TITANIUM AS FREE OXIDE AND SUBSTITUTED FORMS IN KAOLINITES AND OTHER SOIL MINERALS

D. L. DOLCATER, J. K. SYERS and M. L. JACKSON*
Department of Soil Science, University of Wisconsin, Madison, Wisc. 53706

Abstract—Titanium in TiO_2 minerals was differentiated from that isomorphously substituted into minerals by the use of dihydrogen hexafluorotitanate (hydrofluotitanic acid, H_2TiF_6), which selectively dissolved minerals containing substituted Ti^{4+}, leaving free crystalline TiO_2 minerals in the residue. Titanium analyses on the original samples and the residues remaining after H_2TiF_6 treatment, by both wet chemical (Tiron) and neutron activation methods, indicated that an average of 86 per cent of the titanium in seven kaolinite samples was present in the residual TiO_2 form (largely anatase), whereas only 28 per cent in two bentonites was present in the TiO_2 form. Residual Ti accounted for 100 per cent of the Ti in synthetic anatase and for 92 per cent of the Ti in coarse clay sized rutile, the latter value suggesting that about 8 per cent amorphous TiO_2 was removed from the mechanically dry ground rutile by the H_2TiF_6 reagent. The Ti present as residual TiO_2 in a variety of other samples ranged from 0 to 100 per cent.

INTRODUCTION

TITANIUM occurring in aluminosilicate mineral samples has been allocated to isomorphously substituted Ti (Mankin and Dodd, 1963; Weiss and Range, 1966) and to free TiO_2 (Raman and Jackson, 1965) minerals. Rutile occurring as separate grains in micaceous samples interfered with the preparation of platinum–carbon replicas for electron microscopy (Raman and Jackson, 1965). Coatings on the cleavages of micaceous vermiculite have been identified (Roth *et al.*, 1969) as mainly oxides of Fe and Al; the extent, if any, of free TiO_2 occurring in such coatings has not been determined. Inclusions of TiO_2 occur in a wide range of minerals (Deer *et al.*, 1962). Weaver (1968) concluded that Ti in Georgia kaolinites could occur in either the substituted or free oxide form, but in order to differentiate between these forms, a technique would have to be developed which would separate and concentrate each form for individual analysis.

An attempt to differentiate between substituted and free oxide forms of Ti in kaolinites, by the Raman and Jackson (1965) procedure, was unsuccessful because the resistance of standard TiO_2 samples (rutile and anatase) to 48% HF treatment at room temperature was less than that required to make an accurate separation of the two forms. A new procedure was developed that utilized a reagent containing Ti to repress TiO_2 dissolution and F to complex Al and Si, thus minimizing TiO_2 dissolution while maintaining an adequate rate of attack of aluminosilicate minerals. The reagent, dihydrogen hexafluorotitanate (hydrofluotitanic acid, H_2TiF_6), was prepared by the reaction of 48% HF with an excess of TiO_2. This reagent has been used previously in the preparation of amine hexafluorotitanates, which act as high pressure and antioxidation additives in lubricants (Knowles *et al.*, 1966) and in the colorimetric determination of Si, B, Be, Zr, and other elements (Fukamauchi, 1967). None of the literature surveyed, however, relates to the use of H_2TiF_6 for selective dissolution analysis of minerals or soils.

The purposes of this paper are (a) to describe a selective dissolution analysis (SDA) method that utilizes H_2TiF_6 to differentiate Ti isomorphously substituted in mineral structures from that occurring as free TiO_2, and (b) to measure the amount of each crystallographic association of Ti in several types of materials, with neutron activation and Tiron analyses for the Ti content.

MATERIALS

Minerals and other materials were selected to provide Ti in a wide range of crystallographic environments. Titanium controls included synthetic anatase (reagent grade TiO_2, Fisher Scientific Co.); rutile from Kragero, Norway (Wards

*Research Assistant, Assistant Professor and Professor, respectively.

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Scientific Establishment) mechanically dry ground with an iron mortar and pestle, the iron contamination being removed with 0.1 N HCl; and an ilmenite sample from Quebec (Wards). Ten kaolinites analyzed included four from Twiggs Co. in central Georgia and two from Wrens, GA (courtesy J. Iannicelli, J. M. Huber Corporation); a kaolinite from Bordeaux, France; a hydrothermal kaolinite from Cornwall, England; a commercial kaolinite from J. T. Baker Chemical Co.; and the kaolinite from Keokuk, IA geodes (courtesy W. D. Keller). Bentonites analyzed included those from Belle Fourche, SD, Colony, WY, and a commercial bentonite from Mississippi (courtesy L. V. Burns); and one from Upton, WY (courtesy American Colloid Co.). Micaceous materials included biotite and muscovite from Wards; illite from the Blaylock formation, Beavers Bend, OK (courtesy C. Mankin); micaceous vermiculite from Transvaal, South Africa (Wards); and a weathered phlogopite-vermiculite-smectite from Woodson Co., KS (courtesy L. V. Burns). Soil materials tested included Triangle soil from Twin Falls Co., ID (courtesy M. Fosberg); a dust from Kimball Co., NB (courtesy J. E. Dolcater); montmorillonitic soil from Brawley, CA, a diatomaceous earth from Arizona (courtesy L. V. Burns); and micaceous underclay from Kauai and Pauwela soil from eastern Maui, HI.

All samples were used as received except those for which a particular size fraction is indicated. The ilmenite, magnetite, hematite, quartz, albite, and microcline samples were agate mortar ground and sized materials similar to those used by Chapman *et al.* (1969) in a study of the quantitative determination of quartz.

METHODS

Preparation of H_2TiF_6

Hydrofluotitanic acid (H_2TiF_6) was prepared* by the reaction of reagent grade 48% HF with an excess of reagent grade TiO_2. The reaction between these two chemicals is highly exothermic, thereby requiring greater than normal care in the preparation of this reagent. The procedure, which requires approximately 36 hr, can be outlined as follows:

1. 1 lb of reagent grade 48% HF at room temperature is transferred to a polyethylene storage bottle of 1 l. capacity.

2. 10–15 g TiO_2 are added to the HF in the bottle, which is then loosely capped and swirled. CAUTION: Heat is produced at a rapid rate once the reaction between the HF and TiO_2 starts. A cold water bath is used to keep the reaction temperature less than 80°C to avoid melting the polyethylene bottle.

3. Additional increments of TiO_2 are added to the HF and the solution is shaken while the the reaction temperature is maintained between 50 and 70°C (monitored by touch). The temperature is controlled by adjustment of the size and frequency of the TiO_2 additions and by the use of the cold water bath.

4. Once the heating stops (even when more TiO_2 is added), the bottle is placed in a water bath at 80°C. The contents are swirled occasionally, and an excess of TiO_2 is maintained in the bottle.

5. The reaction is complete when (a) no additional TiO_2 is consumed, (b) a "layer" of solution having a density and index of refraction different from that of the bulk solution is no longer visible just above the sedimented TiO_2 which has been reacting for several hours, and (c) the vapor no longer turns moist blue litmus to red. NOTE: The HF must be completely reacted to avoid dissolution of crystalline TiO_2 minerals in the samples to be analyzed.

6. The cool H_2TiF_6 is filtered through a No. 50 Whatman filter paper in a polyethylene funnel and stored at room temperature in a tightly closed polyethylene bottle.

TiO_2 isolation procedure

The procedure for isolating TiO_2 minerals included treatment of duplicate $0.2–2$-g oven dry (110°C) samples in tared 50-ml polypropylene centrifuge tubes with single 30-ml aliquots of H_2TiF_6. The samples were placed in a water bath maintained at 45 ± 2°C for 2 days and were shaken seven times per day at intervals of $2–2.5$ hr. The suspended samples were then centrifuged, the residue being washed three times by centrifugation with 30-ml aliquots of 1 N HCl and twice with 30-ml aliquots of 0.1 N HCl. All supernatant solutions were siphoned off and discarded. The residue which remained in the tube was dried at 110°C and weighed. X-ray diffractograms were prepared with Ni filtered Cu radiation.

Ti determination

Wet chemical (Tiron) method. The original materials and the residues remaining after H_2TiF_6 treatment of sixteen samples were analyzed for Ti by a wet chemical (Tiron) method (Jackson,

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*Since this work was done, it has been learned that this reagent will be synthesized on order, by Ozark-Mahoning Co., Special Chemical Sales (Att. J. B. Beal, Jr., or W. E. White), 1870 S. Boulder, Tulsa, OK 74119.

1958). These samples were digested with reagent grade 48% HF in platinum crucibles on a sandbath at 150°C. After complete dissolution of the sample, 8 ml of 10 N H_2SO_4 were added to each crucible and the digest was heated to light fuming on a sandbath at 230°C. The contents of the crucible were transferred to a 100-ml volumetric flask, diluted to volume with distilled water, and a suitable aliquot was transferred to a second 100-ml volumetric flask, the acidity being adjusted to approximately 0·4 N with 4 N HCl, and then diluted to volume with distilled water. A 5-ml aliquot from this solution was transferred to a 50-ml volumetric flask containing 20 ml of pH 4·7 HOAc-NaOAc adjusted to pH 4·7), 5 ml of 4% Tiron (disodium pyrocatechol-3, 5-disulfonate) solution (Yoe and Armstrong, 1947) were added and the solution was diluted to volume with distilled water. The solutions were allowed to stand for 24 hr, after which approximately 25 mg of $Na_2S_2O_4$ were added to each flask to reduce ferric to ferrous iron. The absorbance of the yellow Ti–Tiron complex was then determined immediately at 410 mμ with a Unicam SP-600 spectrophotometer. Standards prepared from reagent grade TiO_2 were equivalent, whether prepared by $KHSO_4$ fusion techniques or by the HF digestion procedure described above.

Neutron activation analysis. The original materials and the residues remaining after H_2TiF_6 treatment of samples were analyzed for Ti by neutron activation analysis (NAA). All samples were irradiated for 5·0 min in a flux of $4 \times 10^{12} \pm 10$ per cent neutrons-cm^{-2} sec^{-1} and after a 25-min delay were counted for 1000 sec with a Ge–Li detector connected to a 1,024 channel analyzer (0·38 KeV/channel; 60 channel window). The 25-min time lapse between irradiation and counting was necessary to allow for the decay of ^{28}Al and other background-increasing radio-nuclides. The 0·32 MeV gamma ray of ^{51}Ti ($t_{1/2} = 5·8$ min) was used to monitor the Ti content of the samples. Counter deadtime for most of the residues remaining after the H_2TiF_6 treatment was low, but for some of the original samples it was appreciable. A correction was made for all samples whenever necessary. Standards were prepared by the addition of reagent grade TiO_2 to a second sample of the same material or to a material having a neutron absorption comparable to that of the sample being analyzed.

Comparison of methods. Titanium in the original and residual samples of sixteen materials was determined by both the wet chemical (Tiron) and the neutron activation analysis (NAA) methods (Table 1). Because the NAA method was less time consuming but in good agreement with the wet chemical method, the remainder of the samples were analyzed by NAA. Values presented in Table 2 were obtained by single NAA determinations.

RESULTS AND DISCUSSION

Control samples

X-ray diffraction (XRD) analyses (Table 2) confirmed the presence of crystalline anatase and rutile in the residues from one H_2TiF_6 treatment of the anatase and rutile samples, respectively. The residue weight averaged 98 per cent of the original sample weight for synthetic anatase (Table 2). Only 86 per cent was obtained for freshly ground coarse clay sized rutile, but the recovery was 98 per cent after a second treatment of the sample previously treated with H_2TiF_6 for 2 days at 45°C. The loss in weight (14 per cent) during the first H_2TiF_6 treatment probably resulted from dissolution of amorphous TiO_2 produced when the rutile was mechanically dry ground with an iron mortar and pestle. It is well established that the high pestle pressures involved in such grinding of crystalline minerals produces an amorphous "disturbed" layer on the surface (Dempster and Ritchie, 1952). The high values for residual Ti of synthetic anatase and once-cleaned rutile indicated that the majority of the crystalline TiO_2 resists H_2TiF_6 attack.

The residue remaining after treatment of the ilmenite sample was considerably less than might have been expected from an oxidic Ti-containing mineral. It is possible that the Fe^{2+} in combination with the Ti forms a soluble fluoroferrate and renders the Ti susceptible to attack by H_2TiF_6. The Ti of ilmenite thus would be largely classed as a "substituted" form. The purity of this sample was questionable, however, since the Ti content was only 11 per cent instead of the theoretical 32 per cent. The XRD pattern of the residue after treatment of the ilmenite sample indicated that hematite, presumably an impurity, was the dominant mineral remaining.*

Hematite is moderately resistant to the H_2TiF_6 reagent, as shown by its high residue recovery value (Table 2) and its persistence in the residue of other iron oxide rich materials. The 13-fold increase in residue Ti over the original Ti suggests that Ti had been adsorbed into the hematite structure during the H_2TiF_6 treatment. Muscovite (20–5 μ) and the montmorillonitic soil (Brawley,

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*This observation suggested the prior removal of hematite by $Na_2S_2O_4$ prior to the H_2TiF_6 treated, an experiment in progress.

Table 1. Comparison of Tiron and neutron activation methods for determination of Ti in sixteen untreated samples and residues remaining after H_2TiF_6 treatment

| Sample source | Ti* content (% of original sample) | | | |
| | Untreated sample | | Residue | |
	Tiron†	NAA‡	Tiron	NAA
Titanium controls				
Synthetic anatase	56·1	57·2	51·9	57·0
Rutile, 2–0·2 μ	54·9	49·9	46·8	46·1
Kaolinites				
Twiggs Co., GA No. 146-39-A	nd§	0·73	0·66	0·68
Twiggs Co., GA No. 150-110-A	0·97	0·95	0·78	0·72
Wrens, GA No. 150-110-B	1·27	1·32	1·00	0·96
Bordeaux, France	0·92	0·87	0·59	0·61
Cornwall, England	<0·01	0·01	<0·01	0·00
J. T. Baker Chemical Co.	<0·01	0·00	<0·01	0·00
Bentonites				
Ca-bentonite, MS	0·49	0·28	0·07	0·11
Na-bentonite, SD	0·09	0·18	<0·01	0·03
Na-bentonite, WY	0·08	0·00	<0·01	0·02
Other materials				
Montmorillonitic soil				
Brawley, CA	0·41	0·10	0·29	0·23
Illite, Beavers Bend, OK	0·79	0·79	0·60	0·64
Verm.-smect.-phlog., KS	1·62	1·46	22·2‖	22·0‖
Diatomaceous earth, AZ	0·21	0·17	0·10	0·13
Dust, Kimball Co., NB	0·31	0·12	0·14	0·05

*% TiO_2 = % Ti × 1·67.
†HF digestion with Tiron colorimetric procedure.
‡Neutron activation analysis.
§Not determined.
‖Reaction product which contained Ti was formed during H_2TiF_6 treatment.

CA) gave a similar but less extreme result. No reaction product was observed by XRD in any of these three minerals. Magnetitie, however, did not show Ti uptake (Table 2). About 60 per cent of the Ti in magnetite was retained in the residue, suggesting that the sample resisted the H_2TiF_6 treatment.

A white precipitate was encountered when the hypersthene and basalt samples were treated with H_2TiF_6. This reaction product gave a characteristic XRD pattern (Fig. 1), similar to that of the white precipitate formed when magnesium oxide was reacted with H_2TiF_6; also, a similar product formed during treatment of the weathered phlogopite (below). When a smaller hypersthene sample (0·25g vs. 1·23g) was used, no reaction product was formed. These findings, in conjunction with Ti analyses, suggest that insoluble $MgTiF_6$ had formed in the larger hypersthene and basalt samples during the H_2TiF_6 treatment, a result that could be avoided by limitation of the sample size of high-Mg materials.

Although the amount of total Ti in diatomaceous earth was small (0·17 per cent), a high proportion was present in the residual form (76 per cent). This may reflect the presence of detrital TiO_2 minerals, possibly as inclusions in the detrital quartz, laid down during the formation of the diatomaceous earth deposit. Quartz was found in the residue of many other materials, and its persistence in these residues is reflected by a recovery value of 38 per cent for fine silt sized Arkansas hydrothermal quartz (Table 2). Albite and microcline were readily dissolved in the H_2TiF_6 reagent.

Kaolinites

Residue recovery values for ten kaolinites ranged from 2·0 to 43·7 per cent (Table 2). Two Twiggs Co., GA, samples and one Wrens, GA sample had unusually high residue recovery values and very high residual Ti percentages because these samples contained the heavy minerals concentrated from larger kaolinite samples. The kaolinite from
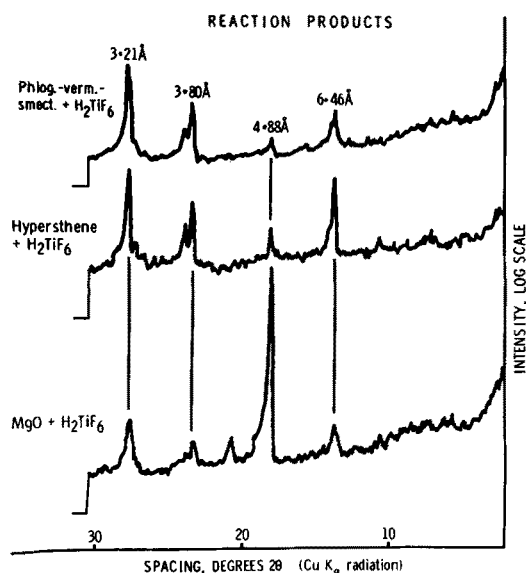
Fig. 1. X-ray diffractograms of the reaction product ($MgTiF_6$?) formed upon treatment of phlogopite, hypersthene, and magnesium oxide with H_2TiF_6.

Fig. 2. X-ray diffractograms of kaolinite and bentonite samples (untreated) and residues after one H_2TiF_6 treatment for two days at 45°C.

Bordeaux, France, contained a large percentage of quartz, an appreciable portion of which remained in the residue. Resistance of kaolinite itself to the H_2TiF_6 reagent is low, but the highly crystalline Keokuk kaolinite dissolved much more slowly than the others.

Seven of the ten kaolinites analyzed contained Ti. Of those seven, an average of 86 per cent of the total Ti was present as TiO_2 (Table 2). X-ray diffraction analysis of residues from these kaolinites indicated that all seven samples contained anatase. The four Twiggs Co. samples contained some rutile in addition (Fig. 2), although there was less rutile than anatase. The presence of anatase and rutile in kaolinites of Georgia has been reported by Weaver (1968). No trace of rutile was found in the two samples from Wrens, GA or in the Bordeaux sample. The residual Ti present as anatase and rutile may have been derived from the parent rock and the anatase formed during weathering. No Ti in any form was found in the Cornwall, Baker, and Keokuk kaolinites. The mica that was found in the residue of several kaolinites was thought to be muscovite on the basis of its resistance to H_2TiF_6 (discussed later) and its relatively large second order XRD peak (Fig. 2).

2:1 Phyllosilicates

Bentonites dissolved rapidly in H_2TiF_6, leaving a small amount of residue, primarily quartz (Fig. 2). All of the medium clay sized montmorillonite
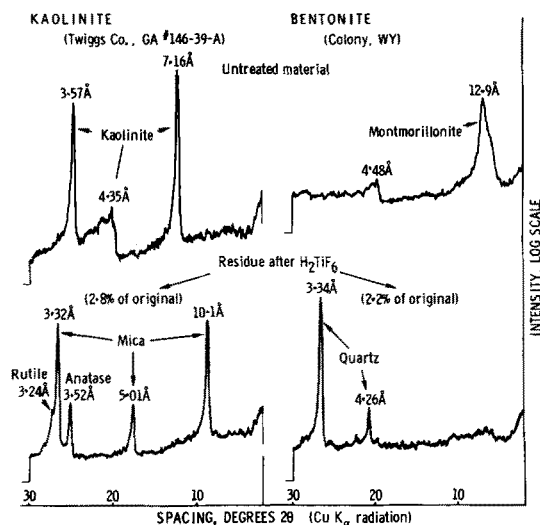
dissolved. In contrast to the kaolinites, the bentonites had the greater percentage of their Ti in the substituted form rather than in the free oxide form (Table 2).

Medium silt sized biotite and fine silt sized muscovite dissolved completely (212 mg of biotite dissolved in 5 hr; 67 mg of muscovite dissolved in approximately 42 hr), whereas only half of the medium silt muscovite was destroyed by one H_2TiF_6 treatment. All of the Ti in biotite was in the substituted form. The presence of rutile in the residue of Beavers Bend illite agrees with the results of Raman and Jackson (1965). The vermiculite and weathered phlogopite samples gave reaction products when treated with H_2TiF_6, and the products appeared to be similar to those produced when basalt, hypersthene, and magnesium oxide were treated with H_2TiF_6 (Fig. 1).

Soil materials

The titanium content of soil materials from the continental U.S.A. differed markedly from that of the materials selected from high-titanium Hawaiian soils (Table 2). Free oxide Ti in the soil materials ranged from 0 to 100 per cent of the total Ti for the Pauwela A2 and Triangle samples, respectively. The Brawley, CA sample apparently adsorbed some Ti from the H_2TiF_6 as mentioned above. A high percentage (74 per cent) of Ti as free TiO_2 was found in the Pauwela A1 horizon while all of the Ti in the A2 horizon of the same profile was removed by the H_2TiF_6 treatment. It is possible that a large portion of the Ti in

Table 2. Titanium content of the original sample and of the residue that remained after one H_2TiF_6 treatment for 2 days at 45°C

Sample source	Residue		Ti*		
	Weight (%)	Composition by XRD†	Of original sample weight (%)	In residue, of original sample weight (%)	Fraction of Ti recovered‡ in residue (%)
Control samples					
Synthetic anatase	97.6	ANA	57	57	100
Rutile, 2-0.2 μ	86.3	RU	50	46	92
Rutile residue (retreated)	98.1	RU	50	nd§	nd
Ilmenite, 20-2 μ	14.7	HEM	11	2.7	26
Hematite, 20-2 μ	65.7	HEM	0.10	1.3	1300‖
Magnetite, 20-2 μ	63.5	HEM, Qtz	0.58	0.35	60
Hypersthene, N.Z. (~4 μ)	19.0	Reaction product‖	11	5.3	
Basalt, HI	32.0	Reaction product	0.00	4.6	
Diatomaceous earth, AZ	11.0	QTZ, mi	0.17	0.13	76
Quartz, AR (5-2 μ)	37.8	QTZ	0.06	nd	nd
Albite, 5-2 μ	0.0		0.00	0	0
Microcline, 5-2 μ	0.0		nd	0	0
Kaolinites					
Twiggs Co., GA No. 142-99-I	43.7	ANA, Qtz, Ru	14	14	100
Twiggs Co., GA No. 159-56-C	15.4	ANA, ru	7.3	7.2	99
Twiggs Co., GA No. 146-39-A, Coarse	2.8	MI, Ana, ru	0.73	0.68	93
Twiggs Co., GA No. 150-110-A	2.2	ANA, Qtz, ru	0.95	0.72	76
Wrens, GA No. 159-54-1B	13.1	ANA, mi (tr)	6.1	5.4	88
Wrens, GA No. 150-110-B	3.2	ANA, MI	1.3	0.96	73
Bordeaux, France	13.4	QTZ, MI, Ana	0.87	0.61	70
Cornwall, England	2.0	MI, Qtz, fld (tr)	0.01	0.00	0
J. T. Baker Chemical Co.	4.6	MI, Qtz, fld (tr)	0.00	0.00	0
Keokuk, IA, from geodes	3.8	QTZ	0.00	0.02	
2:1 phyllosilicates					
Ca-bentonite, MS	5.9	QTZ, Mi, ana (tr?)	0.28	0.11	39
Na-bentonite, SD	2.6	QTZ	0.18	0.03	17
Na-bentonite, WY	2.2	QTZ	0.00	0.02	
Montmorillonite, WY (0.02-0.08 μ)	0.0		0.01	0.00	0
Biotite, 20-5 μ	0.0		1.6	0.00	0
Muscovite, 5-2 μ	0.0		0.00	0.00	0
Muscovite, 20-5 μ	50.7	MI	0.03	0.12	400
Muscovite, 20-5 μ, residue (retreated)	54.2	MI	0.03	nd	nd
Illite, Beavers Bend, OK	8.0	MI, Ru, fld, qtz	0.79	0.64	81
Phlog.-verm.-smect., KS	59.0	Reaction product	1.5	22	

		Reaction product Soil materials			
Vermiculite, Transvaal ($<5\,\mu$)	39·7		0·13	11	
Triangle B2tb, ID ($<5\,\mu$)	3·2	QTZ, ana (tr?)	0·13	0·13	100
Dust, Kimball Co., NB	26·4	QTZ	0·12	0·05	42
Montmorillonitic soil No. 13, Brawley, CA	15·2	QTZ	0·10	0·23	240
Micaceous underclay IIA1 (66-31) Knudsen Gap, Kauai, HI	0·3		nd	nd	nd
Pauwela A1, Maui, HI	37·6	HEM, Qtz	5·5	4·0	74
Pauwela A2, Maui, HI	61·9	HEM, Qtz	6·7	0·00	0
Pauwela B, Maui, HI	7·3	HEM	5·4	0·75	14

*% TiO_2 = %Ti × 1·67.

†Ana = anatase, Ru = rutile, Hem = hematite, Qtz = quartz, Mi = mica, Fld = feldspar, tr = trace; All letters capitalized, first letters capitalized, and all small letters signify prominent, intermediate, and small XRD peak intensity, respectively; XRD peaks listed in order of decreasing prominence, left to right.

‡Because of rounding, the numbers in this column may differ slightly from those calculated from the numbers in the two previous columns.

§Not determined.

‖Ti-containing reaction product formed during H_2TiF_6 treatment.

the Pauwela A2 and B samples was present as amorphous oxides or ilmenite and was subsequently removed by the H_2TiF_6 treatment. Sherman et al. (1964) noted that the transition zone between an indurated surface horizon and the friable B horizon of a Hawaiian soil in the Humic Ferruginous Latosol group had a very high content of colloidal TiO_2. The presence of Ti in the residue of the Pauwela A1 horizon could be explained by a process of TiO_2 crystallization in this horizon possibly as a titanium–iron oxide compound which was resistant to the H_2TiF_6 treatment. The Ti analyses for the Pauwela soil samples concur with the data of Sherman (1952) which indicated that the A2 horizon of this Hawaiian soil contained more Ti than either the A1 or B horizon samples.

CONCLUSIONS

1. Hydrofluotitanic acid (H_2TiF_6) selectively dissolved minerals containing structurally substituted Ti^{4+}, thereby allowing a differentiation of the amount of Ti in the substituted form from that in the crystalline TiO_2 form in samples containing both forms. This differentiation should assist in the allocation of the Ti composition either to substitution in the layer structure associated with modification of the cation exchange capacity or to interleaved crystals of free oxides on the cleavages of weathered micaceous vermiculites, or in part to each.

2. Crystalline TiO_2 minerals were completely resistant to attack by H_2TiF_6, while iron oxides, quartz, and muscovite were moderately resistant; these could, however, be removed by successive treatments.

3. In kaolinites containing Ti, 86 per cent of the total Ti was in the TiO_2 form, primarily as anatase, or anatase with smaller amounts of rutile.

4. All of the Ti in biotite occurred in the substituted form, whereas 81 per cent of the total Ti in Beavers Bend illite was in the free oxide form, primarily as rutile.

5. Amorphous TiO_2, formed by mechanical dry-grinding of rutile, and the whole Ti content (amorphous TiO_2 or ilmenite) in the A2 horizon of a Hawaiian soil were completely dissolved by the H_2TiF_6 reagent.

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Résumé – Le titanium dans les minéraux TiO_2 a été différencié de cleui substitué de manière isomorphe aux minéraux, par l'emploi de dihydrogène hexafluorotitanate-2 (acide hydrofluotitanique, H_2TiF_6), qui a dissout d'une manière sélective les minéraux contenant du Ti^{4+} substitué, en laissant libre les minéraux TiO_2 cristallins dans le résidu. Des analyses de titanium sur les échantillons originaux et les

résidus restant après le traitement H_2TiF_6, à la fois par un procédé chimique humide (Tiron) et d'activation de neutrons, ont montré qu'il y avait une moyenne de 86% du titanium dans sept échantillons de kaolinite, sous la forme résiduelle de TiO_2 (en grande partie l'anatase), alorsqu'il se trouvait seulement 28% dans deux bentonites sous la forme de TiO_2. Le Ti résiduel représentait 100% du Ti dans l'anatase synthétique et 92% du Ti dans de l'argile grossier taillé rutile, la dernière valeur suggérant qu'environ 8% de TiO_2 amorphe étaient enlevés du rutile broyé à sec mécaniquement, par le réactif H_2TiF_6. La présence de Ti en tant que TiO_2 résiduel en une variété d'autres échantillons variait de 0 à 100%.

Kurzreferat — Titanium in TiO_2 Mineralen wurde von isomorph in Mineralen substituiertem durch Verwendung von Dihydrogen Hexafluorotitanat-2 (Hydrofluotitansäure, H_2TiF_6) unterschieden die Minerale, die substituiertes Ti^{4+} enthielten, selektiv löste, unter Zurücklassung von freien, kristallinen TiO_2 Mineralen im Rückstand. Titananalysen an den ursprünglichen Proben und den nach H_2TiF_6 zurückbleibenden Resten, sowohl durch nass-chemische (Tiron) als auch durch Neutronaktivierungsmethoden, zeigten, dass durchschnittlich 86% des Titaniums in sieben Kaolinitproben in der residuellen TiO_2 Form (hauptsächlich Anatas) vorhanden war, während nur 28% in zwei Bentoniten in der TiO_2 Form auftrat. Residuelles Ti stellte im synthetischen Anatas 100% des Ti dar und 92% des Ti in grobem, Tongrösse-Rutil, wobei der letztere Wert andeutet, dass durch das H_2TiF_6 Reagenz etwa 8% amorphes TiO_2 aus dem mechanisch trocken gemahlten Rutil entfernt worden sind. Das als residuelles Ti in einer Anzahl anderer Proben vorhandene Ti bewegte sichin einem Bereich von 0 bis 100%.

Резюме — Титан минералов состава TiO_2 может быть отделен от титана, образующего изоморфные примеси, при использовании гексафтортитановой кислоты H_2TiF_6; эта кислота селективно растворяет минералы, содержащие изоморфную примесь Ti^{4+} оставляя неизмененными кристаллические минералы TiO_2. Определения титана как в необработанных природных образцах, так и в остатках после обработки H_2TiF_6, проведенные методом химического анализа мокрым путем и нейтроно-активационным методом, показали, что в среднем 86% титана в семи каолинитовых образцах содержится в виде остаточного минерала TiO_2 (главным образом, в виде анатаза), тогда как в двух образцах бентонита только 28% титана представлено свободной TiO_2. На долю остаточного титана приходится 100% Ti в синтетическом анатазе и 92% Ti в рутиле грубой глинистой фракции; предположительно около 8% аморфного TiO_2 удаляется из механически растертого в сухом состоянии рутила с помощью H_2TiF_6. Содержание Ti в виде остаточного TiO_2 в ряде других образцов колеблется от 0 до 100%.