with redistilled water. One drop of suspension was transferred by a disposable pipette onto dried silver cement on an aluminum stub. The mounted stubs were covered with a thin conductor film of gold evaporated under high vacuum. The samples were examined with a Cambridge scanning electron microscope.

For elemental analysis of the  $(\text{Ti},\text{Fe})\text{O}_2$  isolates, about 50 mg was fused in 5 g of  $\text{Na}_2\text{S}_2\text{O}_7$  in a silica crucible (Jackson, 1958) and after suitable dilutions,

Table 1. Preparation of a series of H<sub>2</sub>TiF<sub>6</sub> solutions tested by (Ti,Fe)O<sub>2</sub> isolation from two kaolinite samples treated with 30 ml of each H<sub>2</sub>TiF<sub>6</sub> solution for two days at 45 ± 2°C.

Amount of reagent TiO <sub>2</sub> added to 400 ml HF (g)	Residue of 1 g kaolinite samples, of original weight (%)		TiO <sub>2</sub> in impurity (Ti,Fe)O <sub>2</sub> (%)						Fraction of kaolinite TiO <sub>2</sub> impurity recovered in residue (%)	
	a*	b†	In original kaolinite		In residue		In residue, of original sample weight		a	b
			a	b	a	b	a	b		
170	1.03	23.26	1.62	23.28	83.1	73.2	0.85	17.0	52.8	73.2
180	1.47	27.47	1.62	23.28	89.1	75.5	1.30	20.8	80.8	89.2
190	1.59	30.60	1.62	23.28	89.5	74.4	1.41	22.8	87.8	97.9
200	1.53	31.21	1.62	23.28	93.4	67.8	1.41	21.2	88.2	97.3
210	1.46	31.81	1.62	23.28	98.0	74.2	1.41	23.6	88.3	101.5

\* Kaolinite (150-110-A) from Twiggs Co., GA.

† Kaolinite which passed with anatase magnetically concentrated.

the amount of Ti and Fe was determined with a Perkin-Elmer Model 306 atomic absorption spectrophotometer. Another 50 mg of isolate was fused in 1.5 g of Na<sub>2</sub>CO<sub>3</sub> and K and Al were determined by the same technique. Si could not be determined in the same solutions because of its polymerization in the acid treatment after the fusion but the amount was estimated by difference from the content of the other elements in the isolates. Because SO<sub>4</sub> from the Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub> flux interfered with Ti by decreasing absorbance with time, the standards and samples were run in exactly the same conditions and a close standard solution was aspirated alternately between samples. No SO<sub>4</sub> interference with Fe was observed and also, there was no interference of Ti with Al and K. NBS standard samples were run in parallel with the isolates and calibration curves. Ignition loss was determined at 950°C for 12 hr.

#### RESULTS AND DISCUSSION

With increasing amounts of Ti in the H<sub>2</sub>TiF<sub>6</sub>, the (Ti,Fe)O<sub>2</sub> residue amounts went up (Table 1) because of decreasing amounts of free HF remaining to dissolve crystalline anatase and rutile. The TiO<sub>2</sub> content in the residues from kaolinite, ranged from 83 to 98% but ranged from 67 to 75% in the residues from the kaolinitic magnetic concentrate (Dolcater *et al.*, 1970). The residues contain Fe in addition to Ti, evidently with more Fe in the magnetic concentrate. In comparable work, the content of TiO<sub>2</sub> of 90 to 93% were obtained in iron-containing rutile residues from Blaylock argillite and Moorepark soil (Raman and Jackson, 1965). The reagent prepared with 210 g of TiO<sub>2</sub> gave a Ti recovery between 88–101% of the total present (Table 1).

The percentage recovery from reagent grade TiO<sub>2</sub> with the H<sub>2</sub>TiF<sub>6</sub> solution prepared with 210 g of TiO<sub>2</sub> was 82%, increasing to 98% in second-cycle (i.e. the H<sub>2</sub>TiF<sub>6</sub>-treated reagent grade TiO<sub>2</sub>, HCl-washed and retreated, Table 2). This reagent exhibited practically no attack on crystalline TiO<sub>2</sub> (second cycle) and ap-

peared to be suitable for isolation of crystalline TiO<sub>2</sub>. Evidently amorphous TiO<sub>2</sub> in the original anatase was dissolved by the H<sub>2</sub>TiF<sub>6</sub> solution and by subsequent HCl washings. Some crystalline TiO<sub>2</sub> was attacked in the H<sub>2</sub>TiF<sub>6</sub> solutions prepared with lower amounts of TiO<sub>2</sub>.

With increasing amounts of TiO<sub>2</sub> originally added to the HF solution, the Ti percentages in solution went up progressively (Table 3). The H<sub>2</sub>TiF<sub>6</sub> solution to which 210 g of TiO<sub>2</sub> was originally added had a density of 1.5 g/ml and 16.5% Ti by weight, which is very close to the theoretical amount (16.6% of Ti) expected from 49% HF (1.2 g/ml). The reagent hexafluorotitanic acid (or hydrofluorotitanic acid) forms by the reaction:



Only approximately 5% of the H<sub>2</sub>TiF<sub>6</sub> in 30 ml of solution is consumed by 1 g of kaolinite, with the formation of SiF<sub>4</sub> (gas), H<sub>2</sub>SiF<sub>6</sub>, H<sub>3</sub>AlF<sub>6</sub>, H<sub>2</sub>FeF<sub>5</sub> and complexes such as HTiF<sub>5</sub>H<sub>2</sub>O (Buslaev *et al.*, 1967), but not titanil ions (Cotton and Wilkinson, 1972, p. 84). The large excess of H<sub>2</sub>TiF<sub>6</sub> is required to prevent further oxygenation and consequent precipitation of

Table 2. TiO<sub>2</sub> residue amount from reagent grade (Baker) anatase (first-cycle) and the residue anatase (second-cycle) after a two-day treatment at 45 ± 2°C with H<sub>2</sub>TiF<sub>6</sub> solutions of various compositions

Amount of reagent TiO <sub>2</sub> added to 400 ml HF (g)	Reagent grade anatase* (first-cycle)		Anatase† (second-cycle)	
	Amount of sample (g)	Residue (%)	Amount of sample (g)	Residue (%)
190	1.02	49.6	0.22	59.8
200	1.01	65.1	0.22	77.3
210	1.02	81.7	0.22	98.1

\* TiO<sub>2</sub>/H<sub>2</sub>TiF<sub>6</sub> = 1/30.

† TiO<sub>2</sub>/H<sub>2</sub>TiF<sub>6</sub> = 0.2/6 = 1/30.

Table 3. Percentage, molarity and normality of the series of  $H_2TiF_6$  solutions

Amount of reagent $TiO_2$ added to 400 ml HF (g)	By weight (%)		$H_2TiF_6$	
	Ti	$H_2TiF_6$	M	N
170	14.3	49.6	4.5	9.0
180	15.2	51.9	4.7	9.4
190	16.0	53.3	4.8	9.6
200	16.1	55.1	5.0	10.0
210	16.5	56.5	5.2	10.4

$TiO_2$  through reversal of equation (1). With calcareous materials such as Brawley soil,  $CaTiF_6$  precipitates (Dolcater *et al.*, 1970), but pretreatment with 1 N HCl to remove carbonates prevented this. The Mg of mafic minerals such as phlogopite causes a  $MgTiF_6$  precipitate (Dolcater *et al.*, 1970) and this interference was not eliminated in the present study. Treatment of hematite with  $H_2TiF_6$  precipitated  $TiO_2$ , presumably through use of much F of the reagent in fluoroferrate formation. Iron oxide removal from Pauwela soil by citrate-bicarbonate-dithionite dissolved considerable Ti, presumably from (Fe,Ti) oxides.

Anatase was the main crystalline constituent of all the (Ti,Fe) $O_2$  isolates (Fig. 1) but impurities in the isolates included mica and quartz. Mica in the form of muscovite (002 peak present at 5.0 Å) and some quartz (3.34 Å peak enhancement) were especially prominent in the coarse Twiggs County kaolinites and the first and second magnetic concentrates from the Wrens kaolinite. After separation of the isolate from the Twiggs County coarse kaolinite by sedimentation in water, the fine fraction showed more anatase than rutile; the coarse fraction showed more rutile (Fig. 2). Scanning electron microscopy (SEM) pictures of the fine and coarse fractions (Fig. 4c, d) and non-occurrence of rutile in the (Ti,Fe) $O_2$  isolates from the fine kaolinites (Fig. 1, diffractograms 2b, 2c, 3a, 3b, 3c) help to support this conclusion. The presence of cristobalite (Fig. 2) was detected only in this particular isolate which was obtained as a small residue from successive heavy liquid treatments.

The particle size (SEM) of the (Ti,Fe) $O_2$  isolates decreased with kaolinite particle size (Fig. 3) and those from easily separated magnetic fractions were coarser (on the order of a few  $\mu m$  dia, (a) isolates) than those from the second magnetic separates (which included quartz and muscovite, (b) isolates). The anatase isolates from the purified kaolinites were extremely fine, many or most particles being less than 0.2  $\mu m$  in diameter (c isolates, Fig. 3). The shapes of the (Ti,Fe) $O_2$  isolate particles were more polygonal for the coarser, strongly magnetic fractions (Fig. 3, 1(a), 2(a), 3(a)). The finer isolates (consisting of almost pure anatase) tended to flocculate in the SEM preparations. The mica particles (as also revealed in 1(b) and 3(b) isolates by XRD, Fig. 1) appear to be "loaded" with fine anatase particles (Fig. 4e), suggesting that they were brought out in the extensive magnetic separations by co-flocculation with fine (Ti,Fe) $O_2$ . Anatase fractions prepared by drying from 0.1 N HCl were lumpy and the lumps gave much charging (glowing white) in the SEM (photos not shown), while the small aggregates formed by drying from double-distilled water suspension on the mounting stub were much more satisfactory (Figs. 3 and 4). Plateshaped kaolinite crystals and "books" were more abundant in the SEM pictures of both the un-

tation in water, the fine fraction showed more anatase than rutile; the coarse fraction showed more rutile (Fig. 2). Scanning electron microscopy (SEM) pictures of the fine and coarse fractions (Fig. 4c, d) and non-occurrence of rutile in the (Ti,Fe) $O_2$  isolates from the fine kaolinites (Fig. 1, diffractograms 2b, 2c, 3a, 3b, 3c) help to support this conclusion. The presence of cristobalite (Fig. 2) was detected only in this particular isolate which was obtained as a small residue from successive heavy liquid treatments.

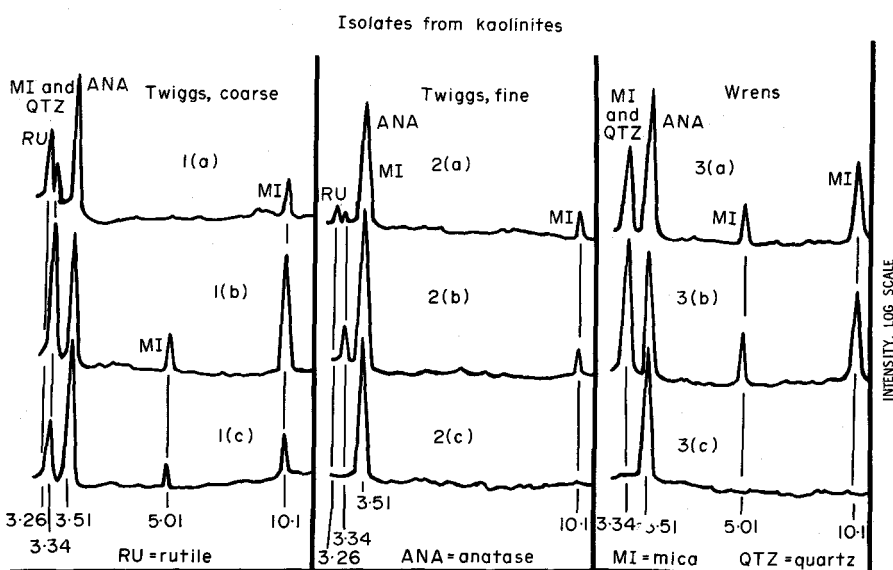


Fig. 1. X-ray diffractograms of (Ti,Fe) $O_2$  isolates after  $H_2TiF_6$  treatments for two days at  $45 \pm 2^\circ C$  of nine kaolinites: (a), first magnetic separate; (b), separate from extensive additional magnetic separations; (c), remaining kaolinite unseparated in b.

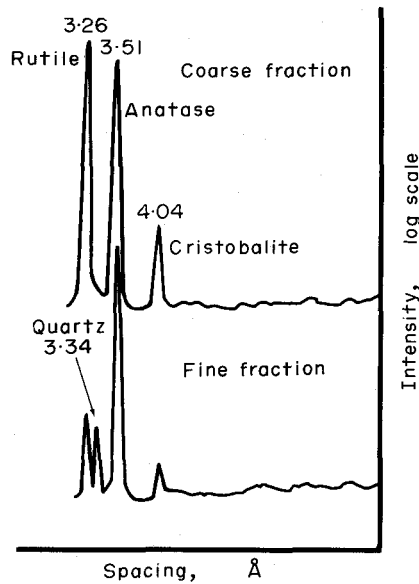


Fig. 2. X-ray diffractograms of the coarse and fine fractions of a  $(\text{Ti,Fe})\text{O}_2$  isolate from Twiggs kaolinite sample 1(a) after extensive heavy liquid treatments and subsequent size separation by sedimentation in water.

treated coarse sample (1a) than in the fine sample (2a) of Twiggs kaolinite, both easily magnetically separated (Fig. 4a, b). The particle size and shape of the other fine kaolinites is illustrated by Fig. 4(b). Uniformity of the kaolinite platelets increased with decreasing particle size.

Chemical analyses of the nine  $(\text{Ti,Fe})\text{O}_2$  isolates (Table 4) yielded 73 and 92% anatase and rutile, which reflects great concentration factors from the kaolinites that originally contained as low as 0.6, 1.0 and 1.7%  $\text{TiO}_2$  (in samples 1(c), 2(c) and 3(c), respectively, Table 5). The remainder of the isolates consisted of isomorphous Fe in the  $(\text{Ti,Fe})\text{O}_2$  and of mineral impurities which did not dissolve in the  $\text{H}_2\text{TiF}_6$  reagent during the isolation procedure.

The Ti and Fe (Table 4) were allocated (Table 5) to  $(\text{Ti,Fe})\text{O}_2$ , responsible for the brownish color of the isolates. The X-ray diffractograms do not show any kaolinite peaks, but the elemental composition implies the presence of 6–19% of amorphous relics of muscovite-derived (K-lost) vermiculite and/or kaolinite. Constituents that may have cation exchange capacity (interleaved mica or vermiculite layers, Lee *et al.* (1975) may be present. The quartz content

Table 4. Total elemental analysis of the  $(\text{Ti,Fe})\text{O}_2$  isolates from nine kaolinites

Sample	No.	%					Ignition loss (%)
		$\text{TiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{K}_2\text{O}$	$\text{SiO}_2^*$	
Twiggs, coarse	1a	82.6	4.4	4.1	0.3	8.6	0.0
	1b	73.4	1.1	6.0	0.7	17.1	1.7
	1c	72.7	0.9	6.1	0.7	14.6	5.0
Twiggs, fine	2a	88.2	2.4	3.6	<0.1	5.8	0.0
	2b	83.5	0.7	7.6	0.1	4.2	3.9
	2c	92.4	0.7	2.5	<0.1	4.4	0.0
Wrens	3a	77.3	4.8	6.1	0.4	10.4	1.0
	3b	75.9	2.1	6.0	0.8	15.4	0.0
	3c	86.6	1.8	2.6	<0.1	5.6	3.4

\* Obtained by subtracting the sum of the percentages of  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ , and ignition loss from 100.0%.

Table 5. Mineral composition of the  $(\text{Ti,Fe})\text{O}_2$  isolates from nine kaolinites

Kaolinite	Sample No.	Anatase and rutile				
		$\text{TiO}_2^*$ (%)	$(\text{Ti,Fe})\text{O}_2$ (%)	Mica (%)	Relic† (%)	Quartz‡ (%)
Twiggs, coarse	1a	14.2	87.0	2.3	8.1	2.2
	1b	1.7	74.5	5.7	9.5	8.5
	1c	0.6	73.6	6.1	9.4	5.8
Twiggs, fine	2a	5.5	90.6	0.6	8.4	0.2
	2b	2.0	84.2	0.8	18.8	0.0
	2c	1.0	93.1	0.3	5.7	0.8
Wrens	3a	10.0	82.1	3.1	12.4	0.6
	3b	3.3	78.0	6.9	8.5	6.4
	3c	1.7	88.4	0.4	6.1	1.4

\* Original in kaolinite samples (analyses by J. M. Huber Corp.).

† Vermiculite weathering product of mica (or kaolinite).

‡ Remaining  $\text{SiO}_2$  after allocating other constituents.



Table 6. Iron extracted (CBD) from kaolinites after boiling in 0.5 N NaOH

Kaolinite sample	Total* Fe <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> † by CBD (%)	Portion dissolved	
			Of Fe <sub>2</sub> O <sub>3</sub> , in CBD (%)	Of sample, in NaOH (%)
<i>Kaolinite with first magnetic isolate</i>				
1a	1.69	0.61	36.2	51.7
2a	0.98	0.33	33.7	74.3
3a	1.78	0.68	38.2	63.2
<i>Kaolinite with successive magnetic isolates</i>				
1b	0.41	0.04	9.7	54.5
2b	0.42	0.05	11.4	65.4
3b	1.04	0.05	4.9	69.0
<i>Purified kaolinite</i>				
1c	0.31	0.01	4.5	40.4
2c	0.35	0.02	6.3	51.8
3c	1.84	0.03	1.5	49.5

\* Original in kaolinite samples (analyses by J. M. Huber Corp.).

† Percentage based on original sample weight (analyses with orthophenanthroline).

(Table 5), which were estimated from left-over SiO<sub>2</sub> after that allocated to mica (by K) and relics (by Al), are in agreement with the XRD (Fig. 1). The mica is mainly in the form of muscovite (5 Å 002 peaks common, Fig. 1) with a little as biotite (no 002 peaks, 1(a), 2(a) and 2(b), Fig. 1). Muscovite is extremely resistant to the H<sub>2</sub>TiF<sub>6</sub> reagent and its resistance increases with particle size. Biotite is not resistant to H<sub>2</sub>TiF<sub>6</sub> solution (Dolcater *et al.*, 1970).

Preconcentration of (Ti,Fe)O<sub>2</sub> by dissolving part of the kaolinite in hot 0.5 N NaOH saves a considerable amount of H<sub>2</sub>TiF<sub>6</sub> reagent. Boiling of about 1 g of kaolinite for 80 min in three successive 300-ml lots of 0.5 N NaOH decreased the sample weight by 40–74% (Table 6), the amount depending upon the kind and/or particle size of the sample. However, titanium was found to be slightly soluble in 0.5 N NaOH through titanate formation. It is very soluble in much stronger NaOH and, therefore the alkali preconcentration was discontinued. Remarkably high resistance of muscovite to this alkali boiling was shown by XRD. Besides some Ti loss by this treatment, NaOH may have some etching effect (Fig. 4f) on (Ti,Fe)O<sub>2</sub> particles and many preferentially dissolve the finer particles.

The dissolution of kaolinite in NaOH released from 2 to 38% of the Fe<sub>2</sub>O<sub>3</sub> contained (Table 6). From the kaolinite passing with the first magnetic concentrate, 34 to 38% of the total iron present was released to citrate-bicarbonate-dithionite (CBD) extraction (Jackson, 1969), after 52–74% of the kaolinite had been dissolved. The iron oxide content of the kaolinite thus may have been instrumental in its passing with the magnetic fraction. Only 2–11% of the iron was released to CBD when 40–69% of the other kaolinites had been dissolved. The non-release of much Fe<sub>2</sub>O<sub>3</sub> by partial dissolution of the purified kaolinite suggests that the iron was mainly in the (Ti,Fe)O<sub>2</sub>.

This suggests one reason for whitening of kaolinite by the magnetic removal treatment, i.e. removal of iron containing kaolinite. The kaolinite would appear to be authigenic while the rutile and much of the anatase appear to be detrital.

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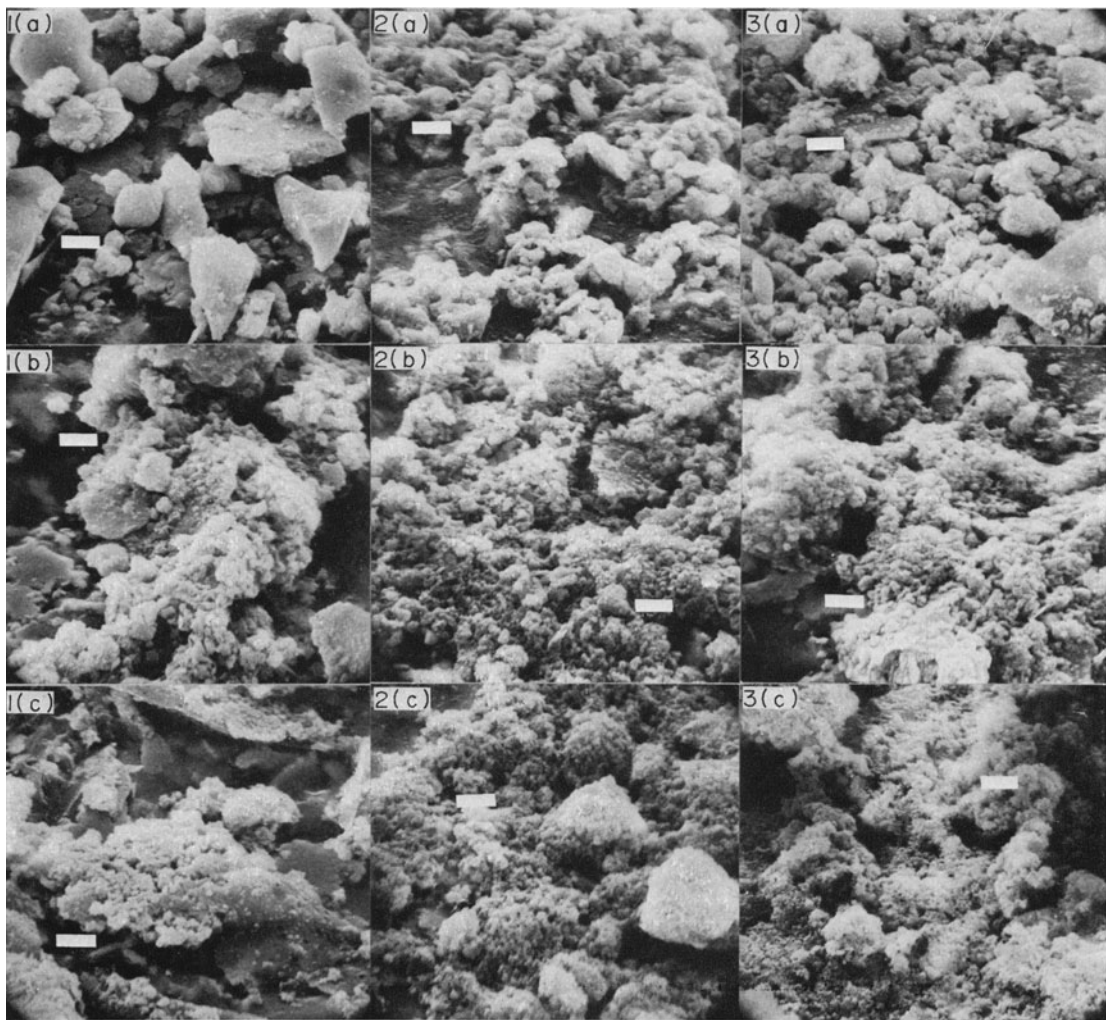


Fig. 3. Scanning electron micrographs of  $(\text{Ti,Fe})\text{O}_2$  isolates from the nine kaolinities (as in Fig. 1) at the same magnification, showing the increasing fineness of the anatase isolate with increasing (i) kaolinite fineness (1,2,3) and (ii) difficulty of magnetic separation (a,b,c). 1a, 1b, 1c represent Twiggs, coarse; 2a, 2b, 2c, Twiggs, fine; 3a, 3b, 3c, Wrens. The bar indicates  $2\ \mu\text{m}$ .



Fig. 4. Scanning electron micrographs: (a) kaolinite sample 1a (Twiggs, coarse), and (b) kaolinite sample 2a (Twiggs, fine), both easily magnetically separated; (c) the coarse  $(\text{Ti,Fe})\text{O}_2$  isolate (rich in rutile, Fig. 2), from kaolinite sample 1a, after extensive heavy liquid treatments and separation by sedimentation in water; (d) the fine isolate (richer in anatase), resulting from the same water separation; (e) a mica particle loaded with fine anatase in the  $(\text{Ti,Fe})\text{O}_2$  isolate from kaolinite sample 3b; (f) a  $(\text{Ti,Fe})\text{O}_2$  isolate (from kaolinite sample 1a), at higher magnification, showing roughness which possibly resulted from hot NaOH etching before the  $\text{H}_2\text{TiF}_6$  treatment. The bar indicates  $2\ \mu\text{m}$ .



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