

AMORPHOUS AND CRYSTALLINE TITANIUM AND IRON-TITANIUM OXIDES IN SYNTHETIC PREPARATIONS, AT NEAR AMBIENT CONDITIONS, AND IN SOIL CLAYS

R. W. FITZPATRICK,* J. LE ROUX† AND U. SCHWERTMANN‡

Department of Soil Science, University of Natal, South Africa

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Abstract—A series of mixed iron and titanium oxide coprecipitates ranging in composition between $0 < \text{Ti/Ti} + \text{Fe} < 1$ was synthesized and aged under varying conditions of pH, temperature and time in order to establish a working model for pedogenic titanium and titano-ferric oxides. X-ray powder diffraction (XRD), selective chemical dissolution, magnetic susceptibility, charge distribution and electron optical data indicate that the freshly prepared Fe–Ti oxides consist of an Fe-rich (Ti-ferrihydrate) phase ($\text{Ti/Ti} + \text{Fe} \leq 0.70$) having pH-dependent positive charge and a Ti-rich phase ($\text{Ti/Ti} + \text{Fe} \geq 0.7$) with permanent and pH dependent negative charge.

Synthetic Ti-ferrihydrate and amorphous TiO_2 were completely soluble in acid ammonium oxalate (2 hr extraction in the dark) whereas poorly crystalline anatase (width at half height, $\text{WHH} > 2.0^\circ 2\theta$) was partly oxalate soluble. NH_4 -oxalate soluble Ti was particularly high in soils developed under a cool montane climate (afro-alpine) and lower in soils of warmer subtropical climate, which contain anatase and rutile.

Several mixed Fe–Ti crystalline phases were identified after aging NH_3 coprecipitates of Fe and Ti nitrate at 70°C and pH 5.5 for 70 days:

- (1) goethite and hematite in the composition range $0 < \text{Ti/Ti} + \text{Fe} \leq 0.20$; at low Ti concentrations (< 5 mole %) goethite was favored and/or hematite inhibited;
- (2) microcrystalline pseudorutile in the composition range $0.20 \leq \text{Ti/Ti} + \text{Fe} \leq 0.70$;
- (3) anatase and ferriferrous anatase in the range $0.70 \leq \text{Ti/Ti} + \text{Fe} < 1.0$; with decreasing proportion of Ti the crystallinity of anatase decreased.

The results suggest that secondary or pedogenic Ti–Fe oxides can form by coprecipitation and crystallization in the weathering solution, and emphasize the essential role of water (as opposed to dry oxidation) in the alteration of primary titaniferous minerals.

Key Words—Anatase, Goethite, Hematite, Iron, Pseudorutile, Synthesis, Titanium.

INTRODUCTION

Regardless of parent material, titanium is invariably detected in soils. Titaniferous oxides generally are considered as inert materials in soil development and this has often been used to establish the degree of depositional uniformity in soils. However, several workers (Sherman, 1952; Sudom and St. Arnaud, 1971; Fitzpatrick and le Roux, 1976) have suggested that Ti may be mobilized in all fractions during soil weathering. Recently Bain (1976) observed high amounts of X-ray amorphous and cryptocrystalline TiO_2 in a peaty podzol. Further work is needed in characterizing the mobile, amorphous and poorly crystalline fractions of Ti in soils.

In recent studies dealing with titanium in soils and clays much emphasis has been placed on the fact that Ti is commonly combined with Fe. Selective dissolution studies by Sayin and Jackson (1975) indicate that anatase in Georgia kaolinite contains small amounts of Fe. Weaver (1976) using electron probe techniques,

supported this view. Moreover, several forms of secondary crystalline iron oxides containing structurally incorporated Ti (e.g. titanomaghemite, titanohematite, pseudobrookite and pseudorutile) have been detected in soils (e.g. Katsura et al., 1962; Walker et al., 1969; Fitzpatrick and le Roux, 1976). Their formation is thought to result mainly from the topotactic oxidation of primary minerals (e.g. titanomagnetite or ilmenite) and not to any great extent by coprecipitation and crystallization of Fe and Ti in the weathering solution. Divergent views exist on the exact nature and genesis of these alteration products, particularly ilmenite (Palmer, 1909; Overholt et al., 1950; Bailey et al., 1956; Lynd, 1960; Bykov, 1964; Temple, 1966; Grey and Reid, 1975). However, there is broad agreement that in nature a distinct intermediate titaniferous product referred to as pseudorutile ($\text{Fe}_2\text{Ti}_3\text{O}_9$ —previously called arizonite) is involved in the alteration of ilmenite (Grey and Reid, 1975). The difficulty in synthesizing pseudorutile free of other Fe and Ti minerals (e.g. hematite and ilmenite) which coincide with some of its XRD lines, together with its poorly crystalline nature, have been major problems in characterizing this intermediate alteration product (Lynd, 1960; Karkhanavala and Momin, 1959; Grey and Reid, 1975). Little information is available on pedogeochemical conditions under which Fe and Ti may coprecipitate and crystallize from the weathering

* Soil and Irrigation Research Institute, Pretoria, based in Natal Region, P. Bag X9059, Pietermaritzburg, Natal, Rep. of South Africa.

† Department of Soil Science, University of Natal, Pietermaritzburg, Natal, Rep. of South Africa.

‡ On study leave from the Institut für Bodenkunde, Techn. Universität, München, Freising 12, West Germany.

solution to form these mixed "alteration" products. Furthermore, it is not yet known what effect Ti and Fe have on the formation of iron (e.g. goethite and hematite) and titanium (e.g. anatase and rutile) oxides, respectively, at ordinary pressures and temperatures.

Numerous synthesis studies have been undertaken at high temperatures and pressures to determine the stability fields of TiO₂ polymorphs and Fe-Ti minerals (Buddington and Linsley, 1964) during magmatic oxidation (i.e. in chemical petrology). Karkhanavala and Momin (1959) hydrothermally crystalized small amounts of pseudorutile at 300°C and 1200 psi and concluded that it was "not the product of atmospheric oxidation." These results are considered to be of little value in determining the conditions and type of Fe-Ti phase which will form during the alteration of titaniferous primary minerals under earth surface conditions.

Except for the work of Weiser and Milligan (1934) on pure Ti systems, little work has been done on the precipitation and crystal growth in Ti (IV) solutions undergoing hydrolysis, particularly in the presence of other metals. Several synthetic studies have been carried out on mixed Fe-Al (e.g. Gastuche et al., 1964) and Fe-Si (e.g. Herbillon and Tran Vinh An, 1969) systems *in vitro*.

The objective of this paper is to study a series of synthetic Ti and Fe-Ti oxides§ aged under different conditions, in order to obtain a better understanding of possible Fe/Ti products and to examine their presence in soils.

EXPERIMENTAL

Synthetic Fe-Ti oxides

Chloride contamination was avoided by employing a titanyl nitrate solution, prepared as follows: a fresh Ti oxide precipitate was obtained by adding a 10% ammonia solution to 0.5 M TiCl₄ (Merck, AR) until the pH of the solution was in the range 5-6. The resulting dense white precipitate was centrifuge-washed five times with deionized water and then dissolved in 5 N HNO₃. A fresh Ti oxide gel was once again precipitated with NH₃ solution, centrifuge-washed with deionized water until a negative chloride test (AgNO₃) was obtained, redissolved in 5 N HNO₃, and diluted to a concentration of 4.79 g Ti/l.

The synthetic fresh titanium oxide (free of chloride) was finally prepared by the addition of a 10% NH₃ solution to the titanyl nitrate solution until the pH was in the range 5-6. The white precipitate was centrifuge-washed thoroughly with deionized water and either freeze-dried immediately or aged in polyethylene bottles as follows: (1) at room temperature (≈25°C) for 30 and 70 days, (2) at 70°C for 70 days, both at pH 5.5 and 12.0.

§ The term oxides in this paper includes all compounds in the system TiO₂·H₂O and Fe₂O₃·H₂O respectively.

The synthetic fresh ferrihydrite (formerly called amorphous ferric hydroxide) was prepared by the addition of a 10% NH₃ solution to 0.1 M Fe(NO₃)₃ solution (Merck, AR) until the pH ranged between 5 and 6. Nine mixed Ti(IV)-Fe(III) coprecipitates of compositions 5, 10, 20, 30, 50, 70, 80, 90 and 95 mole % Ti/Ti + Fe, respectively, were prepared in exactly the same manner except that titanyl nitrate replaced iron in the initial solution in different proportions (for comparison several Fe-Al and Fe-Zr coprecipitates were prepared in a similar way using nitrate salts). The freshly precipitated oxides were centrifuge-washed with deionized water until dispersion and either freeze-dried immediately or aged in polyethylene bottles at room temperature or at 70°C for 70 days. The pH was adjusted to 5.5 by adding HNO₃ or NH₄OH every third day, and water added at intervals to compensate for evaporation. The samples were then washed free of excess salts and freeze-dried.

Fifty mg of sample was dissolved in concentrated HCl to ascertain total Fe and Ti and duplicate samples were extracted (1) with 10 ml NH₄-oxalate (pH 3) in the dark (Schwertmann, 1964) on an end-over-end shaker for 2 hr and then centrifuged; and (2) with one 15-min treatment with citrate-bicarbonate-dithionite (CBD) (Mehra and Jackson, 1960). The extracts were analysed for Fe by atomic absorption and Ti by the Tiron method (tests for NH₄-oxalate interference in Fe and Ti determinations were negative).

X-ray powder diffraction patterns were obtained from gently pressed specimens of random orientation using a Philips PW 1050/70 instrument fitted with a graphite monochromator, and CoK α radiation. Slow scan rates (¼°/min).

Magnetic susceptibility was measured by the Gouy method using mercury (II) cobaltitetrathiocyanate HgCo(CNS)₄ as a calibration standard at 25°C and 2000 gauss.

Charge distribution of the oxides was determined by equilibrating 100-300-mg samples overnight with 10 ml 0.75 N KCl (pH adjusted to 5 or 10 with HCl or KOH) followed by a further two centrifuge washings. The suspensions were then centrifuge-washed five times with 10 ml of 0.05 N KCl adjusted to the appropriate pH. The pH of the final washing was measured, and the tube plus contents weighed immediately after decantation. Suspensions were then centrifuge-washed five times with 10 ml 0.22 N (NH₄)₂SO₄. Potassium and Cl were analyzed in the combined extracts, made up to 50 ml with 0.22 N (NH₄)₂SO₄ by flame emission and with an Aminco-Cotlove chloride titrator, respectively. Negative and positive charges were calculated after correction for occluded salt.

Clay analysis

Twelve soils from a climatoposequence in Natal were selected for study (Table 1). Samples of the clay

Table 1. Sample collection and Ti and Fe extracted from subsoil clays by acid ammonium oxalate (Ti_0 and Fe_0), CBD, (Fe_d) and total Ti (Ti_t).

Soil type	Great group	Location	Parent material	Altitude (m)	Ti_0 (%)	Ti_t (%)	Ti_0/Ti_t	Fe_0 (%)	Fe_d (%)	Fe_0/Fe_d
Peaty podzol	Cryohumod	Ardbrecknish*	Chloriteschists	—	1.95	5.40	0.36	6.09	8.62	0.70
Southwold	Cryumbrept	Lesotho	Basalt	3300	0.12	0.41	0.29	1.87	5.02	0.37
Southwold	Cryumbrept	Sani pass	Basalt	3000	0.11	0.40	0.27	1.58	6.03	0.26
Newport	Haplumbrept	Mikes pass	Basalt	2620	0.05	0.62	0.08	2.09	10.32	0.20
Ouwerf	Fragiaquiltis	Mikes pass	Basalt	2580	0.03	1.26	0.02	0.34	8.66	0.04
Farmhill	Umbriorthox	Richmond	Shale-Dolerite	1050	0.03	0.71	0.04	0.39	10.37	0.04
Farmhill	Umbriorthox	Richmond	Shale-Dolerite	1050	0.02	1.04	0.02	0.37	10.38	0.04
Vazi	Plinthaquept	Piet Retief	Sand stone	1370	0.07	0.81	0.08	1.50	3.60	0.41
Vazi	Plinthaquept	Windy hill	Sand stone	1060	0.04	1.94	0.05	3.04	22.88	0.13
Clovelly	Haplorthox	Dududu	Granite	850	0.05	0.29	0.16	1.51	14.57	0.10
Shortlands	Rhodoxeralf	Albert falls	Dolerite	670	0.01	0.28	0.04	0.32	8.11	0.04
Fernwood	Quartzipsamment	Richards bay	Eolianite	60	0.09	1.05	0.11	3.08	7.40	0.42
Clansthal	Dystrochrept	Umkomaas	Eolianite	50	0.03	0.66	0.06	0.65	15.41	0.04

* Sample from Scotland supplied by Bain (1976).

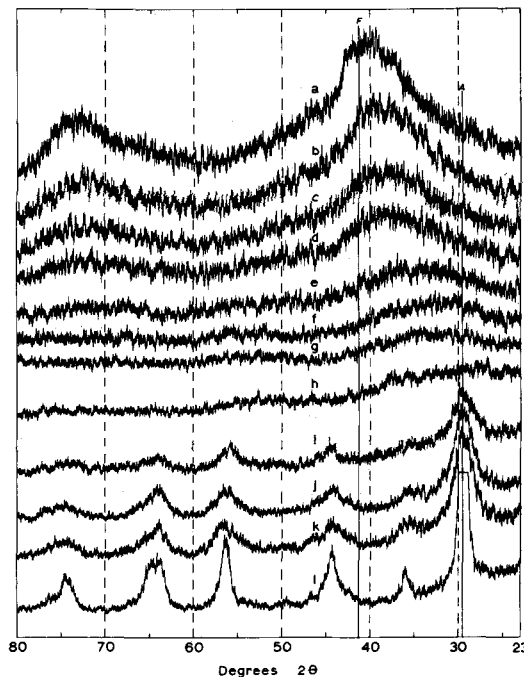


Fig. 1. X-ray powder diffraction patterns from synthetic Fe-Ti preparations. Traces a-h are for freshly precipitated oxides with: (a) 0%; (b) 10%; (c) 20%; (d) 30%; (e) 50%; (f) 70%; (g) 90%; (h) 100% in Ti/Ti + Fe, respectively. Traces i-l are for the freshly precipitated pure Ti oxide: (i) aged at room temperature (pH 5.5) for 30 days; (j) aged at room temperature (pH 5.5) for 70 days; (k) as for (j) but pretreated with 5 N NaOH at 90°C for 1 hr; (l) aged at 70°C and pH 5.5 for 70 days; where A is anatase; F is ferrihydrite.

fraction were obtained by sonic dispersion and sedimentation without pretreatment and freeze-dried. A Ti-rich clay sample ($<1.4 \mu\text{m}$) from a peaty podzol reported on by Bain (1976) was also used. Fifty mg subsamples of clay were (i) dissolved in H_2SO_4 (Pruden and King, 1969), (ii) extracted with CBD, (iii) extracted with NH_4 -oxalate (pH 3); and the extracts analyzed as for the synthetic oxides. Clays (and selected oxides) were also treated with 5 N NaOH at 90°C for 1 hr (Norrish and Taylor, 1961).

RESULTS AND DISCUSSION

Comparison of synthetic and natural Ti oxides

The freshly prepared titanium oxide obtained by precipitating titanyl nitrate (chloride free) with NH_3 , was found to be amorphous to X-rays (Figure 1h) and stayed so after aging at pH 12 for 70 days at room temperature and 70°C. However, at pH 5.5 and at room temperature ($\approx 25^\circ\text{C}$) for 30 days it showed the strong lines of anatase although very broad (Figure 1i). The line broadening corresponds to a mean crystallite dimension (MCD) of 20–80 Å, as calculated from the (101) peak

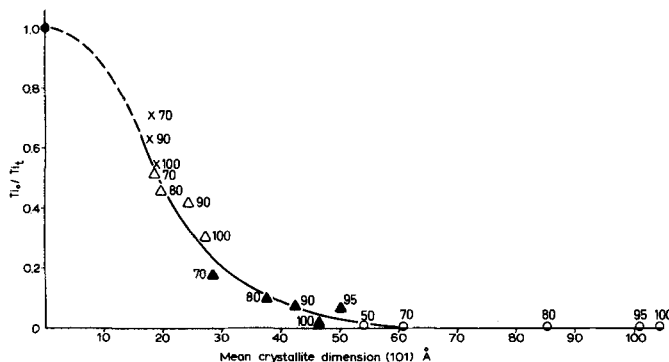


Fig. 2. Relationship between Ti_0/Ti_t and MCD (\AA) for anatase 101 (calculated from the WHH of the anatase 101 X-ray reflection). ● Freshly precipitated Ti and coprecipitated Fe-Ti oxides, × same but aged at room temperature for 10 days; \triangle same but aged at room temperature for 20 days; \blacktriangle same but aged at room temperature for 30 days; \circ same but aged at 70°C and pH 5.5 for 70 days. Numbers refer to % Ti/Ti + Fe.

using the Scherrer formula. The crystallinity of the anatase improves after aging for 70 days at room temperature (Figure 1j). This observation is in general agreement with the results obtained by Weiser and Milligan (1934) after 210 days of aging. We have some evidence that traces of Cl delay the transformation of amorphous Ti-oxide to anatase and this may be the reason for the slower rate of anatase crystallization they observed.

It is difficult to accurately locate the anatase peaks at low levels of crystallinity (Figures 1h and i, $WHH > 2.0^\circ 2\theta$ or $MCD < 50 \text{\AA}$). The rate and degree of anatase crystallization increased greatly when the amorphous oxide was aged at 70°C for 70 days (Figure 1l).

Thus, having demonstrated that X-ray amorphous Ti and anatase with varying MCD could be prepared, these polymorphs were used to monitor and test NH_4 -oxalate (pH 3) and 1 N HCl as extraction reagents for obtaining a measure of the degree of crystallinity. The fresh, X-ray amorphous oxide (Figure 1h) was found to be completely oxalate soluble ($Ti_0/Ti_t = 1$)[#] (Figures 2 and 3), while both the anatase aged for 70 days at 70°C (Figure 1l) and crystalline anatase[¶] are insoluble ($Ti_0/Ti_t = 0$) in oxalate after 2 hr extraction time (Figure 2). The relative dissolution of extremely poorly ordered anatase in oxalate is related to the MCD of anatase [as calculated from WHH of the anatase (101) X-ray reflection] for crystallites $< 50 \text{\AA}$, i.e. $WHH > 2.0^\circ 2\theta$ (Figure 2). Thus, anatase with $MCD > 50 \text{\AA}$ or with $WHH < 2.0^\circ 2\theta$ is resistant to oxalate dissolution (Figure 2) even after successive extractions (Figure 3). The X-ray amorphous Ti-oxide and the anatase with $WHH > 2.0^\circ 2\theta$ was completely soluble in 1 N HCl, but

the HCl-dissolved Ti seemed to hydrolyze extremely rapidly (in some cases after standing for only 5 hr). Both these compounds are soluble in H_2TiF_6 which agrees with previous work (Dolcator et al., 1970; Sayin and Jackson, 1975). Therefore, acid NH_4 -oxalate is the more selective extractant for X-ray amorphous TiO_2 and microcrystalline anatase.

Based on these findings for synthetic materials, this reagent was used to extract selectively similar material from a wide range of soil clays. The results together with Fe_d [#] and Ti_t are given in Table 1. The ratio Ti_0/Ti_t was used because previous work on Transvaal highly weathered soils, (Fitzpatrick and le Roux, 1976) using H_2TiF_6 , indicated that only minor amounts of Ti are associated with kaolinite. The peaty podzol gave the highest Ti_0 and Ti_0/Ti_t . Moreover, the total Ti was only partly oxalate soluble, which probably indicates that it is microcrystalline, as suggested by Bain (1976). From the data in Figure 2 the MCD of the anatase in the peaty podzol appears to be about 25\AA . All the Ti in this soil clay was extracted by H_2TiF_6 .

The Southwold soils (formed under an afro-alpine climate) also have relatively high oxalate soluble Ti values (Table 1). In contrast, most of the other test soils gave low Ti_0/Ti_t and Fe_0/Fe_d values, which suggest that both the Ti and Fe oxides are crystalline. This was verified by detecting anatase (and goethite) by XRD in these samples after removing the dominant kaolinitic material with 5 N NaOH digestion (Norris and Taylor, 1961). According to Sayin and Jackson (1976) NaOH treatment may dissolve or etch finer anatase particles. Since 5 N NaOH pretreatment is used to concentrate the Fe-oxides in sesquioxidic clays, with high amounts of kaolinite and gibbsite, prior to XRD the effect of this pretreatment on poorly crystalline synthetic anatase was tested. The XRD patterns before and after alkali treatment remained essentially the same (Figures 1j and k) and no Ti was detected in the NaOH extract.

There is a significant linear correlation ($r = 0.61$; $p = 0.02$) between Ti_0/Ti_t and Fe_0/Fe_d (Table 1) suggest-

|| $MCD = K\lambda/(B - b)\cos\theta$ in which K is a constant (0.9), λ the wavelength of the X-radiation, B the measured width at half height (WHH), b the instrumental line broadening and θ the Bragg angle of the respective line used.

[#] Ti_t and Ti_0 represent total titanium and NH_4 -oxalate (pH 3) extractable Ti, respectively, Fe_d represents CBD extractable Fe.

[¶] Obtained by courtesy from S.A. Titan Co., Rep. of South Africa.

ing that Ti follows a similar pattern to Fe in the crystallization process in soils. It is further evident that soils of cooler regions have high Fe_o/Fe_d and Ti_o/Ti_t . These observations suggest that crystallization of pedogenic iron and titanium oxides are inhibited by cool temperature conditions and possibly also by interference of organic matter (Schwertmann, 1966) and/or coprecipitation of Fe and Ti.

Freshly prepared Fe-Ti oxides

The colors of fresh and aged mixed Fe-Ti oxides ranging in composition from $0 < Ti/Ti + Fe < 1$ are given in Table 2, and range from brown to pale yellow to white with decreasing Fe content. Compared with these coprecipitates, physically mixing the two freshly precipitated end members resulted in more reddish-pinkish hues suggesting that the coprecipitates are not merely physical mixtures of Ti and Fe but possibly chemical combinations of Ti and Fe. Aging of the freshly prepared oxides at pH 5.5 and 70°C also resulted in color changes (Table 2).

The XRD data are shown in Figures 1a-h. The pure Fe precipitate (Figure 1a) gives a pattern with two broad bands corresponding to proto-ferrihydrate (Chukhrov et al., 1972). The coprecipitates with $0 < Ti/Ti + Fe < 0.30$ also resemble ferrihydrate (Figures 1b and c). However, as the $Ti/Ti + Fe$ ratio increases, the characteristic ferrihydrate pattern progressively weakens (and the two main lines gradually shift towards lower angles, suggesting Ti substitution) to give an essentially X-ray amorphous pattern with a very broad halo between 25 and 35°2θ (Figures 1e-h). The net positive charge measured at pH 4.7-5.0 of the pure ferrihydrate and the "Ti-ferrihydrates" remained fairly constant up to a composition of $Ti/Ti + Fe \approx 0.70$ at which point a net negative charge was measured which continued to increase sharply (Figure 4). A demixing of Fe or substitution of Fe in an amorphous-like titanium phase could account for both the apparent decrease in ferrihydrate (which has a high positive charge at pH 5) and the increase in net negative charge with increasing amounts of Ti. The formation of a separate negatively

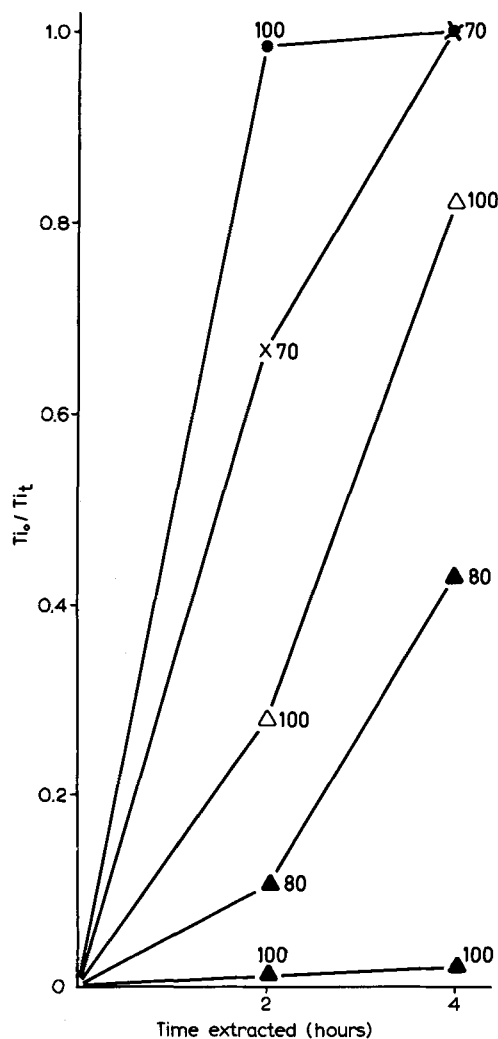


Fig. 3. Relationship between Ti_o/Ti_t and NH_4 -oxalate extraction time (hr). Legend as for Figure 2.

Table 2. Munsell colors of freshly prepared Fe/Ti coprecipitates and after aging at 70°C (pH 5.5) for 70 days.

Ti/Ti + Fe	Freshly prepared coprecipitates		Aged coprecipitates	
	Colour	Munsell notation	Colour	Munsell notation
0.00	Dusky red	10 R $\frac{3}{2}$	Dark red	10 R $\frac{4}{6-3/6}$
0.05	Dusky red	10 R $\frac{3}{3}$	Dark red-red	2.5 YR $\frac{3}{6}$
0.10	Dark reddish brown	2.5 YR $\frac{3}{4}$	Dark red-red	2.5 YR $\frac{3}{6-4/6}$
0.20	Dark red	2.5 YR $\frac{3}{4-3/6}$	Dark red	2.5 YR $\frac{3}{4-3/6}$
0.30	Dark red	2.5 YR $\frac{3}{6}$	Dark red	2.5 YR $\frac{3}{6}$
0.50	Yellowish-red	5 YR $\frac{5}{8}$	Yellowish-red	5 YR $\frac{4}{6}$
0.70	Reddish-yellow	7.5 YR $\frac{6}{8}$	Yellowish-red	5 YR $\frac{5}{8}$
0.80	Yellow	10 YR $\frac{7}{8}$	Reddish-yellow	7.5 YR $\frac{6}{6}$
0.90	Pale yellow	2.5 Y $\frac{8}{4}$	Yellow	10 YR $\frac{8}{8}$
0.95	Pale yellow	5 Y $\frac{8}{3}$	Pale yellow	2.5 Y $\frac{8}{4}$
1.00	White	5 Y $\frac{8}{1}$	White	5 Y $\frac{8}{2}$

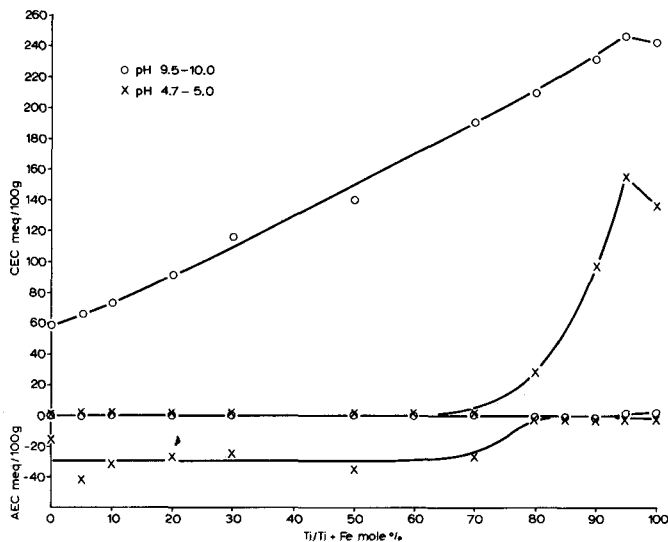


Fig. 4. Negative and positive charge variation with pH in relation to composition of freshly prepared titano-ferric oxides.

charged amorphous Ti-Fe phase and positively charged (pH 5) ferrihydrite phase could be analogous to that proposed for synthetic aluminosilicate (e.g. Cloos et al., 1969).

The pure freshly prepared titanium member has a moderately high negative charge at pH 10 which decreases at pH 5 (Figure 4). This pH-dependent charge is attributed to dissociation of Ti-OH groups. The negative charge of the Ti-Fe phase could play an important role in controlling the Fe or Fe-Ti polymerization. The effect of negatively charged clay minerals in controlling Al polymerization has been discussed by several researchers.

All freshly prepared oxides are completely soluble in oxalate ($Ti_o/Ti_t = 1$, $Fe_o/Fe_t = 1$) which confirms the "poorly ordered" nature as shown by XRD patterns (Figures 1a to h). Furthermore, this conforms with the data of Schwertmann and Fischer (1973) for synthetic and natural ferrihydrites.

In agreement with results of Prasad and Ghildyal

(1975) ferrihydrite has a high magnetic susceptibility (Figure 6) which is probably due to the low degree of order resulting from weak bonding [e.g. exposed Fe (III) polymers]. There is a steady decrease in magnetic susceptibility with increasing Ti content (Figure 6). The titanium which is diamagnetic, simply acts as a diluent in the freshly prepared coprecipitates as far as the magnetic susceptibility is concerned.

Titano-ferric oxides aged at room temperature

In the composition range $0 < Ti/Ti + Fe < 0.3$ where ferrihydrite is present, the XRD pattern remained essentially unaltered after aging at room temperature for 70 days at pH 5.5, and the oxides were also oxalate soluble. However, at $Ti/Ti + Fe$ ratios > 0.70 anatase was detected (Figure 1). With decreasing Fe in the composition range of $0.30 < Ti/Ti + Fe \leq 0.70$, the (101) line of anatase becomes sharper, and the product is progressively less oxalate soluble (Figure 2). This is probably due to decreasing interference of Fe in the

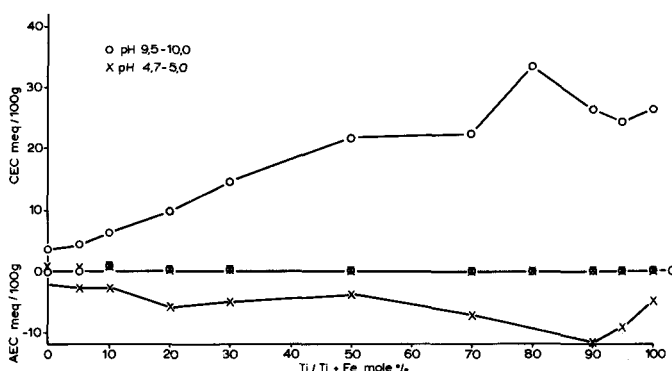


Fig. 5. Negative and positive charge variation with pH in relation to composition of titano-ferric oxides aged at 70°C and pH 5.5 for 70 days.

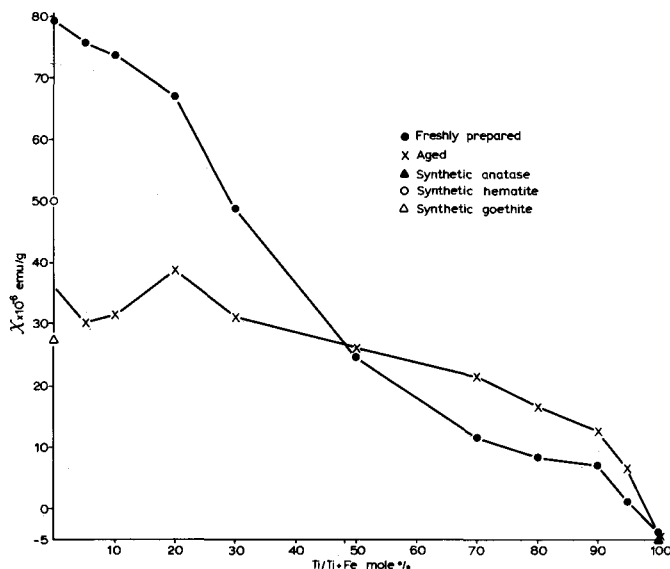


Fig. 6. Variation in specific magnetic susceptibility (χ) with the composition of freshly prepared (●) and aged (70°C at pH 5.5 for 70 days) (×) titano-ferric oxides.

formation of the anatase. Thus, in the high Fe systems which are mainly ferrihydrite, crystallization proceeds slowly, while in the systems rich in Ti, crystallization takes place at a faster rate to form anatase.

The effect of aging at pH 12 and 70°C for 70 days

The coprecipitates in the composition range $0 < \text{Ti}/\text{Ti} + \text{Fe} < 0.30$ aged at pH 12 and 70°C for 70 days, contained relatively high amounts of oxalate soluble Fe and Ti (i.e. amorphous Fe-Ti) while in the oxalate residues large goethite crystals were detected by XRD (WHH of the 111 line = $0.22^\circ 2\theta$) and electron microscopy. These observations are in general agreement with previous oxalate extraction data for oxides prepared from FeCl_3 and TiCl_4 and aged at pH 12 and 60°C for 30 days (Fitzpatrick and le Roux, 1976). Because of the increased aging time and temperature, employed in this study, the oxalate soluble values are slightly lower. The electron micrographs (Figure 7) show the large goethite crystals** coated or embedded in amorphous Fe-Ti oxide.

The effect of aging at pH 5.5 and 70°C for 70 days

The amounts of Fe and Ti removed by oxalate after aging the oxides at pH 5.5 and 70°C for 70 days were extremely low (Figure 8) and constituted less than 1% of the total Fe and Ti in the aged oxides (e.g. $\text{Fe}_0/\text{Fe}_t < 0.01$; $\text{Ti}_0/\text{Ti}_t < 0.002$). Furthermore, compared to the non-aged oxides there is a marked reduction in both

charges (Figures 4 and 5) and magnetic susceptibility (Figure 6). These observations which indicate a marked degree of crystallization for the whole composition range (e.g. $0 < \text{Ti}/\text{Ti} + \text{Fe} < 1$) are confirmed by the XRD results (Figures 1, 9 and 10). Furthermore, aging at 70°C and pH 5.5 resulted in a slight increase in acidity probably as a result of the further hydrolysis.

Composition range $0 < \text{Ti}/\text{Ti} + \text{Fe} \leq 0.20$. When the pure ferrihydrite was aged at 70°C and pH 5.5 for 70 days both goethite and hematite were detected by XRD (Figures 9a and 10) in agreement with previous work (Schellmann, 1959; Schwertmann, 1959). However, on increasing the Ti/Ti + Fe ratio to 0.05, crystalline goethite is favored, with a slightly lower X-ray line broadening while hematite is inhibited (Figures 9 and 10). In contrast goethite rather than hematite was suppressed in the Al-Fe coprecipitates in the composition range $0.05 < \text{Al}/\text{Al} + \text{Fe} < 0.30$ when aged for 70 days at pH 5.5 and 70°C (see also Schwertmann et al., 1977). A possible explanation for this is that the Al-ferrihydrite structure might be less distorted than the Ti-ferrihydrite structure. On increasing the Ti/Ti + Fe ratio in the composition range $0.10 < \text{Ti}/\text{Ti} + \text{Fe} < 0.20$ the goethite peaks become progressively weaker and broader until Ti finally inhibits goethite crystallization. Herbillon and Tran Vinh An (1969) found that SiO_2 inhibited the crystallization of "amorphous Fe_2O_3 " to hematite.

Only a very slight shift was observed in the *d*-spacing of the goethite (111) line with increasing Ti content, possibly because the ionic size of Fe (III) (0.64 Å) and Ti (IV) (0.68 Å) are very similar. However, coprecipitates of Fe and Zr (IV) (0.80 Å) in range $0.05 < \text{Zr}/\text{Zr}$

** Dr. W. J. McHardy (personal communication) has carried out microanalysis on these single goethite crystals, after removing amorphous Fe-Ti with HCl, and found that Ti is incorporated in the goethite structure.

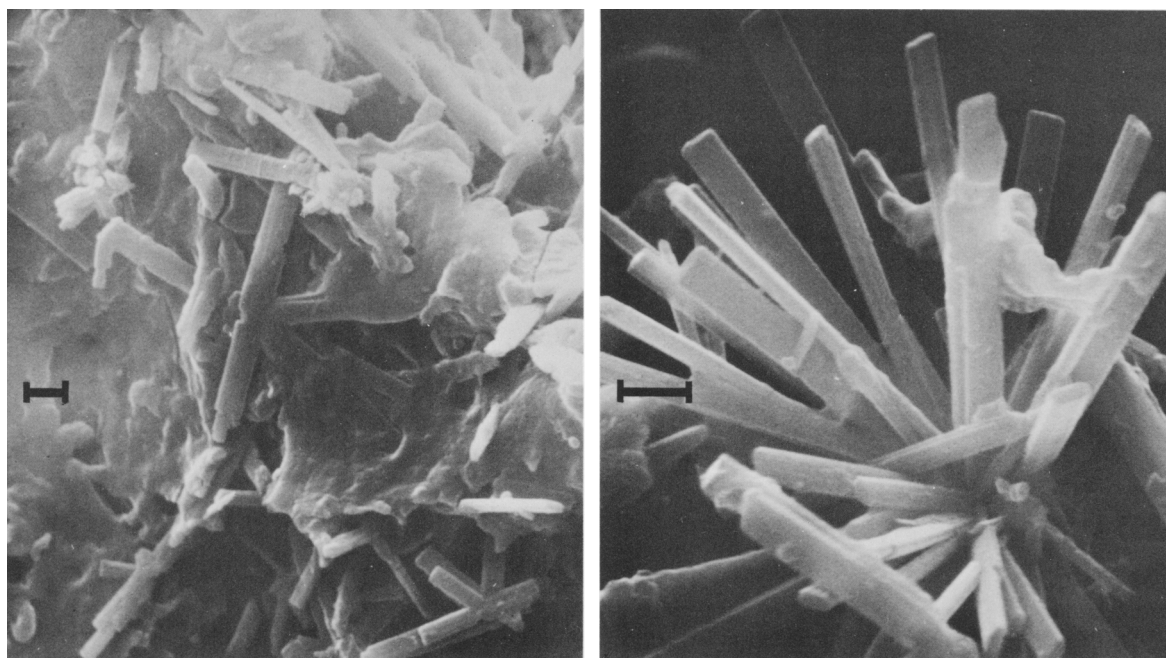


Fig. 7. Electron micrographs of goethite prepared from titano-ferric oxides with 20% in Ti/Ti + Fe pH 13 aged for 30 days (60°C) and dialyzed against distilled water. Line indicates 1 μm .

+ Fe < 0.10, aged for 70 days at pH 5.5 and 70°C once again gave suppressed hematite reflections but the enhanced (111) goethite reflection showed a slight shift towards lower angles, suggesting isomorphous replacement of Zr for Fe in the goethite structure. In addition, the line broadening of the (111) goethite line was larger for the aged Fe–Zr system than for the Fe–Ti system.

Composition range $0.20 < \text{Ti/Ti} + \text{Fe} \leq 0.70$. The complicated nature of the intermediate composition range (i.e. from $0.20 < \text{Ti/Ti} + \text{Fe} \leq 0.70$) with rather broad XRD peaks (Figure 9) which militates precise peak distinction and peak height measurement (hence the hatched area in Figure 9) has a pattern that resembles very closely natural Indonesian pseudorutile (Figure 9l). According to Grey†† and Reid (1975) pseudorutile has only a moderate degree of crystallinity and this is confirmed by the broad diffraction lines in Figure 9 and also by the relatively higher negative and positive charges (Figure 5) observed for this composition range. Furthermore, the magnetic susceptibility values (Figure 6) correspond closely to that for Malayan ilmenite which had undergone marked alteration to pseudorutile or ‘arizonite’ (i.e. $< 40 \times 10^{-6}$ c.g.s., Flintner, 1959).

The success in synthesizing pseudorutile in vitro by

aging a Fe–Ti coprecipitate for 70 days at pH 5.5 and 70°C probably is due to the role of the aqueous solution creating favorable conditions for the rearrangement of the Ti and Fe atoms which essentially is precluded for reactions at higher temperatures and pressures in the dry state (e.g. Buddington and Linsley, 1964) and is only partially successful under hydrothermal conditions (Karkhanavala, 1959; Karkhanavala and Momin, 1959). Under dry conditions and high temperatures (e.g. 1200°C) transformations are mainly topotactic. With increasing titanium content the *d*-spacing shows a shift to higher angles (Table 3) indicating that the unit cell does depend on the Ti/Ti + Fe ratio.

Composition range $0.70 \leq \text{Ti/Ti} + \text{Fe} < 1.0$. In the composition range $0.70 \leq \text{Ti/Ti} + \text{Fe} < 1$ anatase was

Table 3. Comparison between the three sharpest XRD lines for Pseudorutile in the synthetic Fe–Ti oxides of composition $0.20 < \text{Ti/Ti} + \text{Fe} < 0.70$, Indonesian Pseudorutile* and ASTM 19-635 Data reported for Pseudorutile.

Pseudorutile ASTM No. 19-635	Intensity I	Indonesian Pseudorutile* Ti/Ti + Fe = 0.69	Ti/Ti + Fe			
			0.20	0.30	0.50	0.70
\AA		\AA	\AA	\AA	\AA	\AA
1.69	10	1.69	1.71	1.70	1.69	1.69
2.49	6	2.49	2.54	2.52	2.51	2.50
2.19	5	2.19	2.23	2.21	2.20	2.19

* Sample supplied by Grey and Reid (1975).

††According to Grey (personal communication) this sample contains traces of rutile (Figure 9l); for comparative purposes the XRD of all the samples in Figure 9 were run at the same intensity settings).

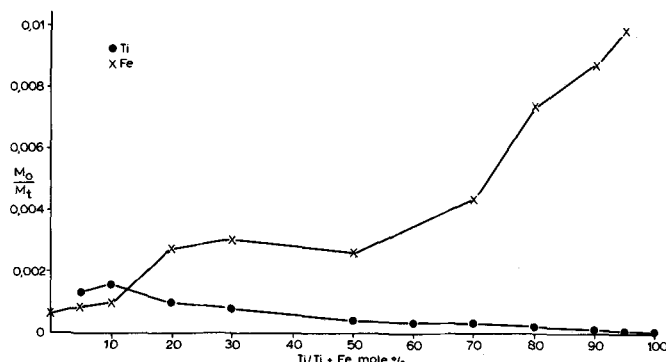


Fig. 8. Relationship between ammonium oxalate extractable Ti and Fe to total Ti and Fe (M_0/M_t) and the composition of titano-ferric oxides aged at 70°C and pH 5.5 for 70 days.

the only phase detected by XRD (Figures 9 and 10). The relatively low Ti_0/T_i ratio (<0.01 ; Figure 8) confirmed the crystallinity of the anatase, while the low Fe_0/Fe_t ratio suggests that the Fe is incorporated in the anatase structure since no other phase was detected. The WHH of the anatase (101) line increases until Fe (at approximately 30–50 mole% finally inhibits crystallization (Figures 9 and 10).

Evidence for possible Fe replacement for Ti in the anatase structure was also obtained by heating the freshly prepared coprecipitates at 250°C for 10 days which once again resulted in smaller anatase crystals with increasing iron content as shown by the general increase in line broadening (Figure 10). Thus, although anatase and ferriferous anatase show similar XRD lines they differ in WHH on heating in air or aging in vitro and this is related to crystallite size. Anatase formed by aging amorphous TiO_2 in vitro at 70°C and pH 5.5 for 70 days has less line broadening than anatase produced by dry heating at 250°C for 10 days (Figure 10). This suggests that the rearrangement of Ti atoms to form crystalline anatase and especially ferriferous anatase is apparently more effective in aqueous suspension than by dry heating even at high temperatures.

Coprecipitates of Zr and Ti and in the composition range $0.05 < Zr/Zr + Ti < 0.10$ aged at 70°C and pH 5.5 for 70 days resulted in anatase with very broad but symmetrical (101) peaks with WHH $4.5^\circ 2\theta$. Furthermore, a slight shift to smaller angles was observed, suggesting that Zr replaces (partly) Ti in the anatase structure. It has been suggested by Valetton (1972) that in bauxites Zr may replace Ti in the anatase structure.

CBD extracts very small amounts of the total Ti ($Fe_d = 0.90\%$) from the pure poorly crystalline anatase phase (e.g. $Ti/Ti + Fe = 1$ with a WHH of 4), whereas oxalate dissolves 30% of the total Ti (Figure 2). There is a fairly good relationship (Figure 2) between Ti_0 and the MCD of anatase (101) below 50 \AA WHH $> 2.0^\circ 2\theta$ regardless of composition. This relationship does not hold for CBD-soluble Ti when Fe is present in the sys-

tem. Thus, a fairly crystalline anatase with a WHH of $2.8^\circ 2\theta$ and a composition of $Ti/Ti + Fe \approx 0.80$ has a $Ti_0 = 4.0\%$ (Figure 2) and $Ti_d = 2.1\%$. The relatively higher amounts of CBD-soluble Ti from the ferriferous anatase phase (regardless of crystallinity) is probably due to preferential removal of Fe from the anatase structure by Fe reduction.

CONCLUSIONS

Titanium may occur in certain soils without being sufficiently crystalline to be detected by XRD techniques. An estimate of these poorly crystalline forms of TiO_2 can, however, be obtained by chemical extraction technique. Extraction of a series of synthetic Ti oxides with acid ammonium oxalate (2 hr in the dark) confirmed that oxalate selectively removes X-ray amorphous TiO_2 and partly dissolves microcrystalline anatase with MCD $< 50 \text{ \AA}$ or WHH $\geq 2.0^\circ 2\theta$. This

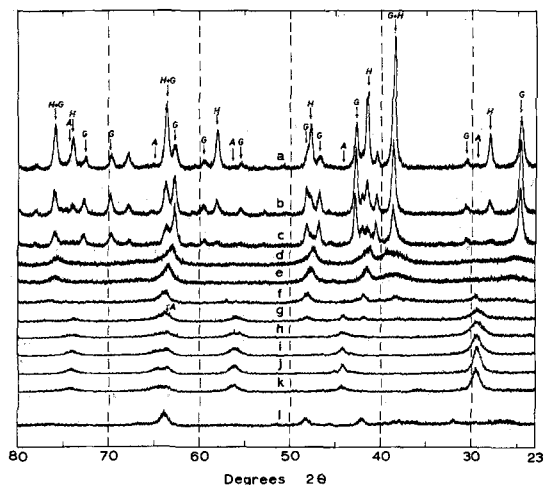


Fig. 9. X-ray powder diffraction patterns of synthetic Fe-Ti preparations aged at 70°C and pH 5.5 for 70 days with: (a) 0%; (b) 5%; (c) 10%; (d) 20%; (e) 30%; (f) 50%; (g) 70%; (h) 80%; (i) 90%; (j) 95%; (k) 100% in $Ti/Ti + Fe$, respectively, and (l) Indonesian pseudorutile where A is anatase; G is goethite; H is hematite.

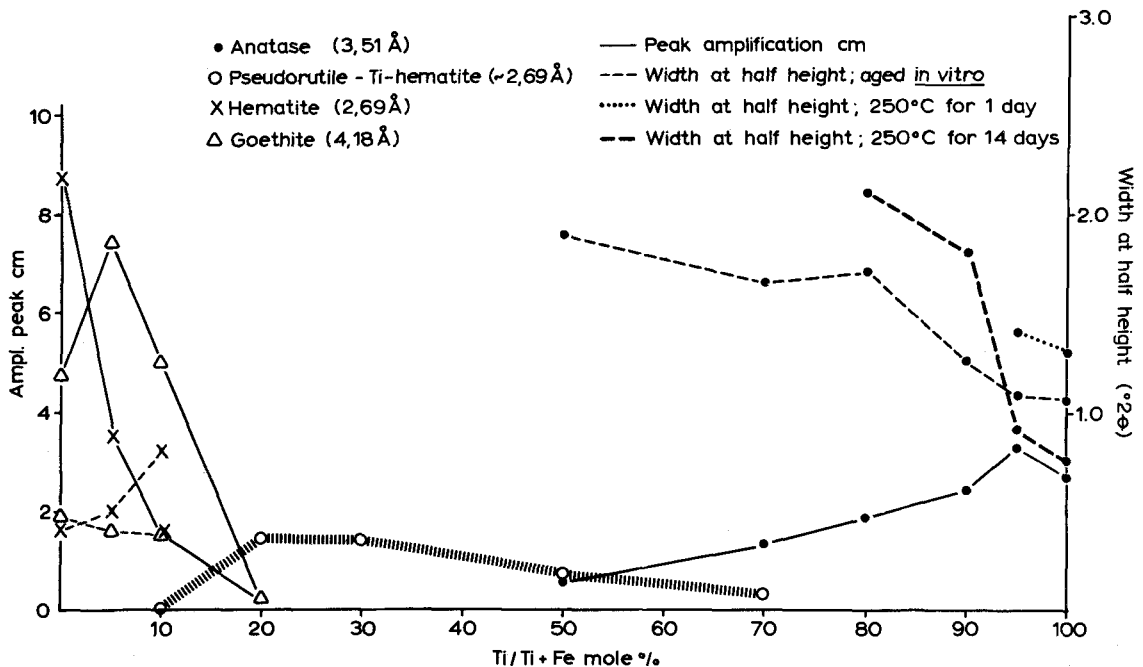


Fig. 10. X-ray diffraction data evaluation (cm relative intensity and width at half height) in relation to composition (Ti/Ti + Fe%) of the crystalline species present in the titano-ferrous system after aging *in vitro* for 70 days at 70°C (pH 5.5) and heating in air at 250°C for 1 day and 14 days.

method is superior to other commonly used reagents (e.g. HCl or H_2TiF_6) and enables one to characterize more fully the nature and amounts of secondary titanium oxides ranging from X-ray amorphous TiO_2 to poorly crystalline and crystalline anatase, and to relate these findings to soil development (e.g. in a soil-climate-toposequence).

The positive and negative charges of the freshly coprecipitated titanoferric oxides appear to be analogous to that proposed for synthetic amorphous aluminosilicates. Furthermore, it is suggested that the composition of the starting Fe-Ti oxide has a pronounced influence on the crystallization of the final product upon aging.

Coprecipitates of Fe and Ti aged at high pH (>10) and 70°C were found to be present primarily as an amorphous phase adsorbed on large goethite crystals (with minor Ti isomorphous substitution). Aging at lower pH (5.5) and 70°C for 70 days, Fe and Ti combined to form crystalline phases (e.g. goethite, hematite, pseudorutile and anatase) depending on the Ti/Ti + Fe ratio. The transformation of freshly prepared oxides to crystalline products was monitored by XRD and showed corresponding decreases in solubility in oxalate, negative and positive charges, and magnetic susceptibility.

Pseudorutile can be successfully synthesized under aqueous conditions at pH 5.5. This suggests that it may form not only from the weathering or decomposition of primary Ti-containing oxides (e.g. ilmenite) but also

from the more weatherable Ti-bearing silicates (e.g. sphene, hornblende or biotite) under earth surface conditions (e.g. in bauxites and Ti-rich beach sands). This would involve removal of Fe and Ti from the primary mineral followed by precipitation and crystallization of Fe-Ti oxides rather than by topotactic oxidation of primary Ti-oxides. Thus, Fe-Ti coprecipitates ranging in composition from $0 < Ti/Ti + Fe < 1$ may be present in the immediate "microweathering zone" (e.g. cracks) of an ilmenite or sphene crystal. The composition of the weathering solution (Ti/Ti + Fe ratio) and hence the crystallization product will be dependent largely on the rate of removal of iron from the primary mineral which is controlled by the prevailing Eh-pH conditions. Under reducing conditions iron is rendered mobile in the ferrous state and is relatively more mobile than titanium. A certain amount of iron is required to form pseudorutile via solution and when the iron is removed by weathering, the titanium atoms rearrange to an anatase structure which may contain small amounts of Fe (<5%).

In the light of these results, an appreciation of synthetic Fe-Ti oxide mixtures, precipitated and aged under conditions comparable to natural environments, is critical in studies on the genesis of weathering processes and soil formation. The application of synthetic studies of this kind to studies of secondary Fe-Ti weathering products is suggested.

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Резюме- Группа смешанных осадков окислов железа и титана, изменяющихся по составу в пределах $0 < \text{Ti}/\text{Ti}+\text{Fe} < 1$, была синтезирована и выдержана во времени при различных значениях pH, температуры и времени, чтобы установить рабочую модель для почвообразующих осадков титанистых и титано-железистых окислов. Порошковый метод дифракции рентгеновских лучей (ДРЛ), селективное химическое растворение, магнитная восприимчивость, распределение зарядов и электронные оптические данные указывают на то, что свежеприготовленные окислы Fe-Ti состоят из обогащенной Fe (Ti-гидрат окиси железа) фазы ($\text{Ti}/\text{Ti}+\text{Fe} \leq 0,70$) имеющей положительный заряд, зависящий от pH, и обогащенной Ti фазы ($\text{Ti}/\text{Ti}+\text{Fe} \geq 0,7$) с постоянным и зависимым от pH отрицательным зарядом.

Синтетический Ti-гидрат окиси железа и аморфный TiO_2 были полностью растворимы в оксалате аммония (2 часа экстракции в темноте), в то время как слабо кристаллический анатаз (отношение ширины к половине высоты, $\text{ШПВ} > 2,0$) был частично растворим в оксалате. Содержание растворимого в NH_4 -оксалате Ti было особенно велико в почвах, образовавшихся в условиях прохладного горного климата (афро-альпийского) и меньше в почвах, образовавшихся в условиях более теплого субтропического климата, которые содержат анатаз и рутил.

Несколько смешанных Fe-Ti кристаллических фаз были определены после выдерживания во времени NH_3 осадков Fe и нитрата Ti при 70°C и pH 5.5 в течение 70 дней:

1) гетит и гематит при составе в пределах $0 < \text{Ti}/\text{Ti}+\text{Fe} \leq 0,20$; при низких концентрациях Ti (<5 молей %) гетит преобладал над гематитом;

2) микрокристаллический псевдорутит при составе в пределах $0,20 \leq \text{Ti}/\text{Ti}+\text{Fe} \leq 0,70$;

3) анатаз и железистый анатаз с пределами $0,70 \leq \text{Ti}/\text{Ti}+\text{Fe} < 1,0$; с уменьшающейся пропорцией Ti с уменьшением кристалличности анатаза.

Результаты показывают, что вторичные или почвообразующие окислы Ti-Fe могут образовываться при совместном осаждении и кристаллизации в эрозионных растворах и что вода играет существенную роль (что противопоставляется сухому окислению) в изменении первичных титано-железистых минералов.

Kurzreferat- Eine Serie von zusammen ausfallenden Eisen und Titanoxyden mit Zusammensetzungen zwischen $0 < \text{Ti}/\text{Ti}+\text{Fe} < 1$, wurde synthetisiert und bei unterschiedlicher Temperatur, Zeitlänge und pH Werten gealtert, um ein brauchbares Modell für pedogenische Titan und Titan-Eisenoxyde herzustellen. Röntgenpulverdiagramme, selektive, chemische Auflösung, magnetische Suszeptibilität, Ladungsverteilung und Elektronen-optische Daten schlagen vor, daß die frisch synthetisierten Fe-Ti oxyde aus einer Fe-reichen (Ti-ferrihydrat) Phase ($\text{Ti}/\text{Ti}+\text{Fe} \leq 0,70$) mit einer pH-abhängigen, positiven Ladung und aus einer Ti-reichen Phase ($\text{Ti}/\text{Ti}+\text{Fe} > 0,7$) mit permanenter und pH-abhängiger, negativer Ladung bestehen.

Synthetisches Ti-Ferrihydrat und amorphes Titandioxyd waren völlig löslich in saurem Ammoniumoxalat (2 Stunden Extraktion im Dunkeln), wohingegen schlecht-krystallisiertes Titandioxyd (Breite bei Halbhöhe $> 2,0$) nur teilweise in Oxalat löslich war. In Ammoniumoxalat lösliches Ti war besonders konzentriert in Böden, die sich in kühlem Klima entwickelt hatten (Afro-Alpine), aber weniger konzentriert in Böden in warmem, subtropischem Klima, die Anatas und Rutil enthalten.

Etliche gemischt Fe-Ti, krystalline Stadien wurden nach dem Altern von mit Ammonia ausgefallenen Fe- und Ti-Nitraten identifiziert: (Das Altern fand bei 70°C und pH 5,5 für 70 Tage statt)

(1) Goethit und Hematit mit Zusammensetzungen $0 < \text{Ti}/\text{Ti}+\text{Fe} < 0,20$; bei niedrigen Ti Konzentrationen (<5 Mol%), wurde Goethit begünstigt und/oder Hematit formation verhindert.

(2) Mikrokrystallines Pseudorutil in der Reichweite $0,20 < \text{Ti}/\text{Ti}+\text{Fe} < 0,70$.

(3) Anatas und Eisen(III) haltiges Anatas mit der Zusammensetzung $0,70 < \text{Ti}/\text{Ti}+\text{Fe} < 1,0$; mit abnehmendem Ti Anteil nimmt die Kristallinität des Anatas ab. Die Resultate schlagen vor, daß sekundäre oder pedogenische Ti-Fe oxyde durch Mitausfallen und Kristallisation in Verwitterungs-Lösungen entstehen können, und betonen die wesentliche Rolle des Wassers (im Gegensatz zu trockener Oxydierung) in der Veränderung von primären, titanhaltigen Mineralien.

Résumé—Une série de coprécipités d'oxides d'un mélange de fer et de titanium s'étageant en composition de $0 < \text{Ti}/\text{Ti}+\text{Fe} < 1$ a été synthétisée et vieillie sous des conditions variées de pH, de température et de temps afin d'établir un modèle de travail pour le titanium pédogénique et les acides titano-ferriques. La diffraction aux rayons-X (X.R.D.), la dissolution chimique sélective, la susceptibilité magnétique, la distribution de charge et les données optiques d'électron indiquent que les oxides de Fe-Ti fraîchement préparés consistent d'une phase riche en Fe (Ti-ferrihydrate) ($\text{Ti}/\text{Ti}+\text{Fe} \leq 0.70$) ayant une charge positive dépendante du pH et une phase riche en Ti ($\text{Ti}/\text{Ti}+\text{Fe} \geq 0.7$) avec une charge négative permanente et dépendante du pH.

La Ti-ferrihydrate synthétique et le TiO_2 amorphe étaient complètement solubles dans l'ammonium oxalate acide (extraction de deux heures dans le noir), tandis que l'anastase pauvrement cristallisé (largeur à demi-hauteur, $\text{WHH} > 2.0^\circ 2\theta$) était partiellement soluble à l'oxalate. Le Ti soluble dans le NH_4 -oxalate était particulièrement élevé dans les sols développés sous un climat frais montagnard (afra-alpin) et plus bas dans les sols d'un climat subtropical plus chaud, contenant anastase et rutile.

Plusieurs phases cristallines de Fe-Ti mélangées ont été identifiées après le vieillissement de coprécipités NH_3 de nitrate de Fe et de Ti à 70°C et à un pH de 5.5 pendant 70 jours: (1) de la goethite et de l'hématite dont la composition s'étageait de $0 < \text{Ti}/\text{Ti}+\text{Fe} \leq 0.20$; à basses concentrations (<5 mole %) de Ti, la goethite était favorisée et/ou l'hématite inhibée; (2) de la pseudorutile microcristalline dont la composition s'étageait de $0.2 \leq \text{Ti}/\text{Ti}+\text{Fe} \leq 0.7$; (3) de l'anastase et de l'anastase ferri-fereux dont la composition s'étageait de $0.7 \leq \text{Ti}/\text{Ti}+\text{Fe} \leq 1$; la cristallinité de l'anastase décroissait proportionnellement à la proportion décroissante de Ti.

Les résultats suggèrent que des oxides Ti-Fe secondaires ou pédogéniques peuvent être formés par coprécipitation et cristallisation dans la solution s'altérant et soulignent le rôle essentiel de l'eau (par opposition à l'oxidation sèche) dans l'altération de minéraux titanifereux.