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Evidence of titanium mobility in soil profiles, Manaus, central Amazonia

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Abstract

Titanium minerals are classically considered to be very resistant to weathering in soils. Consequently, variations of titanium concentrations within the soils were used to estimate rates of weathering of parent material. Mobility of Ti was studied in an Amazonian ferralsol using a large set of techniques. Chemical and mineralogical studies of Ti distribution in the soil profile showed that weathering of Ti minerals follows the mineral sequence: ilmenite, pseudorutile, rutile and anatase. This weathering leads to absolute Ti losses on the profile scale. Mineral bags were located at different depths within the top soil, and removed after 6, 12, 18 months in the soil. In all bags the presence of newly generated anatase was recorded after the exposure periods, showing the rapidity of the processes. The vegetation recycles a significant quantity of Ti, increasing Ti

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mobility in soils. These results indicate that Ti can be mobile under certain conditions and thus should not always be used to estimate weathering rates. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Titanium (Ti) occurs in most of soils and rocks as octahedrally coordinated in oxides (Raman and Jackson, 1965; Saying and Jackson, 1975) or as tetrahedrally coordinated in the structure of silicate minerals (Mankin and Dodd, 1963; Weiss and Range, 1966). It can also occur as inclusions of TiO_2 oxides in numerous minerals (Deer et al., 1962). The most common forms of Ti in soils are residual rutile, inherited from weathering of bed-rock, or neoformed anatase (Weaver, 1976). Titanium content in soils ranges from 0.1% to 0.9% with a mean value of 0.35% (Pendias and Pendias, 1984). However, higher Ti contents occur in tropical soils, particularly in lateritic soils and laterites, e.g., 15% in Hawaii soils (Sherman, 1952); 15% in Norfolk Island soils (Hutton and Stephen, 1956), 3.4% in Australian soils (Stace et al., 1968). The Brazilian soil studied here contains 2.3% Ti. Intense and long term weathering is regarded as the main factor for the high Ti content in tropical soils (Sherman, 1952; Swaine and Mitchell, 1960).

The weathering rate of Ti minerals relative to many primary and secondary minerals is extremely slow (Weyl, 1952; Le Riche and Weir, 1963; Le Riche, 1968). Atmospheric input of Ti is very small. Ti is thus commonly considered to be directly derived from parent material, ilmenite or rutile being the most common primary Ti minerals (Anand and Gilkes, 1984; Kaup and Carter, 1987). Ti released by weathering precipitates as anatase (Berrow et al., 1978). Titanium, as zirconium, is therefore used as a chemically conservative element of soils for mass-balance weathering rate studies (Sudom and St. Arnaud, 1971; Hutton, 1977).

Some studies, however, indicated that Ti is mobile within soils. Ti oxides in soils are more weathered than zircon (McLaughlin, 1954; Barshad, 1964) and Ti mobility was shown in certain environments (Walker et al., 1969). Hutton et al. (1972) found 15% of Ti in silcrete and concluded that this was due to the cementation of quartz by anatase transported over a long time scale. Considering an uptake of 50 mg kg^{-1} Ti (dry matter) by wheat plants, Hutton and Norrish (1974) deduced a Ti concentration of 0.03 mg l^{-1} in soil solution. This concentration is close to the one reported by Livingston (1963) for the major river waters of the world (0.02 mg l^{-1}).

The aim of this study was to determine the mobility of Ti in a tropical environment by combining results from mineralogical studies, in situ test mineral experiments, and chemical analysis of rainforest litter.

2. Materials and methods

2.1. Study area

The study was carried out in a rainforest, located near Manaus (central Amazonia, Brazil). Vegetation cover consists of typical rainforest (Guillaumet, 1987). Climate is characterised by an annual precipitation mean of 2100 mm, and annual temperature mean of 26°C (Nimer, 1989). The area is composed of low plateaux dissected by valleys. Soils on the plateaux are xanthic ferralsols (FAO, 1975), developed on Alter do Chão sedimentary bed rock. The main constituents of this parent material are kaolinite and quartz (Bezerra, 1989). The soils consist of a 17 m thick weathered mantle composed of two main groups of horizons (Lucas, 1989). The upper one is about 7 m thick and mainly consists of kaolinitic clay material. It overlies nodular horizons, richer in gibbsite and Fe oxides with less kaolinite (Table 1). The quartz content in the profile increases progressively with depth.

2.2. Mineralogical study

Samples were observed by optical microscopy on thin sections, by scanning electron microscopy (SEM) and by transmission electron microscopy (TEM). Chemical determinations were also made on these thin sections by microprobe (EDAX Energy Dispersive X-ray Spectrometry, EDS) to determine the distribution of Ti on a centimetric scale. Subsamples were ground for X-ray diffraction analysis (XRD) (Philips PW 1710).

Table 1
TiO₂ and Fe₂O₃ content in the < 2-mm fraction along the profile

Horizons	Depth (m)	Bulk density ^a (g cm ⁻³)	Fe ₂ O ₃ (%)	TiO ₂ (%)	
				In the < 50-μm fraction	In the > 50-μm heavy minerals
Clayey	2	1.25	3.0	2.51	0.04
horizon (0–7 m)	4	1.33	2.5	2.30	0.07
Nodular	7	1.42	2.1	2.09	0.13
horizon (7–17 m)	9	1.44	2.5	1.80	0.16
	12	1.44	1.3	1.23	0.13
	13	1.44	0.7	0.68	0.16
Parent material	20	1.60	0.7	0.55	0.21

^aData are from the work of Lucas (1989).

The > 50- and < 50- μm fractions were separated by sedimentation. From the coarse fraction, heavy minerals were separated by a flotation on bromoform ($d > 2.89 \text{ g cm}^{-3}$). Different electromagnetic fractions were sorted using a Franz apparatus with several separation thresholds (from 0.1 to 1.5 A). As TiO_2 and magnetic Fe oxides are always associated in this type of soils, this method was used in order to separate the Ti–Fe heavy minerals from zircon. The efficiency of the separation was checked by optical identification of minerals in each fraction after sorting. Ti and Fe content of some of the magnetic fractions were determined by atomic absorption analysis after fusion in strontium metaborate.

Some samples of the < 50- μm fraction were boiled in 5 N NaOH to remove kaolinite (Norrish and Taylor, 1961; Schwertmann et al., 1995) and treated by dithionite–citrate to remove iron oxides (Mehra and Jackson, 1960). The Ti minerals were then observed in the residue by TEM. The profile distribution of Ti was determined by chemical analysis of the fine fractions by digesting in a mixture of acids consisting of HNO_3 , HCl and HF and analysing Ti by atomic absorption spectrophotometry.

2.3. Bag experiment

To study mineral reactivity in soils, Durapore filter bags containing test minerals (Ranger et al., 1986) were placed by Cornu et al. (1995) into the topsoil horizons under the litter, at 5, 10 and 20 cm depth, where the biological activity is greatest. Each bag was made by a folded and hot-welded round filter (ϕ 9.5 cm), and contained 1 g of white, well crystalline kaolinite, either from the Alter do Chão sediment or from Georgia. The Durapore material is hydrophilic, non-biodegradable and has a pore size of 0.22 μm . The bags were retrieved after 0.5, 1 and 1.5 years and examined using XRD and TEM coupled with microanalysis by EDS. Titanium concentrations in the samples were measured by ICP–AES after dissolution in lithium metaborate at 1000°C.

2.4. Plant recycling

The fine litter was collected in conical traps emptied weekly or bimonthly throughout a period of two years. The samples were carefully sorted into leaves, reproductive parts (flowers, fruits and seeds), fine woody material and residue (unidentified material). To avoid any contamination, samples were carefully washed, and animal material, adhering mineral material and residue were discarded. The samples were then dried, weighed, finely ground, and stored (Luizão, 1989). Ti concentrations were measured from a bulk sample for the entire 2-year litterfall. Samples were calcinated at 500°C and dissolved by strontium metaborate melting, then analysed by plasma emission spectrometry.

Table 2
Some characteristics of the Fe–Ti heavy minerals in the > 50- μ m fraction

Horizons	Depth (m)	Wt.% of bulk soil	Fe ₂ O ₃	TiO ₂	Fe/Ti
			Percent of the fraction		
Clayey horizon (0–7 m)	2	0.05	13	87	0.089
Nodular horizons (7–17 m)	9	0.19	17	83	0.12
	12	0.17	25	75	0.19
	13	0.21	26	74	0.20
Parent material	20	0.32	34	66	0.30

Details and results for other elements (Si, Al, Fe, Mn, Mg, Ca and P) are given in the works of Luizão (1989), Lucas et al. (1993) and Cornu (1995).

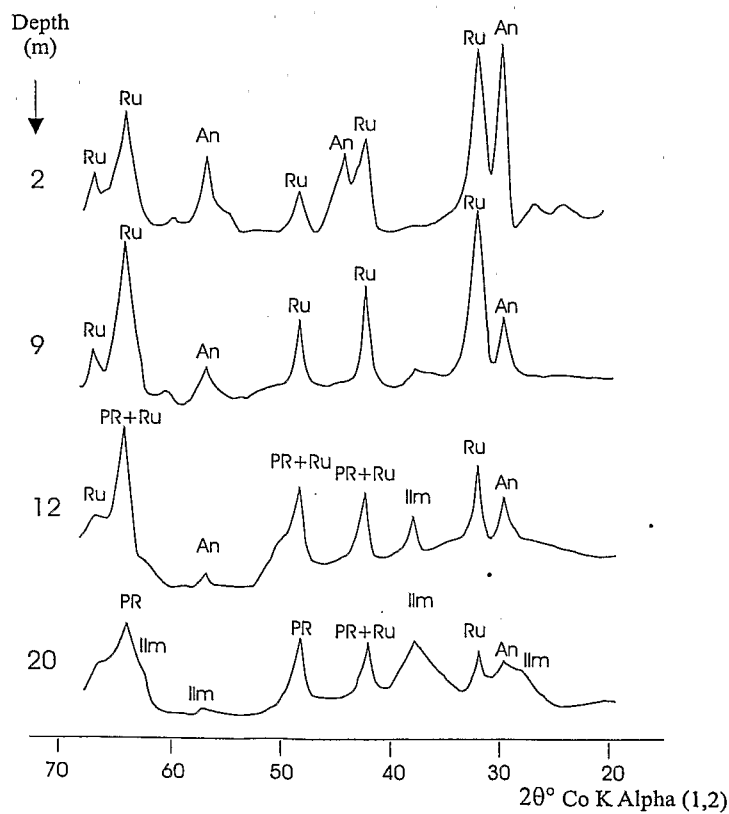


Fig. 1. XRD diffraction patterns of the Ti–Fe heavy minerals in the > 50- μ m fraction.

3. Results

3.1. Ti in the profile (Tables 1 and 2)

In the parent material, most of the Ti (about 70%) is in the fine fraction, as anatase and rutile. TEM observations after dissolution of kaolinite and Fe oxides showed that most anatase forms small pellets (size $< 0.1 \mu\text{m}$), while rutile forms bigger sticks (length up to $1 \mu\text{m}$). About 30% of the Ti is contained in the $> 50\text{-}\mu\text{m}$ heavy minerals (see Table 2). More than 80% of these minerals are zircon. All the rest is composed by opaque, brown or red coloured, layered minerals consisting of rutile, pseudorutile mainly, and small amounts of ilmenite and anatase (Fig. 1). Microscopic observations showed that surfaces of primary Ti–Fe minerals are corroded by weathering (Fig. 2). Semi-quantitative EDS spectra indicate that the weathered areas are depleted in Fe and enriched in Si

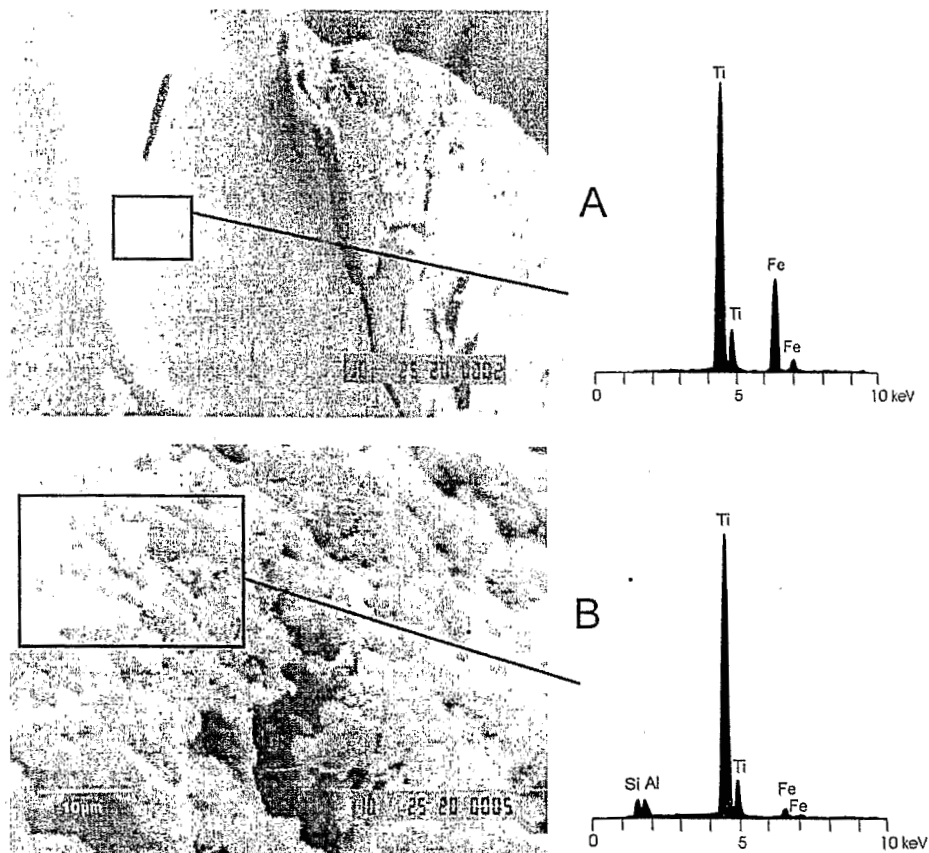


Fig. 2. SEM photograph of Fe–Ti heavy minerals. EDS spectra give the semi-quantitative composition of the indicated area. (A) Poorly weathered grain, (B) weathered grain.

Table 3

Comparison between clay material in quartz dissolution cavities and clay material of the matrix. Spot microprobe analysis on this section. Depth of the sample is 12 m

	Clay material in quartz dissolution cavities ($n = 6$)		Clay material of the surrounding matrix ($n = 10$)	
	Fe ₂ O ₃ (%)	TiO ₂ (%)	Fe ₂ O ₃ (%)	TiO ₂ (%)
Average	1.2	0.7	1.3	1.1
Standard deviation	0.2	0.3	0.3	0.4

and Al. Thus, Ti minerals in the sedimentary parent material are already weathered.

From the base to the top of the profile, the Ti content of the < 50- μ m fraction progressively increase, while the ilmenite and pseudorutile in the > 50- μ m fraction decrease. Corrosion features of Ti–Fe heavy minerals increased, while their main constituents changed from pseudorutile, rutile and a small amount of ilmenite and anatase, to rutile and anatase (Fig. 1). The Ti/Fe ratio of the bulk magnetic fraction is 0.3 in the parent material, and 0.09 in the clayey horizon at 2 m depth. The corrosion cavities of quartz grains in the nodular horizon are filled up with kaolinitic material which presents frequently large-sized booklets and no cutans. Some of these cavities are half-closed, and quartz relics eventually observed in the cavities exhibit the same extinction angle as the corresponding quartz grain (under polarised light). These features mean no physical displacement, thus the kaolinitic material within the quartz

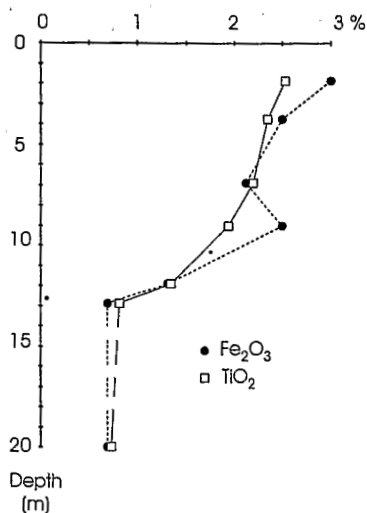


Fig. 3. Fe₂O₃ vs. TiO₂ content in the kaolinitic material.

was likely precipitated in situ. In addition, the Ti content in the quartz cavities was lower than the one of the surrounding matrix (0.7 and 1.1%, respectively, Table 3). At last, in the clayey material, Ti behaviour is close to Fe behaviour along the profile (Fig. 3).

3.2. Bag experiment

In bags, the minerals acquired a yellow-brownish colour becoming darker with residence time within soil. XRD showed no significant mineralogical modifications of the bag kaolinite after 6 months or 1 year. However, TEM observations showed the presence of opaque crystals ranging from 0.1 to 0.4

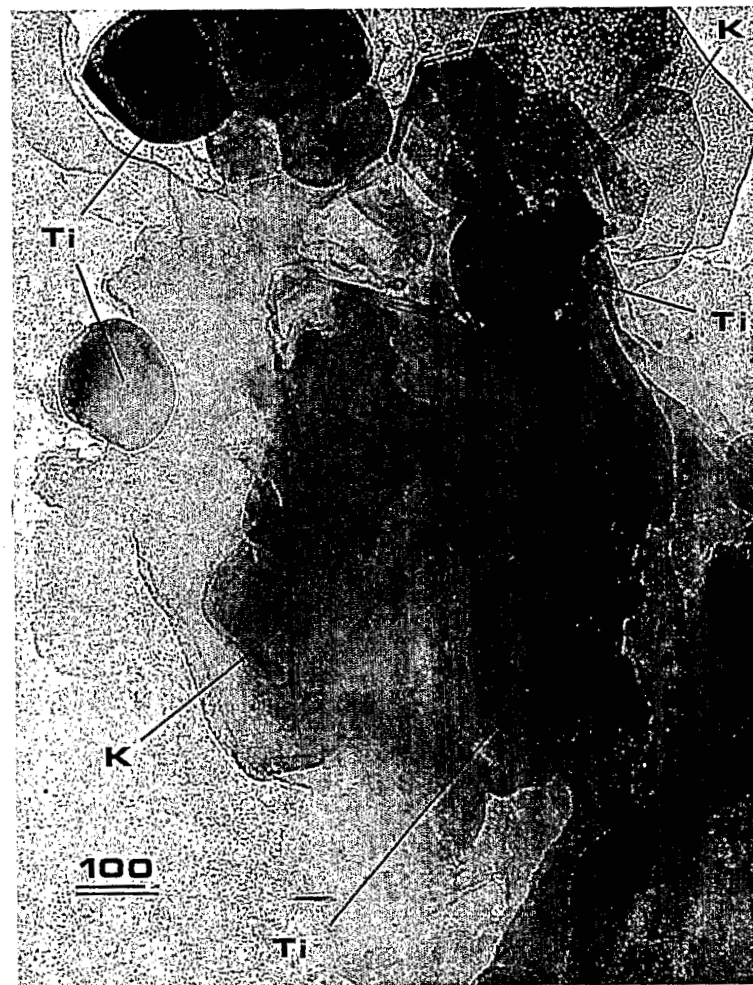


Fig. 4. TEM photograph of the material from a 6-month bag (200 keV). Ti: rounded anatase crystals, K: kaolinite crystals. The length of the bar is 100 nm.

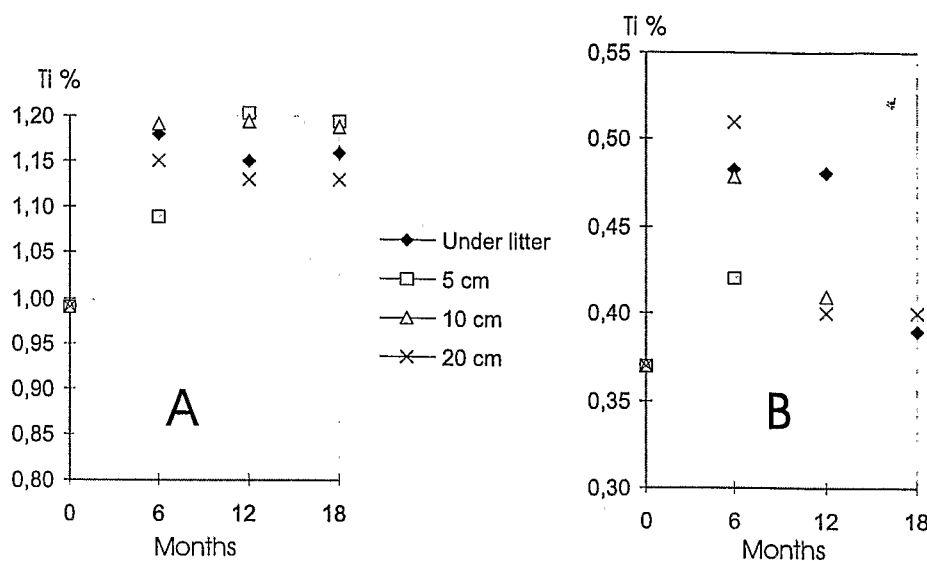


Fig. 5. Ti content (%) in the kaolinite bags after exposure. (A) Kaolinite from Georgia, (B) kaolinite from Alter-do-Chão.

μm in diameter (Fig. 4). Microanalysis and electron diffraction confirmed these crystals to be anatase. Such features were not observed in the Alter do Chão kaolin. Some kaolinite crystals had undergone modifications such as irregular forms, blunted angles, cracked sides, and silica gel was formed (Cornu et al., 1995). The Ti-concentrations increased in the bag material for all samples (Fig. 5). In the kaolinite from Georgia, the Ti content increased 14 to 21% of the initial content. In the kaolinite from Alter do Chão, the Ti content increased 14

Table 4
Necromass production, Ti concentration and Ti fluxes

Organic part	Necromass production ($\text{t ha}^{-1} \text{y}^{-1}$)	Ti concentration (%)	Total amount of Ti in necromass ($\text{kg ha}^{-1} \text{y}^{-1}$)
Fine litter	8.0 ^a	0.0013	0.11
Coarse litter	10.2 ^b	0.002 ^d	0.2
Root turnover	24.6 ^c	not determined	0.25 ^e
Total necromass	42.8		0.56

^aData are from the work of Luizão (1989).

^bEstimation using the data of Cannell (1982), Lucas et al. (1993) and Phillips and Gentry (1994).

^cEstimation using the data of Luizão (1992).

^dFine wood concentration.

^eFlux calculated using the Ti concentration in the fine litter.

to 38% in the 6 months samples, 8, 11 and 30% in the three undamaged 1-year samples, and 5% and 8% in the two undamaged 1.5-year samples. Small elongated Fe oxide crystals (length $< 0.1 \mu\text{m}$) grouped into aggregates (size $< 0.3 \mu\text{m}$) were observed in bags after exposure.

3.3. *Ti cycling by plants*

The quantities of Ti recycled by plants are reported in Table 3. The necromass production consists of fine and coarse litter, and root turnover (see Table 4). Coarse litter and root turnover were estimated from values taken from the literature (Cannell, 1982; Luizão et al., 1992; Lucas et al., 1993; Phillips and Gentry, 1994). Ti recycling by roots was calculated using Ti concentration in the fine litterfall. The fine litter recycles $0.11 \text{ kg ha}^{-1} \text{ y}^{-1}$ of Ti, and the whole quantity of Ti recycled by plants is $0.56 \text{ kg ha}^{-1} \text{ y}^{-1}$.

4. Discussion

4.1. *Ti mobility within the profile*

Corrosion features of the Ti–Fe heavy minerals and Ti patterns along the profile suggest the following weathering sequence of Ti minerals: ilmenite, pseudorutile, rutile, anatase. Ilmenite weathering occurs in natural environments mainly due to iron oxidation, producing pseudorutile (Grey and Reid, 1975). The pseudorutile weathering would in turn lead to rutile (as observed in marine environments by Grey and Reid (1975)) or to anatase formation (e.g., in lateritic environments; Anand and Gilkes, 1984). In our study, pseudorutile and rutile are transitional minerals in the Ti mineral weathering sequence.

Petrographic features indicate that the kaolinite in the corrosion cavities of quartz grains was precipitated in place. The associated Ti was thus also precipitated in place, indicating mobility at small scale (millimeters). Chemical mass balance studies on the whole profiles (Lucas, 1989, 1997) showed that 4 to 8 m^3 of parent material must be weathered to obtain 1 m^3 of the present soil profile. As Ti in the soil is inherited from the parent material, its concentration in the soil should be four- to eight-fold higher than in the bedrock. Calculation from data in Table 1 indicates that the average TiO_2 concentration of the present 15 m deep profile (25 kg m^{-3}) is only about two-fold higher than the bedrock concentration recorded at the profile base (12.8 kg m^{-3}). Thus Ti was likely lost from the profile during weathering, indicating Ti mobility at the profile scale.

4.2. *Anatase formation in bags*

Ti oxides always occur in kaolinite deposits (Dolcater et al., 1970; Weaver and Pollard, 1973; Jepson and Rowse, 1975; Weaver, 1976). Both kaolinites contained Ti before inserting in bags. Ti minerals were, however, not detected

by TEM observations. The Ti contents increased in the bags for both kaolinites after exposure. This could be due to a relative or an absolute Ti enrichment, or both.

Loss in kaolinite is suggested by the weathering features of kaolinite crystals in the bags (Cornu et al., 1995). The Ti released might then precipitate in situ as anatase. The Ti increase after exposure is, however, relatively high: it ranges from 5% to 38% (average 19% and 18% for Alter do Chão and Georgia, respectively). These values are high with regard to the scarcity of kaolinite weathering features. Thus an absolute Ti enrichment is more likely. This implies a Ti mobility at the bag scale (centimeters). The decrease of Ti content in kaolinite from Alter do Chão after 12 and 18 months of exposure also implies Ti mobility at the bag scale. The yellow-brownish colour of the kaolinite after prolonged exposure may be mainly due to Fe oxides formation (Fitzpatrick et al., 1978) or dissolved organic carbon. Anatase may also contribute to this colour (Saying and Jackson, 1975).

The crystal size ($\cong 0.1$ to $0.4 \mu\text{m}$) of anatase in the bags was larger than the size observed by Weaver (1976) which ranges from 0.05 to $0.1 \mu\text{m}$. The pore size of the filter bags was $0.2 \mu\text{m}$, therefore, Ti had to enter the bags as a dissolved form and crystallised afterwards as anatase. These results agree with those of previous studies (Fujimoto et al., 1948; Walker, 1964; Walker et al., 1969; Weaver, 1976). In the top soil, Ti was mainly as anatase. Thus, the origin of the Ti encountered in the bags was probably due to anatase dissolution. Anatase would dissolve and precipitate in the same horizon, either at different microsites, or due to changes in the soil solution chemistry (pH or complexing agent). A such behaviour was frequently observed for other pedogenic minerals as kaolinite or iron oxides (Lucas et al., 1996; Nahon, 1991).

4.3. *Ti recycling by plants*

Several authors found high Ti concentrations in plants (Mitchell, 1954; Cannon et al., 1964; Connor and Shacklette, 1975; Correns, 1978). Lucas et al. (1993) and Rose et al. (1993) showed that the forest cycles numerous chemical elements, particularly Si and Al, which control the mineral–solution equilibria. In our study, the quantity of Ti returned to the soil by the vegetation is about $0.56 \text{ kg ha}^{-1} \text{ y}^{-1}$, which is equivalent to $0.93 \text{ kg ha}^{-1} \text{ y}^{-1}$ of TiO_2 . In the upper 20 cm of the profile, TiO_2 content in the $< 50\text{-}\mu\text{m}$ fraction is 2.5% in mass, corresponding to 62.5 t ha^{-1} of TiO_2 . This quantity may be cycled by the vegetation in about 6.7×10^4 years. This time period is short compared to the time needed for soil formation in most of tropical environments. In the studied areas, the soil formation time was estimated at 3×10^5 to 3×10^6 years (Lucas et al., 1996; Mathieu et al., 1995). Ti is thus mobile over pedological times.

However, the whole of the Ti in the upper soil has certainly not been completely cycled 40–400 times during pedogenesis. Ti contained in the

vegetation is likely more easily mobilised than Ti contained in large heavy mineral particles or Ti closely associated to clay. Anatase and rutile can be dissolved by organic acids such as oxalic acid (Fitzpatrick et al., 1978) and acetic acid in podzol (Swaine and Mitchell, 1960). At low pH, humates retain Ti in solution (Joffe and Pugh, 1934). Soil microorganisms also participate in Ti mineral weathering (Grey and Reid, 1975). Ti mobility is thus likely linked to the complexing capacity of the organic compounds found in the soil solution. The studied soil is quite acidic (pH 4.5, Cornu, 1995) and the soil solution in the upper horizons is rich in organic compounds. These compounds have a significant complexing capacity with regard to metals (Eyrolle et al., 1996; Lucas et al., 1996). These acidic, complexing conditions may lead to the dissolution of anatase in the upper horizons. The organic compounds, however, easily adsorb on the clays or iron oxides surfaces of the soil. In the deeper, clayey horizons, the mobility of Ti as organo-metallic complexes is thus likely small. A SEM study of zircon morphology of this soil showed an evidence of greater weathering of zircon grains in the topsoil where organic acids are most concentrated (Bonnay, 1995). Therefore, even zircon is dissolving and Zr may be mobile in acid environments (Soubiès et al., 1991; Bonnay, 1995).

5. Conclusion

Under strong tropical weathering conditions, Ti may be mobile at centimetric scale as well as profile scale. It moves as a dissolved element or as organo-metallic compounds. The Ti released by weathering of the primary minerals precipitates as anatase. Anatase dissolution and precipitation may occur in the same horizon, depending on the microenvironmental conditions, or on the variation throughout time of the complexing capacity of the soil solution. Vegetation, by recycling Ti, has a significant effect on Ti mobility in the upper part of the profile, and the rate of this process is rapid with regard to pedological time. In assessing weathering rates from mass balance models, the use of Ti as a reference can be sometimes doubtful, at least in tropical environments.

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