Cobalt values were obtained colorimetrically by the formation of a complex with nitroso-R-salt. The iron was determined volumetrically by standardization against potassium dichromate solution and the sulfur was determined gravimetrically. Nickel values were also obtained colorimetrically by the dimethylglyoxime method. The Gutzeit procedure was used for arsenic.

A recast analysis appears at the bottom of Table 2.

DISCUSSION

Figure 1 shows a plot of weight percentage cobalt against the lattice constant in Ångstrom units. The position of the intermediate member is shown relative to normal pyrite and the cattierite of Kerr (1945; anal. by M. Vaes; Kerr's unit cell value converted to Ångstrom units and taken as 5.5346 Å).

Further investigations of a similar nature, into this simple, natural system, are being carried out. Present indications are that the system approximates to a linear series.

REFERENCES

KERR, P. F. (1945) Cattierite and vaesite: new Co-Ni minerals from the Belgian Congo. *Am. Mineral.* **30,** 483–497.

NELSON, J. B. AND D. P. RILEY (1945) An experimental investigation of extrapolation methods in the derivation of accurate unit cell dimensions of crystals. *Proc. Phys. Soc. (London),* **57,** 160–177.

RUTILE AND ANATASE DETERMINATION IN SOILS AND SEDIMENTS

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The titanium oxide minerals, rutile and anatase, often termed "accessory minerals," are usually present as a few per cent of soils and sediments; because of their high resistance to weathering they are used often as index minerals. Their content in soils varies widely, from less than 0.5 per cent in young or little weathered soils of temperate regions to 4 per cent or more in many soils of the tropical regions. Unusually high contents of TiO_2, up to 25 per cent or more have been reported in the highly weathered humic ferruginous latosols of Hawaii (Sherman, 1952). The presence of rutile and anatase in sedimentary kaolins (Nagelschmidt *et al.*, 1949), in fireclay deposits (Ennos and Scott, 1924; Brindley and Robinson, 1947) and in hydrous micas of Swedish origin (Rosenqvist, 1963) have been reported.

The usual method of identification of rutile and anatase is by x-ray diffraction, but detection of their presence is often missed in diffraction patterns, as their contents are relatively low and the x-ray peaks (3.51 Å for anatase and 3.25 Å for rutile) fall very close to those of various silicates in soils. Isolation of the free oxide minerals, rutile and anatase, is necessary as otherwise the entire Ti content may be erroneously allocated as the octahedral cation in layer silicates. For example, Mankin and Dodd
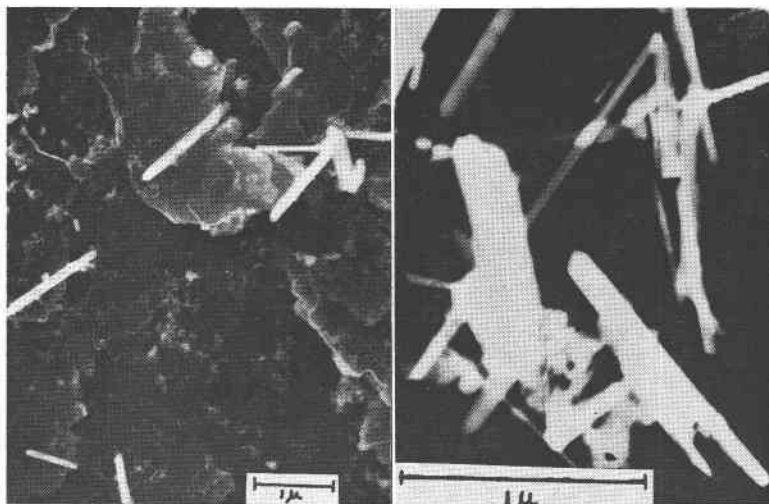

Fig. 1. Electron micrographs of samples containing rutile. a. Left. Cleavage surface of illite from Blaylock formation. Needleshaped crystals, identified as rutile, which are present on the surface stick to the replica when the siliceous materials are dissolved by HF and HCl. b. Right. Residue from the above sample after treatment with HF, showing the same sharp, euhedral crystallographic features of rutile.

(1963) in their proposed reference illite from the Blaylock formation allocated the entire Ti content to octahedral positions.

In an investigation on the surface structure of clay minerals, it was found that the surfaces of several micaceous deposits examined contained a number of needle shaped particles, highly opaque and not easily soluble in HF (Fig. 1). The sharp crystalline features of this material indicated the presence of a separate mineral species in the original mineral. The material was therefore treated with HF, and the siliceous minerals were dissolved. Since the new mineral was not very soluble in HF, it accumulated in the residue. An x-ray pattern of this concentrated residue showed the presence of rutile in the sample (Fig. 2). Electron micrographs of the residue showed the same sharp crystallographic features of needles present in the original material (Fig. 1).

Based on this and other studies, a method for the qualitative detection and quantitative estimation of rutile and anatase in small amounts has been developed for the selective dissolution of the siliceous materials in the sample by treatment with HF at room temperature, which leaves the TiO_2 accessory minerals relatively unattacked. The presence of rutile and
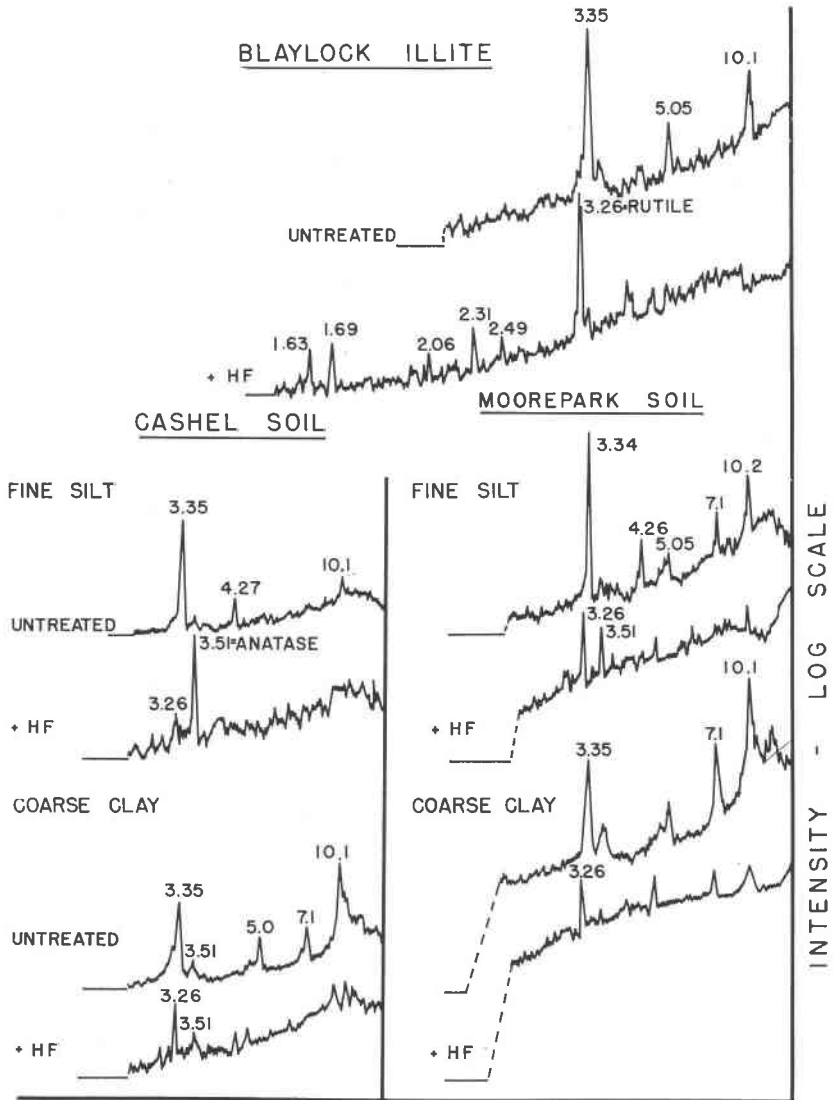

Fig. 2. *X*-ray diffractograms of fine silt and clay fractions of soils and sediments before and after treatment for selective dissolution of rutile and anatase.

anatase is then easily established by *x*-ray techniques. Prior to the HF treatment, exchangeable bases are replaced with hydrogen and free (Ca, Mg)CO_3 is dissolved to eliminate the formation of Ca and Mg fluorides which would form insoluble precipitates and coat the siliceous minerals. The coated material resists further action of cold HF on the silicate minerals. The *x*-ray diffraction peak of anatase is at 3.51 Å and of rutile is at 3.26 Å. These spacings change slightly with isomorphous substitutions in the lattice. Selected area electron diffraction of the needle-shaped structures (Fig. 1) gave the pattern characteristic of rutile, commonly occurring as clusters of crystals intergrown with anatase.

METHOD

Reagents

1. Hydrochloric acid (HCl): Concentrated HCl (approximately 12 N) diluted with water to give a stock of approximately 6 N.

2. Hydrofluoric acid (HF): Reagent-grade 48% HF.

3. Perchloric acid ($HClO_4$): 60% reagent.

4. Tiron reagent: The reagent is prepared daily by dissolution of 4 g. of Tiron in 75 ml. of distilled water and dilution of the solution to 100 ml.

5. Buffer solution of pH 4.7: Equal volumes of 1 N HOAc (60 ml. of glacial acetic acid per liter) and 1 N NaOAc (82 g. of anhydrous NaOAc per liter) are mixed and the pH is adjusted to 4.7 by a glass electrode.

6. Standard Ti solution: A solution is made by fusion of 0.1668 g. of standard TiO_2 in $K_2S_2O_7$ and taking up the melt with 10 ml. of 6 N HCl. This solution is diluted to 1 liter with 50 ml. of 6 N HCl and water. The concentration is 100 mg. of elemental Ti per liter in 0.4 N HCl. After thorough mixing, 10 ml. of this solution is diluted to 100 ml. with 0.4 N HCl, to give a standard Ti solution of 10 ppm. Aliquots (2, 4, 6, 8 and 10 ml.) of this standard are taken for the standard curve, giving 20 to 100 micrograms of Ti.

Procedure. The sample is lightly ground in an agate mortar and a weighed 0.5-g sample is transferred to a polypropylene centrifuge tube (50-ml capacity). It is washed three times, each with 30 ml of 6 N HCl by centrifugation. The sample is treated with 30 ml of HF at room temperature and allowed to stand 24 hours, with occasional stirring in the initial few hours. The sample is centrifuged down and the supernatant liquid decanted. It is then washed twice with 30 ml of distilled water, once with 30 ml of 6 N HCl, and twice more with distilled water. The residue is dried and weighed, then *x*-rayed. The peaks are indexed to detect the presence of rutile or anatase.

If rutile or anatase is present in the sample, a duplicate sample treated in the same manner as above is used for quantitative colorimetric determination of the titanium present according to a semimicrochemical system of silicate analysis (Jackson, 1958). To the weighed sample of the residue in the platinum crucible (or teflon beaker), two drops of 60% $HClO_4$, 1 drop of 18 N H_2SO_4 and 10 ml of 48% HF are added. This solution is evaporated to dryness on a sand bath in a fume hood at a temper-

ature not greater than 225° C. Care is taken to see that the solution does not boil vigorously, lest spattering cause a loss of sample. When the HF has evaporated, the crucible is cooled and another 5 ml of HF is added and the content is evaporated to dryness. Next, 7 ml of 6 N HCl is added and the solution is warmed slightly, the sides of the crucible or beaker being rubbed with a rubber tipped glass rod. This solution is then brought nearly to boiling by holding in a hot air bath over a burner. Heating is continued for 5 minutes to effect the dissolution of perchlorates and sulfates in the residue. The solution is made up to a volume of 100 ml and aliquots used for colormetric analysis.

To develop the color of the Ti-Tiron complex, first, 10 ml of buffer solution of pH 4.7 NaOAc-HOAc is pipetted into a clean 50-ml volumetric

TABLE 1. TITANIUM OXIDE CONTENT IN THE ORIGINAL SAMPLE AND THE RESIDUE
AFTER TREATMENT WITH HF

Sample	TiO_2 in original sample %	Residue %	TiO_2 in residue %	TiO_2 in residue expressed is % of TiO_2 in original sample
Blaylock illite	1.46	1.74	78.2	93.2
Rutile (isolated and retreated)	78.2	92.4	79.1	93.5
Moorepark—fine silt	1.76	2.42	66.3	91.2
Moorepark—Coarse clay	1.37	2.08	59.8	90.8

flask. The volume is adjusted to approximately 30 ml with water, and 5 ml of the Tiron solution is added. An aliquot containing 10 to 100 micrograms of Ti in 0.4 N HCl is transferred to the volumetric flask. The flask is swirled and the solution is diluted to volume with water and mixed. The percentage light transmission of the yellow Ti complex with Tiron is determined within 10 minutes with the 4000 Å light maximum. The concentration of Ti (micrograms per 50 ml) is then obtained from the standard curve.

Calculation of results. About 93% of the original Ti of rutile and anatase is recovered analytically (Table 1) after the cold HF-HCl procedure for concentrating these oxides. The TiO_2 content determined by elemental analysis is therefore multiplied by 1.08 to obtain the percentage of rutile plus anatase.

RESULTS

The titanium oxide content of Blaylock illite and other soil samples before and after the treatment described above are presented in Table 1.

The content of TiO_2 remained constant, 78.2 and 79.1%, within the limits of experimental error, in the isolation and retreatment of rutile from Blaylock illite. The TiO_2 recoveries were 93.2 and 93.5%, respectively, while the weight recovery was 92.4% for the retreatment. These data suggest an impurity or ionic substitution in the rutile phase amounting to about 7%. In the soil samples examined, the TiO_2 recovered in the residue after the treatment is about 91% of the amount originally present, indicating that almost all the titanium in the original samples was present as the oxide mineral, as judged from the Blaylock recoveries.

DISCUSSION

The applicability of this procedure for determining the rutile and anatase content of soils and sediments was tested by examining fine silt and clay fractions of soils containing appreciable amounts of titanium. X-ray diffractograms of these specimens (Fig. 2) do not show positively the presence of rutile and anatase. In some samples, TiO_2 peaks appear as shoulders of the dominant peaks of the other clay minerals present in the samples, and are therefore left unrecognized. X-ray diffractograms of the samples after the treatment described above shows the presence of anatase and rutile. The nature of the titanium mineral may vary considerably. Thus the Moorepark soil, a weakly developed podzol (Spodosol), contained both rutile and anatase in the fine silt fraction and mainly rutile in the coarse clay fraction. Cashel soil, a gray-brown podzolic (Alfiisol), had mainly anatase with a little rutile in the fine silt fraction with both rutile and anatase in the coarse clay fraction. Fine silt and coarse clay fractions from the following other soils were also examined, though the diffractograms are not presented here:

Kilcolgan soil—a rendzina (Mollisol)
Leitrim daub soil—a low humic gley (Inceptisol)
Ferruginous humic latosol (Oxisol) containing about 25 per cent TiO_2

The results obtained were, in general, the same as reported above except that varying amounts of titanium were present in the different samples.

It is suggested that this method (procedure given also in Jackson, 1965) can be successfully used for the determination of rutile and anatase content in a wide variety of soils and sediments. Where detailed formula calculations of the minerals and soil clays are involved, the presence of rutile and anatase may be tested and estimated if the sample contains appreciable amounts of titanium.

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REFERENCES

BRINDLEY, G. W. AND K. ROBINSON (1947) Note on the occurrence of anatase in some fire clay deposits. *Mineral. Mag.* **28,** 244–247.

ENNOS, F. R. AND A. SCOTT (1924) Refractory materials: Fire clays—analyses and physical tests. *Spec. Rep. Min. Res. Geol. Surv. Great Britain,* **28.**

JACKSON, M. L. (1958) *Soil Chemical Analysis,* Prentice Hall, Englewood Cliffs, N. J.

———— (1965) Free oxides, hydroxides, and amorphous aluminosilicates. Sec. 45, in *Methods of Soil Analysis,* Agronomy Monograph, Vol. 9, (C. A. Black, Ed.) American Society of Agronomy, Madison, Wisconsin.

MANKIN, C. J. AND C. G. DODD (1963) Proposed reference illite from the Ouachita Mountains. In, *Clays and Clay Minerals,* 10th Conf. Pregamon Press, New York, 372–379.

NAGELSCHMIDT, G., H. F. DONNELY AND A. J. MARCOM (1949) On the occurrence of anatase in sedimentary kaolin. *Mineral. Mag.* **28,** 492–495.

ROSENQVIST, I. TH. (1963) Studies in position and mobility of the H atoms in hydrous micas. In, *Clays and Clay Minerals,* 11th Conf. Pergamon Press, New York, 117–135.

SHERMAN, G. D. (1952) The titanium oxide content of Hawaiian soils and its significance. *Soil Sci. Soc. Am. Proc.* **16,** 15–18.

A CORDIERITE-RICH MAGNETITE-HÖGBOMITE-ORTHOPYROXENE HORNFELS FROM CURRYWONGAUN, CONNEMARA, IRELAND

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During recent re-mapping of the Currywongaun noritic intrusion (Ingold, 1937), North Connemara, Co. Galway, Ireland, by Dr. N. S. Angus, an interesting hornfelsed pelitic xenolith, largely composed of partly pinitised cordierite, with lesser magnetite and accessory högbomite, orthopyroxene and biotite was discovered. The nearest exposure of basic rock is about 10 yds away, but the contact of the two rocks is not exposed. The xenolith is about 30 yds from the inferred edge of the intrusion, which is intruded into a series of pelitic and semipelitic sillimanite-garnet-staurolite-bearing schists.

The rock has an almost equigranular texture dominated by cordierites which average 1–2mm in mean diameter. The cordierite only rarely shows lamellar twinning. The magnetite has grown along the cordierite grain boundaries and frequently presents concave surfaces to the cordierite.