Study of current dynamics of soils from a podzol–oxisol sequence in Tahiti (French polynesia) using the test-mineral technique

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Abstract

The current soil dynamics of a podzol–oxisol climosequence located in Tahiti on basaltic and pyroclastic parent rocks has been investigated using the ''test-mineral'' technique. The test-mineral, a vermiculite with a high exchange capacity (161 meq/100 g) was placed in recoverable bags in the A and B horizons of three members of the sequence, for periods of 1 to 3.5 years.

Changes in the chemistry and mineralogy, enabling complexing acid environments to be distinguished from non-complexing, were determined following the in situ reaction with natural soil leachates. A set of leachates from the same horizons were collected and chemically analysed at the end of 3.5 years. The results indicate that the current acid environment is only weakly complexing. This suggests that the podzolisation processes which led to the development of a unique A2 horizon containing gibbsite, anatase and rutile, and a placic horizon, in the upper podzol member of the sequence, is no longer operating.

Keywords: dynamics; podzols; oxisols; Tahiti

1. Introduction

The basaltic planezes of Tahiti, which are gently sloping relics of the original surface of the Hawaiian-type volcanic cone, have a soil mantle which comprises two successive soil units. The lowest part, up to an altitude of 800 to 900 m depending on orientation, is occupied by oxisols which are ferrallitic soils associated, on this type of rock, with pedogenesis in a low altitude humid tropical climate. At higher altitudes, in an

increasingly cool climate, litter begins to appear and above 1100–1200 m, the organic accumulation is such that conditions for podzolization might develop. The soils at this elevation are unique in that the colour of the leached A2 horizon does not depend, as in classical podzols, on a concentration of quartz sand (which is non-existent in basalts), but on considerable amounts of residual gibbsite associated with anatase and rutile (Fig. 1).

The characteristics of the soils covering the planezes, the most stable morphological units, have already been studied (Jamet, 1986, 1987a,b). The oxisols (Typic Gibbsihumox) are characterized by an almost exclusive accumulation of metallic oxides and hydroxides and are almost devoid of clay minerals. This results from a strong dissolution of bases and silica caused by the abundant, warm percolating water passing through the soil as a result of the gentle slope and permeability of the material. The location of the podzols (Typic Placohumod) within the sequence appears to show that podzolization is more influenced by the cool climatic conditions induced by altitude than by the current composition of the plant cover. In the transition area between 800–900 m and 1100–1200
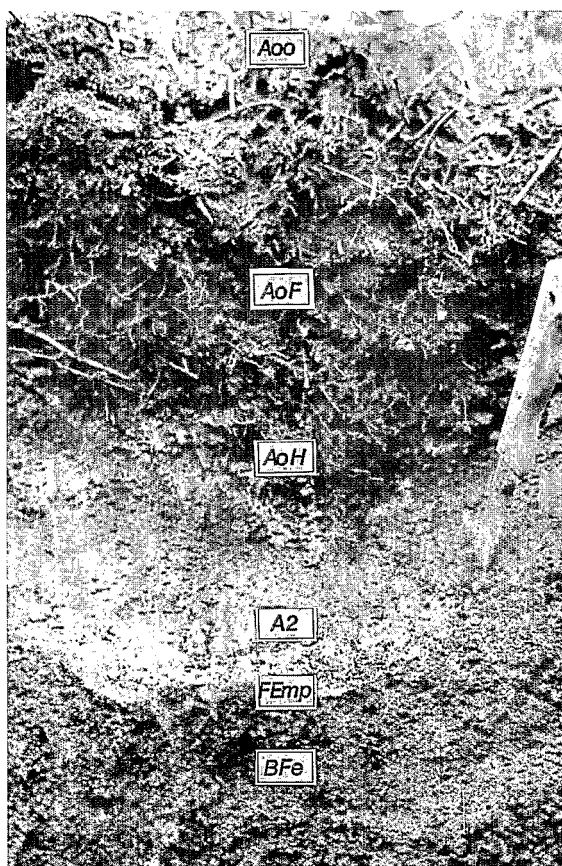

Fig. 1. The MAU1 profile (Podzol). The whiteness of the A2 horizon is due to gibbsite.

m, where temperatures are still too high to slow down the decay of the organic matter, the transitional soils are highly humiferous oxisols (Umbric Gibbsihumox). The main characteristics of these soils are described below.

The distinction between past and currently active soil forming processes is generally not possible by analysis of solid-phase soil. Currently active soil-forming processes should be investigated through soil solution studies.

Water is a dynamic component functioning as a solvent and as a transporting agent for other elements within the soil. Therefore, the collection and analysis of soil solutions, followed by a study of their in situ action on recently introduced highly reactive minerals, will make it possible to investigate the characteristic processes of the current soil dynamics (Vedy et al., 1977; Bartoli et al., 1981; Ugolini et al., 1987, 1988; Ranger et al., 1992).

The study aims at establishing

(1) whether podzolisation processes still operate under current environmental conditions in soils with a podzolic morphology, which date back 1000 to 1500 years B.P. (radiocarbon (^{14}C) datings on placic and B Fe horizons) and which are located on the summit of the planeze, and

(2) the extent to which the highly weathered and mature sesquioxidic oxisols of the lower planeze still display continuing or potential soil processes which affect their development.

For this purpose, solutions which circulate freely through the soil are collected at the base of the characteristic horizons and analysed. Clay minerals, which have both a potential high exchange reactivity and are subject to rapid transformation of the crystal lattice, in the soil solution, are exposed to the migratory water flow by intercalation within the soil profile. This is called the "test-mineral" experimental method and has been used in France for more than ten years in order (a) to follow the weathering of different minerals under natural conditions (Berthelin et al., 1983) and (b) to study seasonal or annual soil dynamics under the influence of various types of vegetation cover (Ranger and Robert, 1985; Dambrine et al., 1989; Righi et al., 1990; Ranger et al., 1992).

2. Experimentation principle

Experimental studies conducted in the laboratory by Robert et al. (1979), followed by numerous field applications (Ranger and Robert, 1985; Dambrine et al., 1989; Ranger et al., 1986, 1991, 1992) have shown that 2:1 phyllosilicates can, under the influence of acid solutions, evolve differently according to the conditions of reaction within the immediate soil environment.

The test-mineral (vermiculite), whose exchange sites have been previously saturated with sodium ions, is allowed to react in the soil until an equilibrium is established. If the soil environment is acid and complexing, the less complexable cations (Mg^{2+}) accumulate in the interlayer region, while the aluminium ions extracted from the mineral are removed in solution in the form of a complex. If the soil environment is acid but non-complexing, the vermiculite is altered by the loss of Mg from the octahedral sheet,

while the aluminium released from the mineral structure migrates and accumulates in the interlayer region, and rapid hydroxylation leads to the formation of an Al intergrade mineral easily detectable by X-ray diffraction.

Gravitational water, which percolates through the horizons and is collected at their base, shows the modes of transfer of aluminium, iron and possibly titanium in the cationic or complexing form, enabling an evaluation of the contribution of these elements to the two forms (Bartoli et al., 1981).

3. Materials and methods

3.1. Environment and soils

The study deals with the western, leeward side of Tahiti island (17°40′S–149°30′W) and more precisely, the Faaa planeze, a morphological unit on the shoreward fringe of the island, which is the relic of the primitive surface of the volcano (Fig. 2).

This planeze, which decreases in area as one moves away from the shore, extends over 9 kms from the coastal plain up to its summit which culminates at 1400 m (Fig. 3).

The soils of the lower planeze overlie Pleistocene basaltic flows while those of its upper part overlie Recent pyroclastic rocks (lapilli and ash), both of them with a moderate slope of about 15%, under a vegetation characterized along the sequence mainly by a herbaceous stratum with *Gleichenia linearis*, a fern that grows as a monospecific population with a complete ground-cover. At altitudes above 900 m the heath, with dense, tall *Gleichenia* is enriched with relatively low woody species (2 to 5 m) which give a 30 to 40% ground cover. This is the "cloud forest" (Florence, 1983).

The climate is humid tropical but is strongly moderated by the proximity of the ocean and the high relief. The mean annual temperature is 25.7°C at sea level, decreasing to
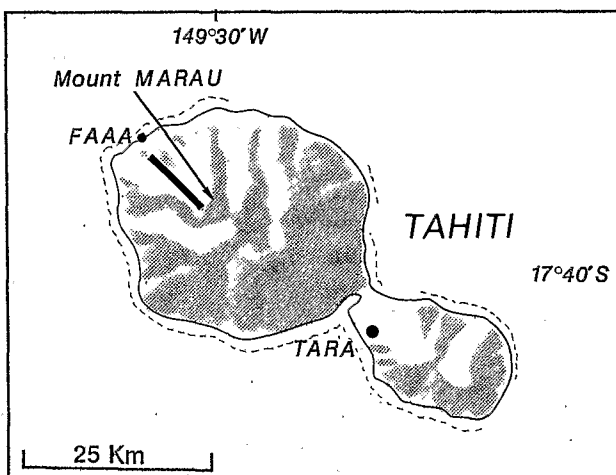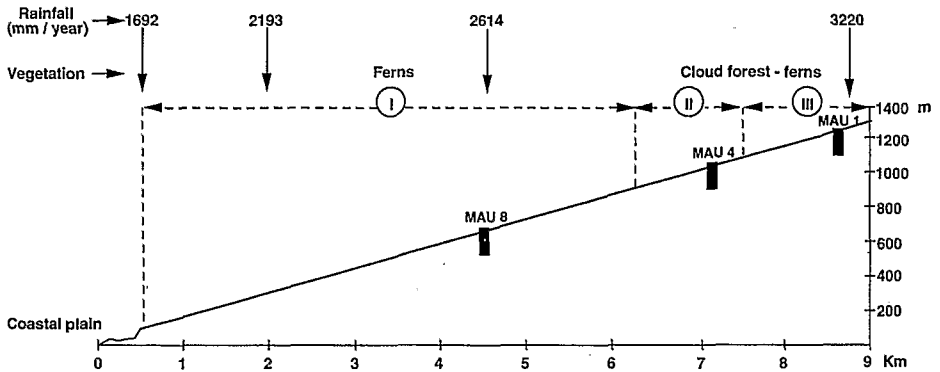

Fig. 2. Map of Tahiti with our working areas.

Fig. 3. Diagram of the soil sequence (Faaa planeze) and location of the experimental sites; I = Oxisols, II = Transitional oxisols, III = Podzols.

about 18°C at 1400 m. Rainfall at sea level to the leeward is low (1692 mm) compared to 3220 mm on Mount Marau, which is the planeze summit (Fig. 3).

The soils as a whole are not very deep (60 to 150 cm to C horizons); the fine texture of their mineral horizons ranges from silty clay to clay. These terms refer to the particle size, as the material in the upper horizons is generally devoid of clay minerals. They are acid to very acid soils: the $pH(H_2O)$ of the podzol organic horizons (MAU1) does not exceed 4.0; in the A and B horizons of the transitional oxisol MAU4 and the oxisol MAU8 it ranges from 4.1 to 6.2 and 5.9 to 6.1 respectively. The CEC of the B mineral horizons is variable and highly dependent on the pH. At pH 7.0, it ranges from 4 to 15 meq/100 g and retains less than 5 meq/100 g of exchangeable bases, in places as little as 0.5 meq.

The mineral fractions of the A and B horizons in both podzol and oxisols are almost exclusively composed of iron, aluminium and titanium oxihydroxides including 8–9% TiO_2, the SiO_2 content being generally lower than 5%.

The uniqueness of the A2 horizon of the podzol will be emphasized, as it is very rich in gibbsite (32%) and titanium oxide (17% as anatase and rutile), i.e. 50% and 27% of the mineral fraction respectively. It is rich also in phlobaphenes (fossil resin).

The placic horizon underlying the A2 horizon displays the characteristics of a spodic horizon as defined by Soil Survey Staff (1975), i.e. a horizon where organo-metallic materials, which have accumulated by illuviation, can be extracted by sodium pyrophosphate (Higashi et al., 1981; Mokma, 1983; Buurman, 1985).

All these soils are well structured and well drained, except for the barrier represented by the placic horizon.

The main analytical data for these three soil profiles, characteristic of three stages of development, are given in Table 1.

3.2. The test-mineral

This was a trioctahedral vermiculite from Santa-Olalla (Spain), selected for its high reactivity under acid conditions. This reactivity is linked to the existence of an interlayer region which gives the mineral a high exchange capacity (161 meq/100 g).

Table 1
Some analytical data for the soils from the podzol–oxisol sequence and the TARA profile (oxisol)

Soil	Horizon [a]	Depth (cm)	Particle size (μm) distribution (% of whole soil)					pH (H$_2$O)	C %	C/N	CEC (meq/ 100 g)	Total oxides %		Fe ox. % [c]	Al ox. % [c]
			< 2	2–50	50–200	200–1000	> 1000					SiO$_2$	Others [b]		
Podzol	Aoo	5–0													
MAU 1	AoF	0–18						3.5	48.8	32.3	168.9	1.0	0.7		
	AoH	18–21						4.0	37.5	24.5	100.0	1.6	28.0	8.6	0.5
	A2	21–26	41.6	31.6	9.4	11.4	5.4	4.3	21.7	26.3	52.8	1.1	47.2	2.1	0.7
	FEmp	26–27						4.5	4.2	24.7	n.d.	4.6	69.6	17.5	1.5
	BFe	27–48	41.4	48.8	5.0	3.9	0.2	5.4	4.7	26.3	36.6	8.6	64.2	11.6	5.0
	C	48–	8.3	43.5	27.7	19.0	1.9	5.9	0.3	10.5	23.0	21.1	53.4	5.2	8.2
Transitional	Aoo	5–0													
oxisol	A1	0–15	44.1	27.8	6.4	14.7	5.5	4.1	15.1	21.9	48.9	1.2	47.2	0.8	0.3
MAU 4	A3	15–25	24.0	10.0	7.2	32.2	24.7	5.9	5.2	31.4	23.9	1.2	69.6	4.3	0.5
	B1	25–40	38.0	22.0	12.6	21.9	4.2	5.9	3.1	30.1	14.9	1.4	73.2	8.6	2.4
	B2	40–70	14.7	52.8	9.0	22.3	1.2	6.2	1.1	34.3	5.8	1.4	76.4	10.4	3.4
Oxisol	A1	0–15	44.8	42.3	7.4	5.5	0	5.9	8.5	16.9	30.2	1.3	64.2	2.2	1.4
MAU 8	A3	15–35	34.6	49.6	9.1	6.6	0	5.9	4.6	16.9	17.1	1.0	70.7	2.0	1.0
	B1	35–55	30.0	49.0	9.4	11.7	0	5.9	1.7	19.8	6.9	1.6	74.4	1.4	1.0
	B2	55–75	39.8	36.9	7.7	13.9	1.3	6.1	0.9	25.2	4.0	2.0	77.8	0.8	0.5
Oxisol	A1	0–18	22.8	64.9	5.9	5.8	0	4.8	3.5	16.4	21.8	0.4	85.3	5.3	1.0
TARA	A3	18–40	27.6	69.3	2.0	1.1	0	5.3	2.0	24.3	18.9	1.6	80.5	3.2	0.5
	B1	40–72	21.9	51.3	11.8	14.3	0.7	5.6	1.8	21.8	21.3	3.5	81.7	6.6	0.5
	B2	72–95	37.1	55.8	2.9	4.0	0	5.5	1.0	11.6	14.6	13.3	68.4	2.8	1.4

[a] Soil horizon designation according to CPCS (1967) and AFES (1992).

[b] $Fe_2O_3 + Al_2O_3 + TiO_2$.

[c] ox = Tamm's method (Tamm, 1922).

Its chemical composition (1) and structural formula (2) are as follows:

(1) SiO_2: 31.46; Al_2O_3: 13.89; TiO_2: 0.63; Fe_2O_3: 3.63; FeO: 0.30; MnO: 0.11; MgO: 19.65; CaO: 0.15; K_2O: 0.04; Na_2O: 0.16; BaO: 13.50.

(2) (Si 2.71, Al 1.29) (Al 0.12, Fe^{III} 0.24, Fe^{II} 0.02, Mg 2.52, Mn 0.01, Ti 0.04) Na 0.03, Ca 0.01, Ba 0.46.

The vermiculite (3 g) was used as particles of 200–500 μm diameter. It was saturated with Na^+ ions, mixed with quartz (1g with a particle size of 200–400 μm) to improve the percolation of the soil solution, and placed in rot-proof polyamide bags (5 × 10 cm) with a cloth mesh of 20 μm.

In a specially prepared pit, soil was hollowed out from the wall at the base of characteristic soil horizons and the sealed bags were carefully seated in these cavities so that no discontinuity was created between the soil and the bag. These hollows were then sealed off and the pit was refilled, retaining the original horizons.

Two sets of 8 bags each were introduced in July 1987, each set being distributed as follows (Fig. 4):

(a) 5 bags in the MAU1 profile (podzol) at the base of the AoF, AoH and A2 horizons, in the upper part of the BFe horizon and at its base.

(b) 2 bags in the MAU4 profile (transitional oxisol) at the base of the A1 and A3 horizons.

(c) 1 bag in the MAU8 profile (oxisol) at the base of the A1 horizon.

The first set of 8 bags was collected in July 1988 (dry season), one year after introduction. The second set was collected in January 1991 (hot, humid season), three and a half years after introduction.
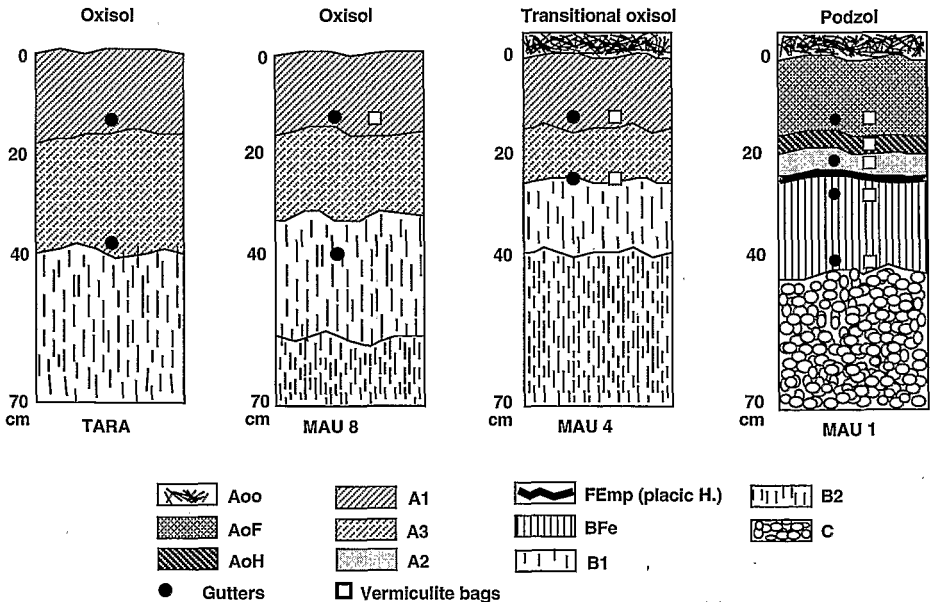

Fig. 4. Schematic representation of the soils morphology and location of the gutters and test-mineral bags.
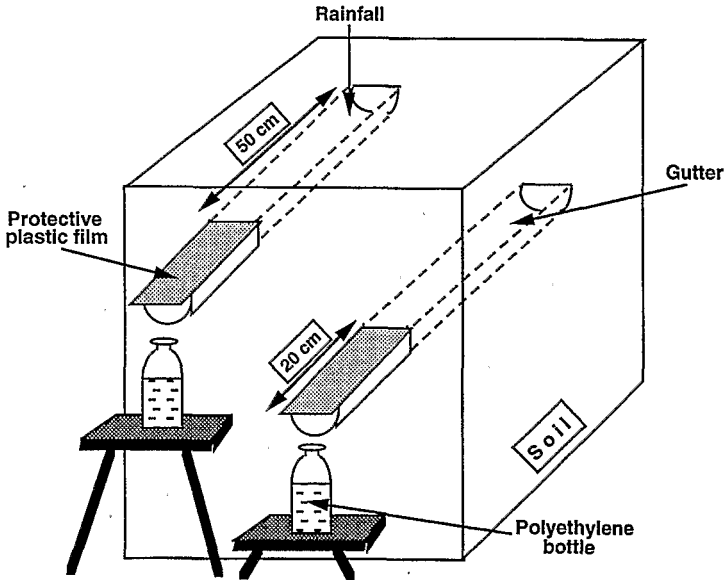
Fig. 5. Schematic représentation of the gutters in soil.

The experiment was not repeated, as experiments of this kind, by Ranger and Nys (1994), are reproducible.

3.3. Gravitational water

This was collected through a system of permanent, buried PVC gutters, most often in the same positions as those adopted for the bags of test-minerals and parallel to the soil surface (Figs. 4 and 5).

(a) 4 gutters were set up in the MAU1 profile at the base of the AoF and A2 horizons and at the upper part and the base of the BFe horizon.

(b) 2 gutters were set up in the MAU4 profile at the base of the A1 and A3 horizons.

(c) 2 gutters were set up in the MAU8 profile at the base of the A1 horizon and in the B1 horizon.

Finally, two additional gutters were set up at the base of the A1 and A3 horizons of the TARA profile, which is another oxisol particularly rich in titanium, (19% on average in the A and B horizons). It is situated at the base of the Taravao planeze in the west of the peninsula (Fig. 2). Its main morphological and analytical characteristics are given in Fig. 4 and Table 1.

Depending on the horizon, between 1.5 and 3 liters of water were collected during 24 hours of heavy rain, in February 1991 (rainy season). The samples remained in the containers for three weeks and throughout that time, including the transport, they were kept at low temperature (2 to 5°C).

3.4. Analytical methods

3.4.1. The test-mineral

The following determinations were performed on the recovered samples:

(1) exchangeable cations (Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Fe^{3+}, Mn^{3+}) through KCl exchange, K^+ through $SrCl_2$ exchange, and the free Al and Fe contents through sodium citrate extraction (Tamura's method; Tamura, 1958), carried out subsequently on the same subsample.

(2) X-ray analysis (a) after saturation with the potassium ion (KCl), and (b) after extraction of the free Al and Fe by sodium citrate.

3.4.2. Gravitational water

The free soil solutions collected at the bottom of each soil horizon were passed through a 0.45 μm filter and the color measured for optical density at 330 nm in a 10 mm path long cell. The concentrations of Ca^{2+}, Mg^{2+}, K^+, and Na^+ were determined by atomic absorption spectrometry, whereas Fe and Al were determined by ICP atomic emission spectrometry, and the mineral anions (NO_3^-, SO_4^{2-}, Cl^-) by ionic chromatography. Alkalinity was determined according to the Gran titration procedure and the dissolved organic carbon with the TIC–TOC Carlo Erba device.

To evaluate the strength of the association between the metallic ions Al and Fe and the organic ligands, soil solutions were percolated slowly through columns filled with acidic cation exchangers (Amberlite 120 resin in H^+ form). The concentrations of Al and Fe were determined before and after percolation. The association ratio (AR) represents that part of cations found in solutions after percolation, this part being assumed to be strongly linked to organic compounds. Molar ratios C/Al and C/Fe were computed from the concentration values of Al and Fe of the solutions after percolation and the organic carbon concentration in the initial solutions. We therefore assumed that the resins did not retain organic substances.

4. Results

4.1. Transformation of the test-mineral

4.1.1. Geochemical transformation (Fig. 6)

(1) Exchangeable cations and free Al.

Changes concerning the ions adsorbed in the vermiculite differ according to whether it was buried in A horizons or in the underlying soil horizons and also according to the residence time.

Loss of Na. After one year in the organic horizons of soils situated above 1000 m (MAU1 and MAU4 profiles) there is a drop in the Na^+ content (from 130 to about 50 meq/100 g). After 3.5 years, the exchange complex is almost completely devoid of Na^+ and this removal occurs to the same extent in the podzol A2 horizon and the oxisol A1 horizon at the bottom of the planeze.

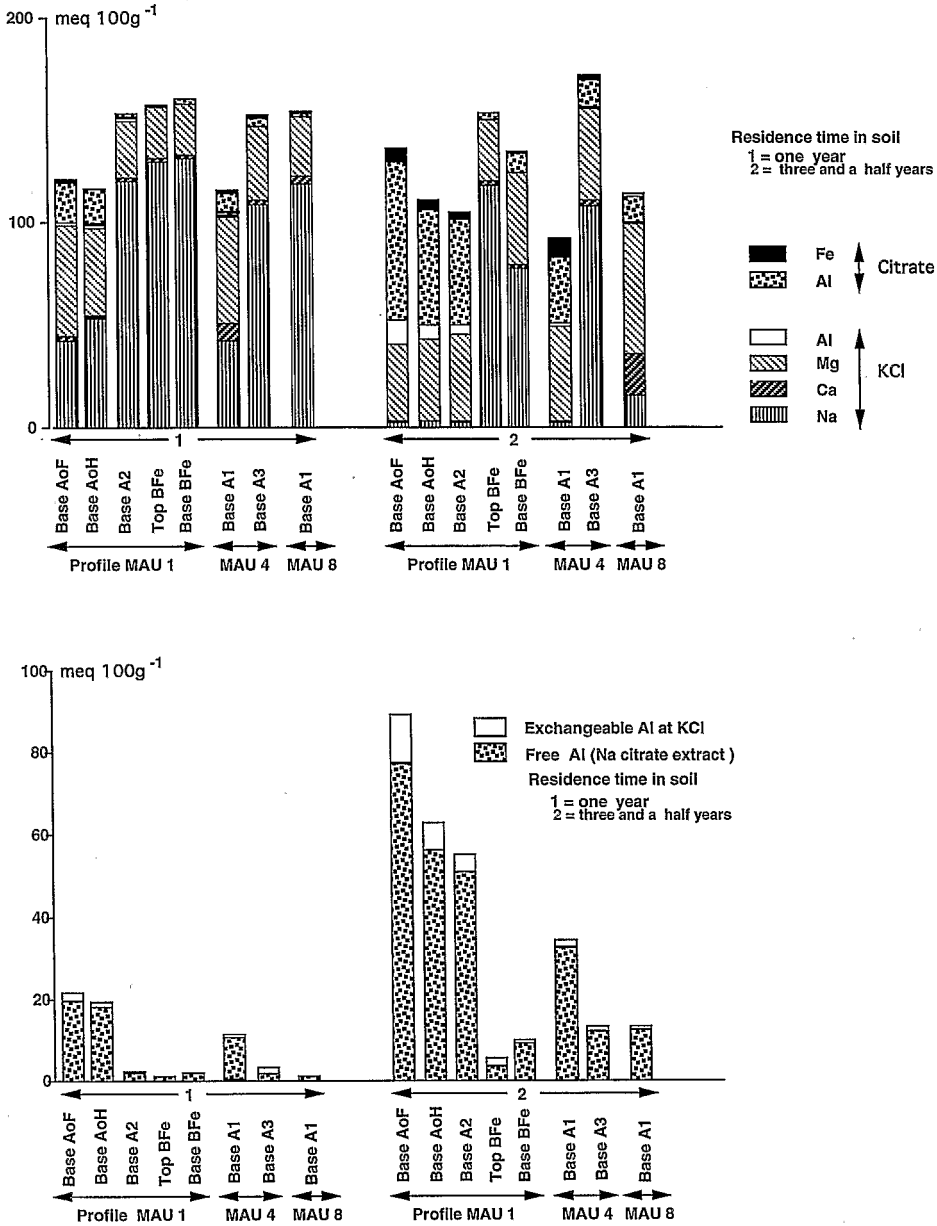Mg^{2+} has partly replaced the Na^+ ions of the vermiculite buried in these horizons:

Fig. 6. Geochemical transformation of the test-mineral (vermiculite) after 1 and 3.5 years residence time in soils.

40 to 55 meq/100 g at the end of the first year, tending to decrease over time except in the test-mineral from the oxisol (MAU 8), which retains more than 60 meq/100 g of exchangeable Mg^{2+} associated with a high Ca^{2+} content (20 meq/100 g).

The exchangeable aluminium is clearly identifiable only after a long residence time, in the vermiculites from the A horizons of the podzol, with its maximum increase nearer to the surface (12 meq/100 g in AoF). There are low amounts only in profiles MAU4 and MAU8.

Free Al (extractable by a complexing agent: Na citrate). The changes at the exchange sites of the test-mineral correlate with the occurrence of free Al, of which the vermiculite is originally devoid. Once the vermiculite has been introduced into the soil, the retained Al content increases hand in hand with the desaturation of the adsorbing complex, except in the oxisol.

The test-mineral from the oxisol Al horizon retains only a rather small amount of free Al (12 meq/100 g) after 3.5 years in the soil. The same holds true for the test-mineral from the A3 horizon of the transitional oxisol and from the BFe horizon of the podzol.

In vermiculites from the A horizons of the podzol and the A1 horizon of the transitional oxisol, the content of fixed free Al, which was already significant after 1 year (except for A2) has increased greatly at the end of 3.5 years residence time. For the podzol, the levels are highest in the AoF horizon (80 meq/100 g) and decrease from the surface down to A2 (51 meq/100 g). The free Al and the exchangeable ion Al^{3+} follow a similar trend, each on its own scale.

(2) Free Fe. The free iron content is at its maximum in the vermiculite introduced into the Al horizon of the transitional oxisol where it amounts to only 10 meq/100 g. Fe in vermiculites from the podzol follows a similar trend to Al, though Fe content is only one twelfth the Al content.

4.1.2. Mineralogical transformation (Fig. 7)

X-ray diagrams are presented for samples of vermiculite which were originally saturated with Na^+ and extracted after 3.5 years in the soil. Before X-ray analysis, each sample was treated successively with potassium chloride, which extracts the exchangeable elements, and sodium citrate (Tamura reagent, 1958), which extracts the non-exchangeable aluminium. The X-ray diagrams clearly distinguish vermiculites recovered from the Ao, A2, A1 horizons of the podzol and transitional oxisol compared with those from the BFe and A3 horizons of the same soils, while the vermiculite introduced into the oxisol is also markedly different.

These differences are as follows:

(1) The Ao, A2 and A1 horizons of the podzol and transitional oxisol: after treatment with KCl, the diagram shows an intense diffraction line at 13,5 Å, while treatment with sodium citrate leads to a closure partly towards 11,3 Å (major line), and partly towards 10 Å.

(2) The BFe and A3 horizons of the podzol and transitional oxisol: after treatment with KCl, a less intense line occurs at 10.5/10.7 Å or 11.1 Å and for the BFe base sample a shoulder appears at 14.2 Å. Treatment with citrate leads to a general closure near 10.3 Å.

(3) The oxisol A1 horizon: the closure under the influence of KCl is median at 12,8 Å, while citrate leads to a behaviour similar to that of the A horizons of the other soils, with the occurrence of a doublet at 11 and 10 Å.
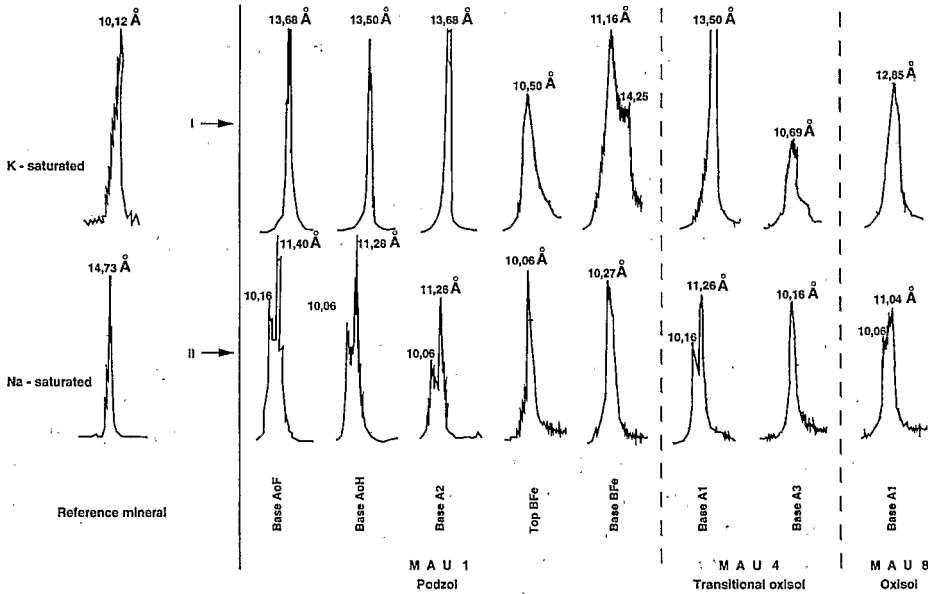
Fig. 7. Mineralogical transformation of the test-mineral (vermiculite) after 3.5 years residence time in soils. X-Ray diffraction diagrams of the Na-saturated and K-saturated reference mineral and of the test-mineral samples inserted in the upper horizons of the profiles under study: I, K-saturated; II, Na citrate saturated.

4.2. Characteristics of soil solutions

The chemical analyses of soil water and rainfall are presented in Table 2. All samples are colorless except for soil solutions collected in the podzol, where it appears that the optical density values are not correlated with the organic carbon concentration.

The solutions collected in the podzol are very acid (pH from 3.95 to 4.30) so that the titratable alkalinity takes negative values, indicating that the proton concentration is higher than the concentration of the titratable alkalinity such as carboxylate groups and conjugate anions of weak mineral acids. Except for Al, the dominant cation is Na^+; whereas the major mineral anions are Cl^- and SO_4^{2-}.

The maximum organic carbon concentration is found in the solutions from deep horizons in the podzol (Table 2) and corresponds to the highest values of Al (Table 3). As indicated in Table 3 by the values of the association ratios (AR), most of the Al and Fe present in the soil solutions is not retained on resins and could correspond to non-ionic forms mainly associated with soluble organic substances and/or organized under polymeric forms. The Al and Fe of the solutions collected at the AoH and A2 horizons boundary appear to be strongly linked to organic substances and, according to the molar values of C/Al (186) and C/Fe (1048), one can assume that numerous sites of these organic substances are still protonic. At the base of the A2 horizon, the strong acidity of the solution (pH = 3.95 and 3.75 before and after resin treatment respectively) could explain the relatively low AR values of both Al and Fe. Ionic and monomeric forms could be more abundant. Water collected in the BFe horizon exhibits high AR

Table 2
Chemical characteristics of soil solutions and rainfall

	Location of zero-tension lysimeter	Organic carbon (mg/l)	Optical density ($\lambda = 330$ nm)	pH	Ca^{2+} (μeq/l)	Mg^{2+} (μeq/l)	K^+ (μeq/l)	Na^+ (μeq/l)	Cl^- (μeq/l)	NO_3^- (μeq/l)	SO_4^{2-} (μeq/l)	Alkalinity (μeq/l)
MAU 1	G1 At the base of AoF	11.95	0.523	4.00	7.8	10.6	4.8	27.3	71.8	4.2	44.8	−87.9
	G2 At the base of A2	9.65	0.260	3.95	15.6	28.1	3.4	39.5	112.1	2.0	49.6	−97.3
	G3 At the top of BFe	13.35	0.462	4.20	4.0	35.4	1.9	35.0	66.2	7.0	36.5	−51.5
	G4 At the base of BFe	15.95	0.684	4.30	6.6	19.0	2.8	38.9	70.4	8.5	19.8	−46.9
MAU 4	G1 At the base of A1	2.15	0.027	4.85	7.0	44.7	3.7	65.2	46.5	31.5	49.0	−8.7
	G2 At the base of A3	4.45	0.071	4.95	4.7	18.5	3.8	50.0	28.0	14.0	33.0	4.1
MAU 8	G1 At the base of A1	1.65	0.018	5.60	7.6	11.1	16.8	50.9	50.7	1.0	30.0	8.8
	G2 In B1 horizon	n.d.	0.009	6.85	157.0	160.5	75.2	615.0	564.4	15.6	75.0	324.7
TARA	G1 At the base of A1	3.40	0.051	5.85	72.5	49.0	3.5	36.0	66.9	13.0	37.0	36.1
	G2 At the base of A3	2.00	0.024	5.20	67.0	44.0	5.0	71.0	54.5	60.0	53.0	12.8
MAU 1	Rainfall	<1.00	0.000	5.85	13.7	13.4	3.3	31.3	30.6	5.0	17.0	12.5
TARA	Rainfall	1.10	0.007	5.70	8.9	6.7	9.6	37.1	33.8	4.0	11.0	27.2

Table 3
Aluminium and Iron in soil solutions before and after treatment with H^+-resin. The association ratio describes the element concentration after and before H^+-resin treatment. The molar ratio C/Al and C/Fe are computed with elements supposed to be associated with soluble organic substances

		Before H-resin treatment		After H-resin treatment			Association ratio		Al and Fe associated with organic substances	
		Al μmol/l	Fe μmol/l	Al μmol/l	Fe μmol/l	pH	Al	Fe	C/Al (molar ratio)	C/Fe (molar ratio)
MAU 1	G1	5.80	1.10	5.35	0.95	3.90	0.92	0.86	186	1048
	G2	11.85	5.20	6.80	3.25	3.75	0.57	0.63	118	247
	G3	19.35	4.55	13.20	3.00	3.90	0.68	0.66	84	371
	G4	30.45	5.85	20.40	4.50	3.95	0.67	0.77	65	295
MAU 4	G1	3.65	0.45	1.20	0.15	3.95	0.33	0.33	149	1194
	G2	7.35	1.45	4.20	0.70	4.00	0.57	0.48	88	530

(0.68 for Al, and up to 0.77 for Fe). The relatively low molar C/Al ratios suggest that the high mobility of Al is related to its stronger linkage with acidic sites of organic substances of a fulvic type.

The soil solutions from the transitional oxisol (MAU 4) are less acid and their organic carbon concentration lower than in those collected in the podzol. Na^+, Mg^{2+}, Cl^- and SO_4^{2-} are still the major ions (Table 2) and the Al concentration has greatly decreased. As observed in Table 3, the association ratio of Al gives 0.33 and 0.57 for the A1 and A3 horizons respectively, the highest value being related to the highest concentration of organic carbon (4.45 mg/l in the A3 horizon against 2.15 mg/l in the A1 horizon).

Water percolating the oxisols MAU8 and TARA is neutral. It has a very low organic carbon concentration, high positive alkalinity and no detectable amounts of Al and Fe. Especially at Tara, Ca^{2+} and Mg^{2+} are the dominant cations (Table 2). This is probably due to the high level of biological cycling of these elements.

The high ionic concentration of the soil solution collected in the B1 horizon of MAU8 cannot be easily explained. The Na/Cl and SO_4/Cl equivalent ratios (1.1 and 0.13, respectively) being close to those of sea water (0.86 and 0.10: Michard, 1989), there is evidence of an influence of sea salt aerosols. Ca/Na and K/Na ratios of 0.25 and 0.12, respectively (0.04 and 0.02 in sea water), suggest another origin of Ca and K, probably related to the weathering of mineral phases.

5. Discussion

5.1. The contribution of test-minerals to the study of current soil dynamics

The considerably reduced reaction of the test-minerals introduced below the placic horizon of the podzol confirms the field observations, that this horizon is a barrier which

considerably slows down the movement of solutions, so leading, in the case of high rainfall, to temporary obstruction and hence to a lateral rather than vertical flow.

The results obtained with vermiculite buried for more than three years, reveal a marked reaction and alteration of this mineral in the upper A horizons of the three soil types concerned.

First, it results in a displacement of Na^+ ions from exchange sites, which is more rapid in the organic horizons of the podzol and the transitional oxisol and is incomplete and/or slower in the other horizons of these soils and in the oxisol. This desaturation in sodium ions correlates with a considerable decrease in the CEC (KCl removing in a ratio vermiculite : solution = 0.25 : 1). And the more acid the environment, the greater and faster the desaturation.

Such is the case for the A horizons of the *podzol*, where the pH of both soil and percolating solutions is close to 4,0. This acidification is due to a mixture of strong mineral acids and weak and very weak organic acids produced by the AoF and AoH organic horizons. The solution resulting from maceration of a sample of these horizons in distilled water (soil : water = 1 : 2), for 24 hours, gives a pH of 3.5. This acidity (4.45 meq/l) is more mineral (two thirds being sulphuric) than organic, in a ratio of 1.6 : 1 (Brunelot et al., 1989).

The experiments show that this acidity decreases once the solution has percolated through the mineral horizons (A2 and BFe) but that the proportion of mineral acids increases and, in the case of the A2 horizon, the ratio increases to 2.5 : 1. Further analyses show that solutions, derived from these organic horizons, do not contain organic anions capable of chelating metals, but do contain carbon compounds of the humic acid type.

These analysis show that the environment, to which the vermiculite has been subjected, contains mineral acids that are increasingly prevalent with depth. They are associated with organic acids capable, according to experimental studies by Robert and Razzague-Karimi (1975), of exerting only an acid chemical, a protonization effect, thus leading merely to the opening and aluminization of the sheets.

These observations are consistent with the analyses of test-minerals interpreted in the light of the results obtained by Ranger and Robert (1985), Dambrine et al. (1989), and Ranger et al. (1991, 1992). The high accumulation of both free and exchangeable aluminium (Ranger and Robert, 1985) in vermiculite, which has remained for a certain lengh of time in the A horizons of the podzol, gives evidence of an acid medium which is not complexing enough to completely sequestrate this element, but is rich in protons which can, through exchange with other cations, diffuse within the structure and lead to a partial migration of the aluminium. The latter hydroxylates and migrates from the tetrahedral and octahedral layers to the interlayer region of minerals, thus contributing to the formation of an aluminous vermiculite (Jackson, 1963; Robert and Razzague-Karimi, 1975; Robert et al., 1987). It is also possible that some of the interlayer aluminium derives from external sources but, whatever the origin of the Al, the dynamics are the same.

This mineralogical change is confirmed by X-ray diffraction. After treatment with potassium chloride, which removes exchangeable elements, the diffraction line of vermiculite at 14 Å closes only to 13.5 Å, showing that the interlayer region is weakly

occupied by these elements which occupy exchangeable sites between the hydroxylated Al. By contrast, treatment with sodium citrate leads to the closure of the interlayer region to 10 or 11 Å. This confirms that it is the aluminium in the interlayer region that halts the closure of the sheets at 13.5 Å after treatment with potassium chloride.

Here, the medium is acid and solutions neither complex nor release the aluminium of the test-minerals, but on the contrary, integrate it into the interlayer region. Considering that only a complexing acid system, destroying minerals and releasing aluminium, seems to be characteristic of the podzolization process (Robert et al., 1987), it can be said that this medium is not as strongly podzolizing.

The changes in the vermiculite at the end of 3.5 years in the A1 horizon of the *transitional oxisol* show that the latter functions like the A horizons of the podzol. The accumulation of hydroxylated aluminium, though it is less marked here, still amounts to 32 meq/100 g and therefore gives evidence of the same acid, but not very complexing, medium. It is confirmed by the study of the X-ray diagrams: the K-saturated vermiculite closes only to 13.5 Å, while it collapses to 10 and 11 Å after treatment with sodium citrate.

In the A3 horizon, the vermiculite still shows 13 meq/100 g of free aluminium, although its exchange capacity, closely bound up with the interlayer region, is already almost saturated by the exchangeable elements (157 meq/100 g — Na mainly). It is therefore likely that the free aluminium revealed by the analysis has, at least partly, another origin, or at least another position relative to the sheets. The X-ray diagrams seem to confirm this hypothesis, the K-saturated vermiculite collapsing to 10.7 Å and to 10.1 Å after citrate treatment.

In the oxisol, the vermiculite is in equilibrium with a less acid medium (pH = 5.9). The free aluminium, though present in rather small quantities compared to the exchangeable elements (Mg^+, Ca^{2+}), occupies a large number of sites in the interlayer region as indicated by the X-ray analysis of the K-saturated mineral: it closes only to 12.8 Å. According to this test, the medium seems to be more complexing than the previous ones, which seems inconsistent with the results obtained from the collected gravitational water.

6. Conclusion

As revealed by the in situ experiment, the soil with a podzol morphology and podzol characteristics, is no longer developing as a podzol. The soil's environment is today an acid environment, but too weakly complexing to maintain the preexisting podzolization. A new balance is probably being establishing.

Since the podzol dates back to 1000–1500 BP and no significant climate change has been identified for that period, this soil was probably produced under the influence of a vegetation cover different from today's. This is suggested by the presence in the A2 horizon of phlobaphenes, which are fossil resins unknown in the present-day vegetation; they may be associated with *Ericaceae*, whose past existence is revealed by the palynological analysis.

Though oxisols represent the final stage in the pedogenetic evolution or "the residual

process of weathering'' (Chesworth, 1973), they are not, mineralogically, as inert as might be thought. Gravitational water contains neither iron, nor aluminium, but can become enriched at the surface in Ca^{2+}, Mg^{2+} and K^+ ions, probably originating from the biological cycling of these elements, and can carry them down to greater depths. This is confirmed by the fact that they can be found fixed in test-minerals introduced into the soils. A marine origin seems improbable, the Ca/Na and K/Na ratios being six times higher than those of sea water.

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GEODERMA

Study of current dynamics of soils from a podzol–oxisol sequence in Tahiti (French polynesia) using the test-mineral technique

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