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Pedogenesis by clay dissolution on acid, low-grade metamorphic rocks under mediterranean forests in southern Tuscany (Italy)

B. van Wesemael ¹, J.M. Verstraten, J. Sevink

*Laboratory for Physical Geography and Soil Science, University of Amsterdam, Nieuwe Prinsengracht 130,
1018 VZ Amsterdam, Netherlands*

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Abstract

Pedogenesis on acid, low-grade metamorphic rocks under well-developed forests was studied in the meso-mediterranean climatic zone. To that purpose three representative soil profiles on phyllite and sandstone under sclerophyllous oak, pine and heathland were selected. The major soil forming processes consisted of transformation of part of the K-mica (muscovite) to (hydroxy-inter-layered) vermiculite and smectite, impoverishment both in major elements (Al, K, Mg and Fe) and fine particles, and redistribution of sesquioxides as organic complexes. These processes indicate clay hydrolysis under acid conditions and subsequent removal of solutes by lateral subsurface flow. The resulting impoverishment of the soil profiles could be mainly attributed to hydrolysis under acid conditions brought about by slow decomposition of organic matter. The proposed mode of pedogenesis deviates strongly from the current concept of fersiallisation, and is probably restricted to acid parent materials in mediterranean climates where lateral removal of soluble weathering products is ensured throughout the largest part of the year.

1. Introduction

In contrast to the major part of the mediterranean basin, vast areas of southern Tuscany are still covered with well-developed oak and pine forest. The soils in this hilly area are best developed on the broad crests, while erosion dominates on steep upper slopes and colluvial soils occur on the foot slopes (Pedroli et al., 1988). The soil profiles on these crests provided an excellent opportunity to study soil formation under mediter-

¹ Present address: Laboratory for Experimental Geomorphology, Catholic University Leuven, Redingen-straat 16 bis, 3000 Leuven, Belgium.

anean climatic conditions, whence the mineral composition of the acid, low-grade metamorphic parent rock varies within a narrow, well-known range (Turner, 1968; Weaver and Beck, 1971; Winkler, 1974).

Recently, research on the dynamics of organic matter decomposition and soil conditions was carried out in mediterranean forests on acid parent materials [phyllite and sandstone in southern Tuscany (Pedroli et al., 1988; Van Wesemael and Veer, 1992) and granite, granodiorite and schist in north-eastern Spain (Sevink et al., 1989)]. These studies showed that in both areas litter decomposition is slow and that the dominant humus form is a moder. Sequential analysis of the soil solution in a sclerophyllous forest in southern Tuscany revealed that the mobility of metal organic complexes of aluminium and iron in the topsoil is considerable (Van Wesemael and Verstraten, 1993). Soil formation is therefore likely to be influenced by water-soluble organic acids, of which a part counterbalances the basic cations in the ectorganic layer (L, F and H horizons). Furthermore, seasonal sampling of various soil profiles in three forest stands in southern Tuscany (up to 10 km apart; Van Wesemael, 1993b) indicated that the effective CEC and base saturation of the topsoil are large, which can be attributed to the release of basic cations from decomposing organic matter and the large nutrient retention by organic matter. Nutrient supply by capillary rise can be ignored because of the low base saturation and the acid nature of the mineral subsoil (Van Wesemael, 1993a,b). This combination of mobile organic acids and rich nutrient status is uncommon in soils of temperate and cool, humid climates (Ulrich et al., 1979; Duchaufour, 1982; Mokma and Buurman, 1982) and its influence on weathering is therefore not mentioned in the literature.

According to Duchaufour (1982, p. 373), organic matter decomposes rapidly under mediterranean climatic conditions. This leads to an effective cycling of bases and the formation of eutrophic mull humus forms. Leaching of bases is limited in such soils, while weathering occurs out of reach of organic acids and is relatively weak. Soils formed under these conditions are classified as fersiallitic soils (CPCS, 1967) and exhibit several characteristic features: an argillic Bt horizon due to clay perversion (relocation, lessivage; Paton, 1978) and often accompanied by impoverishment of the surface horizons, a red colour due to the formation of complexes of free iron oxides with clay, a high base saturation also as a result of capillary rise during the dry summer, and a clay fraction composed of inherited and neoformed 2:1 clay minerals (Duchaufour, 1982). The theory on fersiallisation (Duchaufour, 1982, pp. 375 and 389–390) is primarily based on the study of well-developed soils on older (pre-Holocene) land surfaces, whereas little attention has been paid to young, Holocene soils. The older soils represent the combined effect of pedogenic and morphogenic processes, active over a long period of time and under a wide range of climatic conditions. Therefore, the question may arise, whether fersiallisation is indeed the dominant process under present-day climatic conditions.

In this paper, attention will be paid to soil formation and weathering in three mediterranean, forest soils on low-grade metamorphic rocks. Without attempting a budget study for the entire forested area, the hypothesis that decomposing organic matter is the dominant proton source for the hydrolysis of clay minerals will be discussed. The results will be evaluated with reference to the current theory on pedogenesis.

2. Research area and soils

The largely forested research area is situated south of the Farma river (boundary between Siena and Grosseto province) in southern Tuscany (Italy). The topography is hilly with broad crests (maximum elevation: 800 m above sea level). The area is underlain by the mainly non-carbonatic rocks of the Middle Triassic Verrucano formation (Signorini, 1968). This formation consists largely of pelitic sediments, which were subjected to folding and regional metamorphism, resulting in low-grade metamorphic phyllites, with some sandstone and anagenite (a reddish coarse grained sandstone) layers (Nardi and Nardi, 1975; Azzaro et al., 1976). The Verrucano formation extends over a largely forested area of more than 160 km². The forests in the research area now are largely state-owned and have not been coppiced since about 1950 (Bernetti, 1987). According to the estimated age of the thickest shrubs, 30–37 years, destruction of the understory by forest fires or felling, which leads to erosion of the humus profile and the mineral topsoil (Sevink et al., 1989), is very rare.

A landscape ecological study of the Farma valley by Pedroli et al. (1988) revealed that the regolith on the broad crests is still mainly in situ (Fig. 1). While on the steep slopes the regolith can be considered to be a stony slope deposit, the regolith of the profiles on the flat crests is relatively deep and contains small amounts of stones and gravels where they are underlain by phyllite or sandstone (Fig. 1). Colluvial soils are restricted to the foot slopes. Previous research on the spatial distribution of humus

Fig. 1. Catena across the Farma valley (Pedroli et al., 1988) and location of profiles studied.

Table 1
Some characteristics of the soil profiles

profile	depth (cm)	O.M. (%)	pH _{H₂O}	pH _{CaCl₂}	fine clay to clay ratio	gravel (%)	description	
1	L	+4.5	92.9	4.52	4.15	—	intact leaves and few twigs; no roots no droppings;	
	F1	+4.5	87.5	5.06	4.22	—	wavy clear to:	
	F2	+3.5	61.1	5.79	4.61	—	leaf fragments; few very fine roots; common droppings;	
							few mycelia; wavy clear to:	
	H	+2.5	0	57.2	5.55	4.40	—	amorphous humus; many very fine roots; abundant droppings;
	AEh	0	22.6	5.00	4.58	5	common mycelia; clear wavy to:	
	Bw1	2.5	4.4	4.39	3.74	35	loam (7.5YR 4/2); abundant fine roots; clear wavy to:	
							gravelly loam (7.5YR 4/4); common fine and medium roots;	
							smooth gradual to:	
	Bw2	20	33	4.28	3.68	0.35	15	gravelly loam (7.5YR 5/4); common small mottles (7.5YR 6/2);
2							few fine and medium roots; smooth gradual to:	
	C	33	0.9	4.14	3.62	0.30	<1	silty clay loam (10YR 7/4); abundant medium mottles (2.5Y 6/1; 5YR 5/8); few roots.
	L&F	+3.5	87.6	4.35	3.44	—	—	loose twigs and needles; no roots; no droppings; smooth clear to:
	H	+2.5	0	74.9	4.42	3.36	—	amorphous humus; abundant fine and medium roots; common droppings; no mycelia; smooth clear to:
	AEh	0	16.4	4.15	3.58	0.51	0	loam (7.5YR2/2); common fine roots; smooth clear to:
	Bw1	2	4.7	4.50	3.82	0.51	1	loam (10YR 4/4); common small mottles (10YR 5/2);
								common fine to medium roots; smooth gradual to:
	Bw2	15	28	4.57	3.87	0.44	7	loam (10YR 5/4); abundant small mottles (2.5Y 5/1; 2.5YR 4/6);
								few fine and medium roots; wavy gradual to:
	C	28	0.6	4.34	3.65	0.29	3	silt loam (10YR 6/6); abundant medium mottles (7.5YR 6/1; 2.5YR 3/6) ; very few roots.
3								intact needles and few twigs;
	L	+5	95.8	4.34	3.69	—	—	no droppings; no roots; smooth clear to:
	F1	+4	94.4	4.27	3.47	—	—	needle fragments and amorphous humus; common very fine roots;
	F2	+3	0	76.9	4.63	3.56	—	common droppings and mycelia; wavy gradual to:
	AEh	0	28.4	4.16	3.63	0.54	2	slightly gravelly loam (7.5YR 3/2); many fine roots; clear wavy to:
	Bw1	1	5.4	4.88	4.21	0.52	35	slightly stony loam (7.5YR 4/3) few coarse mottles (7.5YR 4/4);
								common fine and medium roots; wavy gradual to:
	Bw2	25	48	4.80	4.51	0.44	39	gravelly loam (7.5YR 5/6); few small mottles (7.5YR 4/4);
								very few medium roots; wavy gradual to:
	C	48	0.7	4.87	4.16	0.58	54	gravelly loam (10YR 6/8); abundant small mottles (5YR 5/6); very few medium roots.

profiles (Van Wesemael and Veer, 1992) and on soil pH and adsorption complex in several forest stands helped us to select three relatively deep and non-stony profiles on the broad crests. These three soil profiles are in typical mediterranean forests: sclerophyllous oak forest, 390 m a.s.l., 9° slope, NE exposition (profile 1), secondary heathland, 450 m a.s.l., 0° slope (profile 2) and pine forest, 480 m a.s.l., 6° slope, W exposition (profile 3). Profiles 1 and 2 are on phyllite while profile 3 is on sandstone. The dominant humus form is a moder with well-developed ectorganic horizons. The soils have an ectorganic layer (i.e. L, F and H horizons) of about 5 cm and a characteristic thin (1–3 cm) greyish AEh horizon (Table 1). The fine roots are concentrated in the lower part of the ectorganic layer and in the uppermost 5 cm of the mineral soil. The soils are medium textured without any macro- and microscopic signs of clay illuviation. The occurrence of mottles in the lower part of the profiles suggests that some hydromorphism occurs during the wet season. This is most prominent in profile 2, which is in a flat position (Table 1). The soils of profiles 1 and 3 are classified as Dystric Cambisols (FAO, 1988) or as Dystric Xerochrepts (Soil Survey Staff, 1990). The soil of profile 2 belongs to the Gleyic Cambisols (FAO, 1988) or Aquic Xerochrepts (Soil Survey Staff, 1990).

Climate is attenuated meso-mediterranean (UNESCO-FAO, 1963) with an average annual precipitation of 988 mm (Torniella, 1962–1978). The rainfall distribution shows maxima in October/November and in May. The average January maximum temperature is 5.6° C, the minimum is 1.7° C; in July these values are 27.0° C and 17.8° C respectively (Pedroli et al., 1988). The average water balance over a 20 years period (1955–1974) was calculated by the Thornthwaite–Mather method for the nearby station of Chiusdino with an annual precipitation of 956 mm and an annual potential evapotranspiration of 754 mm (Bigi and Rustici, 1984). The potential evapotranspiration largely exceeds precipitation from June till August. For soils with an available water capacity of 80 mm (comparable to that of the investigated soil profiles, unpublished data) the soil moisture control section (Soil Survey Staff, 1990) remains dry for 109 consecutive days. However, for the largest part of the year a leaching regime prevails. The rainfall excess at the station of Chiusdino with a calculated actual evapotranspiration of 561 mm/yr (Bigi and Rustici, 1984) is 42% of the annual precipitation. This corresponds very well with the average runoff to precipitation ratio of 40% measured near Torniella in the Farma river (runoff data from 1962 to 1978; Pedroli et al., 1988), which means that an average water depth of 400 mm/year rainfall leaches through the soil profiles.

3. Methods

3.1. Soil sampling

Samples were taken from profile pits over the entire depth of the soil horizons (Table 1). After air drying and gentle crushing, gravel (> 2 mm), stones and roots were removed (fine earth fraction: < 2 mm). The clay fraction (< 2 μm) was separated after oxidation of organic matter by H_2O_2 and dispersion with a few drops of 4 M NaOH. The fine clay (< 0.2 μm) was separated from the coarse clay (0.2–2 μm) by repeated

centrifugation. The masses of both fractions were used to calculate the fine clay to total clay ratio. The major types of rocks in the Verrucano formation, violet phyllite and sandstone and a reddish coarse grained sandstone (anagenite), were sampled in a road cut in the vicinity of the sites. The rocks were powdered and used for elemental analysis and X-ray diffraction.

3.2. *Granulometric analysis*

Organic matter, as the major cementing agent in non-carbonate soils, was removed by treatment with 10% H_2O_2 on a boiling water bath. Salts were removed by suction and washing. The clay and silt fractions were dispersed by addition of sodium pyrophosphate. The fractions $< 2 \mu\text{m}$, $2\text{--}16 \mu\text{m}$, $16\text{--}32 \mu\text{m}$ and $32\text{--}63 \mu\text{m}$ were obtained by the pipette method, using settling times calculated from Stokes law. Amounts in each fraction were expressed as percentage of the sum of the mineral fractions. pH was determined potentiometrically in 1:2.5 (weight/volume) dilutions with either distilled water or 0.01 M CaCl_2 solutions.

3.3. *Organic matter content and water from decomposition of minerals*

Loss on ignition (16 hours at 375°C) was used to estimate the organic matter content of AEh horizons. In addition, loss on ignition (16 hours at 1000°C) was used to determine water from decomposition of minerals. Organic carbon content of the other mineral horizons was determined by wet oxidation (Allison, 1960).

3.4. *Elemental analysis*

Total element contents were determined after digestion with HF and H_2SO_4 (Lim and Jackson, 1982). Al, Fe, Mn, Na, K, Ca and Mg were determined by atomic absorption/emission spectrometry, whereas Ti and P were estimated colorimetrically. A distinction between Fe(II) and Fe(III) was made by digesting the samples for 15 seconds in HF and measuring Fe(II) colorimetrically. Immediately after the Fe(II) estimation, the solution was reduced by adding a solid reductant (hydroquinone) and total iron, as Fe(II) was measured (Begheijn, 1979). Total Si was estimated by AAS after fusion with sodium carbonate (Lim and Jackson, 1982). All elements were expressed in weight percentages of their oxides. The CEC of the clay fraction was determined by shaking Ba saturated clays (pH 7) with a 0.025 M MgSO_4 solution (1:20 w/v) and measuring the decrease of Mg in the equilibrium solutions. Analytical errors were estimated to be about 2% for the individual elements.

3.5. *Selective extractions*

Al and Fe in sodium dithionite–citrate, ammonium oxalate and sodium pyrophosphate extracts (Al_d , Fe_d , Al_o , Fe_o , Al_p and Fe_p ; McKeague et al., 1971; Verstraten, 1980) were determined by atomic absorption. The extracts were checked for the occurrence of suspensions with a laser beam, and if required some KCl crystals were

added. In addition, carbon was estimated in the sodium pyrophosphate extracts (C_p) by evaporation and wet oxidation according to Allison (1960).

3.6. X-ray diffraction analysis

X-ray analyses were carried out on non-oriented clay, fine clay and powdered rock samples with a Guinier–De Wolff camera. Diffractograms were made of well oriented clay samples saturated with Mg, Mg-ethylene glycol, K, K heated to 300° C and K heated to 550° C respectively. The mineralogical composition of the samples was estimated from the height of the peaks in the diffractograms and by reflection intensities on the Guinier–de Wolff camera films.

3.7. Acid neutralising capacity (ANC)

The ANC of the soil is calculated from the sum of the molar concentrations using Eq. 1 (Van Breemen et al., 1983):

$$\begin{aligned} \text{ANC} = & 6(\text{Al}_2\text{O}_3) + 2(\text{CaO}) + 2(\text{MgO}) + 2(\text{K}_2\text{O}) + 2(\text{Na}_2\text{O}) + 6(\text{Fe}_2\text{O}_3) \\ & + 2(\text{FeO}) \end{aligned} \quad (1)$$

The concentrations are derived from the elemental analysis of the fine earth fraction (see above). The Δ ANC, reflecting the impoverishment of the soil profile, is calculated in $\text{kmol}_c \text{ ha}^{-1}$ from the difference in ANC between each horizon and the unweathered C-material, using the thickness and bulk density of each horizon. Considering the analytical errors for the individual elements the error on the ANC is about 5%.

4. Results and discussion

4.1. Mineralogy of the parent rocks

The X-ray analyses of the powdered rocks reveal that the parent rocks consist mainly of quartz, K-mica, chlorite, pyrophyllite and hematite (Table 2). The K-mica is dioctahedral and shows a sharp 1.0 nm reflection which is characteristic for muscovite. The difference between the various rock types is small, being a larger K-mica and pyrophyllite content and a smaller quartz content in the phyllites (Table 2). Such a mineralogical composition is characteristic for pelitic sediments, consisting of clay minerals, which were subjected to low-grade metamorphism (Turner, 1968; Winkler, 1974). The typical K-mica of low-grade metamorphism is a muscovite of so called phengitic composition, which means that the Si/Al ratio in the tetrahedra is large, caused by substitution of octahedral Al by Fe and Mg and the occurrence of some chloritic inter layering (Weaver and Beck, 1971; Verstraten, 1980).

4.2. Particle size distribution and mineralogical composition of the soils

Clay ($< 2 \mu\text{m}$) and fine silt ($2\text{--}16 \mu\text{m}$) contents decrease gradually in all profiles from C to AEh horizons (Fig. 2), while sand ($63\text{--}1000 \mu\text{m}$) increases (Fig. 2). The ratio

Table 2

Clay mineralogy and mineralogical composition of powdered rocks estimated by X-ray diffraction

profile		smec- tite	vermi- culite	hydrox. interl.	K-mica	chlo- rite	kao- linite	pyro- phyllite	halloy- site	quartz	free iron minerals
1	AEh	28	—	—	63	3	6	x	tr	2–4	—
	Bw1	tr	17	tr	74	5	4	x	tr	2–4	—
	Bw2	—	9	—	83	6	2	x	tr	1–3	tr
	C	—	tr	—	94	6	tr	tr	tr	1–3	tr
2	AEh	15	tr	—	75	5	5	tr	tr	2–4	—
	Bw1	tr	13	—	79	4	4	x	tr	2–4	tr
	Bw2	—	8	—	86	3	3	x	tr	1–3	tr
	C	—	—	—	98	2	—	x	tr	1	xx ^a
3	AEh	11	tr	—	71	—	18	—	tr	2–4	tr
	Bw1	—	27	tr	50	1	23	—	tr	2–4	tr
	Bw2	—	tr	13	59	9	19	—	tr	2–4	tr
	C	—	—	20	50	7	23	—	tr	2–4	tr

Parent rocks

phyllite	—	—	—	xx	tr	—	x(x)	—	xx	x ^b
sandstone	—	—	—	x	tr	—	tr	—	xxx	tr
anagenite	—	—	—	x	tr	—	tr	—	xxx	x ^b

^a Lepidocrocite.^b Hematite.

All figures are percentages of the crystalline part estimated from diffractograms (tr: traces).

When the percentages are not given: tr: traces; x: present; xx: common; xxx: abundant.

Some illite/vermiculite interstratification is present in all horizons (not estimated).

of fine clay to total clay decreases with depth in profiles 1 and 2. This trend is less evident in profile 3 (Table 1). The data clearly point to impoverishment of fine particles with some residual enrichment of the coarser fractions in the topsoils. Indications of clay

Fig. 2. Cumulative particle size distribution of the fine earth fraction.

Table 3

Mineralogy of the fine clay fraction ($< 0.2 \mu\text{m}$) estimated by X-ray diffraction

profile		sum of > 1.0 nm ^a	K-mica	kaolinite	pyro- phyllite	halloysite	free iron minerals ^b
1	AEh	48	41	11	tr	tr	—
	Bw1	39	51	10	tr	x	—
	Bw2	22	68	10	tr	x	x
	C	2	81	17	—	x	x(x)
2	AEh	36	56	8	tr	—	tr
	Bw1	28	64	8	tr	—	tr
	Bw2	27	67	6	tr	x	tr
	C	tr	100	tr	—	—	x

^a Sum of (hydroxy interlayered) vermiculite, smectite and interstratified minerals.^b Goethite and some lepidocrocite.

All figures are percentages estimated from diffractograms (tr: traces).

When the percentages are not estimated: tr: traces; x: present; xx: common; xxx: abundant.

In profile 3 K-mica, (hydroxy interlayered) vermiculite, smectite, kaolinite and halloysite are present, percentages were not estimated due to the poor crystallinity.

translocation such as a larger clay or fine clay content in the B horizon lack (Fig. 2). Moreover, in thin sections from the B horizons clay illuviation features are absent.

The mineralogical composition of the clay fractions of profiles 1 and 2 closely resembles that of the powdered phyllite (Table 2). The clay fraction of the C horizons contains of 94 to 98% K-mica, with some chlorite and small amounts of pyrophyllite, halloysite and free iron minerals (Table 2). The K-mica is a well crystallised muscovite with a phengitic composition, characterised by a sharp 1.0 nm reflection with a somewhat asymmetric base. This is in agreement with the results of Azzaro et al. (1976), who found that in the bulk of the Verrucano formation the K-mica is phengitic. Apparently, weathering in the C horizons is still in its initial stage, as is also evidenced by the absence of clay minerals such as kaolinite, smectite and vermiculite. Towards the surface the amount of K-mica decreases, and (hydroxy-interlayered) vermiculite, and eventually in the AEh horizons, smectite appear. The sum of the 2:1 minerals [K-mica, (hydroxy-interlayered) vermiculite and smectite], however, remains constant. The amount of primary chlorite remains virtually constant (2–6%), and some kaolinite is present (2–6%). In addition, small amounts of interstratified K-mica/vermiculite were found (Table 2). The crystallinity of the fine clay fraction ($< 0.2 \mu\text{m}$) is weak, which makes it very difficult to distinguish between (hydroxy-interlayered) vermiculite, smectite and illite/smectite interstratifications (Table 3). The trends in the mineralogical composition of the fine clay fraction are, however, comparable to those of the total clay fraction: towards the (mineral) soil surface there is an increase in vermiculite and smectite at the expense of K-mica (Table 3).

The essentially constant sum of 2:1 minerals and also the alteration of micaceous minerals to (hydroxy-interlayered) vermiculite and smectite as seen in Table 2 are typical for weathering in podzols and some podzolic soils (Brown and Jackson, 1958; Allen and Hajek, 1989). This weathering sequence, from K-mica to vermiculite and

smectite, is attributed to leaching out of K^+ , substitution of some octahedral Al [by Fe(II), Fe(III) and Mg] and replacement of the K-interlayer by a hydroxy-interlayer and, ultimately, dissolution of the hydroxy-interlayer in an acid environment (Jackson, 1964; Douglas, 1989). The small amounts of kaolinite can be due to weathering of halloysite or pyrophyllite (Allen and Hajek, 1989). Iron oxide minerals (goethite, hematite and lepidocrocite) are common in the parent rock and their amount decreases upon weathering (Table 2).

The mineralogical composition of the clay fraction of profile 3 differs considerably from that of the parent rock (Table 2). Clay minerals (hydroxy-interlayered vermiculite and kaolinite) constitute 40% of the total clay fraction, and pyrophyllite is absent in the C horizon. The parent rock of profile 3 (yellowish sandstone) was probably subjected to high grade diagenesis rather than metamorphism, as a result of which clay minerals were conserved (Winkler, 1974). This is confirmed by the absence of pyrophyllite, associated with low-grade metamorphism, in the C material. Except for the abundance of inherited kaolinite, the weathering sequence is comparable to that of profile 1 and 2 but more pronounced. This can be seen from the large amount of hydroxy-interlayered vermiculite in the lower part of the profile and the disappearance of chlorite in the upper horizons of profile 3. The mineralogical composition of the fine clay fraction is comparable to that of the total clay fraction, but, within the profile no clear trends can be observed (Table 3).

4.3. Chemical composition of the fine earth and clay fractions

The decrease in amount of fine particles from the C horizon to the surface, indicated by the data in Fig. 2, is also reflected in the elemental composition of the fine earth fractions: the SiO_2 content increases from the C horizon upward, whereas the content of Al_2O_3 , MgO and K_2O , which occur mainly in the clay fraction, decrease (Table 4). Contents of other elements, like Fe(II), Ca, Mn and P are small in the parent rock and increase from bottom to top in the soil profile (Table 4). This increase is either due to weathering and organic complexation (Fe(II)), or to cycling of these elements in the biological system (Ca, Mn and P; Van Wesemael, 1993a). The large amount of CaO in the AEh horizon of all profiles can probably be attributed to deposition of calcium rich aeolian dust (Pye, 1992).

The elemental composition of the total clay fraction shows a decrease in Al_2O_3 , Fe_2O_3 and K_2O combined with an increase in FeO, MgO, CaO and TiO_2 concentrations towards the (mineral) soil surface (Table 5). The trends in the FeO, MgO, K_2O and Al_2O_3 contents can be explained by the transformation of K-mica into (hydroxy-interlayered) vermiculite and smectite. These trends will be treated in more detail in the next paragraph. The increase in TiO_2 concentration towards the (mineral) soil surface is caused by residual enrichment and points to dissolution of clay. The increase in CEC towards the surface is due most probably to the increase in vermiculite and smectite and to a lesser extent to the incomplete removal of organic matter (Table 5). This is best expressed in profiles 1 and 2 with a C horizon consisting entirely of K-mica with a small CEC. The elemental concentrations in the coarse clay fraction show approximately the same trends as those in the total clay fraction (Table 6).

The decrease in K_2O/MgO ratios in all fractions can only be seen in profiles 1 and 2 (Table 7). It corresponds with the transformation of K-mica into vermiculite and smectite due to the leaching of K from the interlayers (Douglas, 1989; Table 2). The K_2O/MgO ratios in profile 3 are rather constant throughout the profile and are generally smaller than in the other profiles (Table 7). This corresponds with the smaller and rather constant K-mica contents (Table 2). The increase in FeO towards the surface, as witnessed from the FeO/MgO and the FeO/TiO_2 ratios in all fractions, can be explained by the increase in (hydroxy-interlayered) vermiculite and smectite, in which substitution of some octahedral Al occurs, and Fe(II) is trapped in the hydroxy-interlayers (Jackson, 1964; Carstea et al., 1970; Verstraten, 1980; Barnhisel and Bertsch, 1989). The sharp increase in the FeO content in the AEh horizons of the fine earth fraction is mainly due to the larger organic matter content. The typical behaviour of aluminium is best expressed in the Al_2O_3/TiO_2 ratios of the fine clay fraction (Table 7). These are largest in the Bw horizons, which corresponds with the appearance of (hydroxy-interlayered) vermiculite in these horizons (Table 2). This corroborates with the weathering sequence of the soil minerals: formation of aluminium hydroxy-interlayering in the lower part of the soil profile and dissolution of these interlayers in the acid environment of the topsoil (Table 2; Douglas, 1989).

4.4. Selective extractions of the fine earth fraction

Both total iron (Fe_t) and dithionite extractable iron (Fe_d) decrease from C horizons to AEh horizons in all profiles (Fig. 3), while total iron is largest in the parent rock (Table

Table 4
Loss on ignition (LOI) and elemental composition of the fine earth fraction (< 2 mm)

profile		LOI (1000° C)	elemental concentrations in weight percentage on ash free base (LOI 1000° C)										
			SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅
1	AEh	25.8	78.5 ^a	9.5	2.9	0.85	0.2	0.57	1.39	0.25	1.55	0.73	0.08
	Bw1	6.5	83	9.5	3.4	0.25	0.03	0.37	0.05	0.22	1.63	0.70	0.04
	Bw2	3.9	77.5	12.1	4.4	0.27	0.01	0.49	0.02	0.26	2.57	0.77	0.03
	C	4.7	65.5	17.3	6.0	0.10	tr	0.83	tr	0.28	4.25	0.91	0.03
2	AEh	17.9	86	6.8	1.8	0.57	tr	0.36	0.29	0.21	1.14	0.61	0.04
	Bw1	6.4	82.5	7.9	2.6	0.25	tr	0.31	0.04	0.22	1.34	0.65	0.03
	Bw2	4.3	84	9.1	3.2	0.17	tr	0.31	tr	0.26	1.58	0.70	0.03
	C	3.2	79	13.3	4.4	0.14	tr	0.37	tr	0.43	2.71	0.83	0.03
3	AEh	29.2	86	6.0	1.8	0.47	0.01	0.43	0.73	0.26	1.11	0.54	0.05
	Bw1	6.9	83.5	7.0	2.6	0.25	0.01	0.37	0.13	0.27	1.18	0.61	0.02
	Bw2	4.4	77.5	10.8	3.3	0.28	0.02	0.68	0.13	0.47	1.70	0.80	0.02
	C	5.1	72	14.2	5.3	0.16	0.02	0.77	0.09	0.36	2.08	0.91	0.03
<i>Parent rocks</i>													
	phyllite	3.6	61	20.4	8.2	0.08	tr	0.34	0.03	0.52	4.17	1.15	0.06
	sandstone	1.3	84	8.0	1.7	0.06	tr	0.18	0.02	0.23	1.71	0.51	0.03
	anagenite	1.2	81	6.5	5.0	0.06	tr	0.25	0.02	0.19	1.31	0.36	0.04

^a Value probably too low.

tr: trace.

Table 5
CEC, loss on ignition (LOI) and elemental composition of the total clay fraction (< 2 μm)

profile	CEC _{pH7} (mmol _c kg ⁻¹)	LOI (1000° C)	elemental concentrations in weight percentage on ash free base (LOI 1000° C)								
			Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂
1	AEh	10.6	32.0	4.4	0.54	0.04	1.11	0.07	0.63	5.90	1.05
	Bw1	61	33.2	7.1	0.28	0.05	1.00	0.02	0.96	5.80	0.99
	Bw2	173 ^a	34.5	8.0	0.29	0.02	0.93	0.03	0.81	7.15	0.85
	C	20	33.5	10.4	0.35	tr	0.89	0.02	0.58	7.77	0.77
2	AEh	10.8	31.9	4.2	0.45	0.01	1.11	0.04	0.90	6.24	1.27
	Bw1	63	33.1	6.7	0.59	0.01	0.95	0.03	1.10	6.21	1.15
	Bw2	55	33.5	8.9	0.35	0.01	0.80	0.02	1.13	6.46	1.10
	C	12	34.4	8.7	0.26	tr	0.55	0.03	1.29	7.59	0.94
3	AEh	20.7	28.4	2.8	1.50	0.02	1.60	0.06	0.34	5.36	1.69
	Bw1	80	28.8	13.1	0.72	0.02	1.44	0.04	0.39	4.50	1.50
	Bw2	102	32.4	10.1	0.48	0.03	1.44	0.04	0.33	4.15	1.42
	C	141	10.1	32.6	10.6	0.51	0.02	1.36	0.03	3.94	1.22

^a Unrealistic value.
tr: trace.

Table 6
Loss on ignition (LOI) and elemental composition of the coarse clay fraction (0.2–2 μm)

profile	LOI (1000° C)	elemental concentrations in weight percentage on ash free base (LOI 1000° C)								
		Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂
1	AEh	32.1	2.6	0.48	0.01	0.70	0.06	0.70	6.36	1.14
	Bw1	32.8	4.3	0.35	0.02	0.68	0.03	0.82	6.64	1.05
	Bw2	34.4	3.8	0.34	0.01	0.79	0.02	0.74	8.12	0.87
	C	35.3	3.5	0.33	tr	0.82	0.01	0.61	8.96	0.68
2	AEh	32.6	2.5	0.49	0.01	0.82	0.04	0.92	7.10	1.55
	Bw1	33.1	3.7	0.53	0.01	0.71	0.03	1.07	7.07	1.26
	Bw2	33.5	4.4	0.33	tr	0.62	0.02	1.07	7.27	1.37
	C	35.3	3.8	0.28	tr	0.47	0.02	1.30	8.33	0.95
3	AEh	27.3	2.0	1.09	0.01	1.09	0.08	0.49	6.66	2.10
	Bw1	27.4	6.8	0.73	0.02	1.24	0.06	0.40	5.59	1.88
	Bw2	11.9	6.6	0.71	0.02	1.37	0.05	0.38	5.10	1.74
	C	10.1	6.4	0.58	0.02	1.34	0.04	0.38	5.40	1.61
trace.										

tr: trace.

Table 7
Molar ratios of the total clay (< 2 μm) and fine clay (< 0.2 μm) fraction

profile	total clay fraction (< 2 μm)					fine clay fraction (< 0.2 μm)				
	Al ₂ O ₃ / Fe ₂ O ₃	Al ₂ O ₃ / TiO ₂	K ₂ O / MgO	FeO / MgO	FeO / K ₂ O	Al ₂ O ₃ / Fe ₂ O ₃	Al ₂ O ₃ / TiO ₂	K ₂ O / MgO	FeO / MgO	FeO / K ₂ O
1										
AEh	11.5	24	2.3	0.27	0.12	6.0	34	1.0	0.24	0.23
Bw1	7.3	36.5	2.5	0.16	0.06	3.0	37	1.1	0.11	0.10
Bw2	6.8	31.5	3.3	0.18	0.05	2.4	40.5	1.7	0.11	0.06
C	5.1	34	3.7	0.22	0.06	1.5	37	1.9	0.16	0.09
2										
AEh	12	19.5	2.4	0.23	0.09	6.9	33.5	1.4	0.17	0.12
Bw1	7.8	22.5	2.8	0.35	0.13	4.2	39.5	1.5	0.19	0.13
Bw2	5.9	24	3.5	0.24	0.07	2.8	38	1.8	0.14	0.08
C	6.2	28.5	6.0	0.26	0.04	2.0	45.5	4.4	0.24	0.06
3										
AEh	16	13	1.4	0.53	0.37	9.0	20	0.86	0.29	0.33
Bw1	3.5	15	1.3	0.28	0.21	2.3	22	0.82	0.14	0.17
Bw2	5.0	18	1.2	0.19	0.15	3.4	32.5	0.79	0.07	0.09
C	4.8	21	1.2	0.21	0.17	3.4	30.5	0.85	0.10	0.12

Fig. 3. Dithionite (d), oxalate (o) and pyrophosphate (p) extractable iron combined with total iron (t) and silicate bound iron (t-d).

4). Pyrophosphate extractable iron (Fe_p) is almost equal to oxalate extractable iron (Fe_o) and shows an increase in the Bw horizons (Fig. 3). The silicate bound iron (Fe_{t-d}) decreases from bottom to top of the profiles (Fig. 3). However, this decrease is less than the decrease in clay content, which implies that iron is built in the clay structure upon weathering. This corresponds with the transformation of pure K-mica into (hydroxy-interlayered) vermiculite and smectite, which is accompanied by an increased substitution of octahedral Al and trapping of iron in the hydroxy-interlayers (Jackson, 1964; Carstea et al., 1970; Brinkman, 1977; Verstraten, 1980). The Fe_o/Fe_d ratio indicates the degree of crystallinity of the free iron oxides (Blume and Schwertmann, 1969). Its clear decrease with depth in all profiles confirms the relative importance of amorphous and organic iron complexes in the AEl and Bw1 horizons (Table 8).

The amounts of pyrophosphate and oxalate extractable iron are comparable, indicating the relative importance of metal organic complexes (Fig. 3). According to Mokma and Buurman (1982) the solubility of organo-metal complexes depends on the ratio between carbon and metal ions. They found that for podzols, the atomic ratio between total carbon and aluminium in selective extracts ($\text{C}_t/\text{Al}_p = 40$, $\text{C}_p/\text{Al}_p = 30$) is a measure for the discrimination between eluvial (> 40 and 30 respectively) and illuvial horizons (< 40 and 30 respectively). In the studied mediterranean soil profiles, these values distinguish between AEl and B horizons, provided that the critical C_p/Al_p is set at about 20 (Table 8). Free iron and aluminium to clay ratios, which are used as diagnostic property for spodic horizons, are relatively constant in profiles 1 and 2 (Table 8). The Al_d/clay ratio in profile 3 is generally larger and both Al_d/clay and Fe_d/clay increase from C to Bw1 and are again less in the AEl horizon (Table 8). These trends can be ascribed mainly to mobility of organo-metal complexes rather than to a strong degradation of clay minerals considering the small Al_d/clay ratios (0.01–0.03; Verstraten, 1980). Although a spodic horizon has not (yet) developed, it can be concluded that the mobility of iron and aluminium has been considerable, in particular in soil profiles 1 and 3 which have a well-developed moder humus profile (see also Van Wesemael and Verstraten, 1993).

5. Soil formation on low-grade metamorphic rocks under mediterranean climatic conditions

According to current concepts (Paquet, 1970; Duchaufour, 1982), in the mediterranean zone, degradation of illite (K-mica) to vermiculite is restricted to leaching environments in which cations are lost, while the transformation of illite to montmorillonite is restricted to environments which are rich in basic cations. Moreover, a rapid turnover of organic matter and high base saturation clearly exclude migration of aluminium and iron through complexation.

The catena of Fig. 1 indicates that, although some lateral drift of the regolith on steep slopes and some colluviation in the valley bottom occurs, the trends in the investigated profiles on the crests can be attributed to in situ pedogenesis (Pedroli et al., 1988). Furthermore, previous work on spatial distribution of humus profiles (6 forest stands up to 10 km apart; Van Wesemael and Veer, 1992) and on soil conditions in various soil profiles (within 3 forest stands; Van Wesemael, 1993b) indicates that slow decomposition of organic matter and acid conditions in the mineral soil with low base saturation are characteristic for an extensive area underlain by acid low-grade metamorphic rocks. The soil profiles showed a prominent impoverishment of both fine particles and elements other than silica. Considering the similar trends in molar ratios of all fractions and the relative increase of the fine clay towards the surface, acid dissolution of clay minerals rather than selective lateral eluviation of fine particles is the most important process. Furthermore, clear evidence for complexation and migration of Al and Fe was found, although these processes did not lead to the development of a spodic horizon. The weathering sequence of clay minerals is similar to that of podzols and podzolic soils and is most clearly expressed in the soil profiles on phyllite (profiles 1 and 2):

Table 8

Ratios between dithionite (d), oxalate (o) and pyrophosphate (p) extractable and total iron, aluminium and carbon

profile		weight ratios				atomic ratios			
		Fe _o /Fe _d	Fe _d /clay	Al _d /clay	(Fe _p + Al _p)/clay	C _t /Al _d	C _t /Al _o	C _t /Al _p	C _p /Al _p
1	AEh	0.13	0.07	0.01	0.02	163	140	226	25
	Bw1	0.20	0.07	0.01	0.02	34	30	39	8.5
	Bw2	0.14	0.07	0.01	0.01	10	18	21	3.0
	C	0.09	0.10	0.01	0.00	3.9	5.9	18	7.4
2	AEh	0.35	0.07	0.01	0.02	143	165	195	31
	Bw1	0.38	0.07	0.01	0.01	41	43	61	3.8
	Bw2	0.29	0.06	0.01	0.01	17	24	34	5.3
	C	0.07	0.07	0.01	0.00	5.1	13	23	5.8
3	AEh	0.20	0.06	0.02	0.02	154	265	309	18
	Bw1	0.17	0.09	0.03	0.04	18	23	26	6.5
	Bw2	0.05	0.08	0.03	0.03	3.6	4.6	7.2	2.3
	C	0.03	0.07	0.02	0.01	1.9	3.3	6.0	1.4

transformation of K-mica to (hydroxy-interlayered) vermiculite and eventually to smectite (Brown and Jackson, 1958). The soil on sandstone (profile 3) is probably too shallow to display a complete weathering sequence, since hydroxy-interlayered vermiculite is already present in the C horizon. Kaolinite in this soil profile was probably not destroyed during diagenesis, and is therefore inherited (Weaver and Beck, 1971).

The observed phenomena evidently do not comply with the current concepts (Paquet, 1970; Duchaufour, 1982) and in fact are typical for acid soils in temperate humid and cooler climates, in particular for podzols and podzolic soils (Brown and Jackson, 1958; Allen and Hajek, 1989). However, the simple assumption of podzolisation being the main process in the soils studied conflicts with two other important features: the high base saturation of the topsoil and a prominent impoverishment of the mineral soil in the absence of a distinct spodic B horizon.

Soil conditions and litter decomposition are such that a high level of nutrient cycling is maintained in the ectorganic horizons and upper part of the mineral soil (Van Wesemael, 1993a,b). The concentrations of basic cations and organic anions in the soil solution decrease rapidly with depth (Van Wesemael and Verstraten, 1993). This can be explained as follows: the major part of the basic cations and organic anions are released during decomposition of organic matter in the ectorganic layer and are leached into the mineral soil. These basic cations and ammonium (the dominant inorganic N species) are partly exchanged for hydrogen ions through root uptake, whereas the major part of the organic anions are mineralised. The remaining organic acids probably form complexes with aluminium and iron (Van Wesemael and Verstraten, 1993). This vertical, spatial de-coupling of mineralisation and root uptake after the formation of a well-developed ectorganic layer results in acidification of the upper part of the mineral soil (Ulrich et al., 1979). A high base saturation and CEC is maintained by the insoluble organic matter in the AEh horizon, while in the lower soil horizons the CEC is small and aluminium is the most important exchangeable cation (Van Wesemael, 1993b).

As stated before, signatures of clay translocation were not found. Moreover, soil conditions are such that transport of fine particles by lateral subsurface flow is very improbable. The well-developed ectorganic layer protects the topsoil against drop impact and erosion, and in the B horizon peptization of clay is very unlikely to occur considering the acid nature of these horizons and the abundance of exchangeable Al. Although some lateral transport of fine particles may have occurred during initial soil formation, it must be concluded that the impoverishment is largely due to dissolution of clay minerals and the subsequent removal of solutes by lateral subsurface flow.

Although a budget study in this hilly terrain is beyond the scope of this paper, it still is useful to evaluate whether the production of acids in the organic horizons can be responsible for the impoverishment of the soil profiles by acid hydrolysis. To that purpose the loss of acid neutralising capacity (ΔANC) of the soil profile was compared to proton inputs by decomposition of organic matter in three forest types.

The maximum amount of acidity ($\text{kmol}_c \text{ ha}^{-1}$) required to cause the decrease in acid neutralising capacity (ΔANC) in the soil profiles was calculated from the sum of the differences in ANC (Eq. 1; Van Breemen et al., 1983) between the soil horizons (AEh, Bw1 and Bw2) and the C horizon (Table 9). The ΔANC ranges from about 14,000 $\text{kmol}_c \text{ ha}^{-1}$ in profile 2 to almost 22,500 $\text{kmol}_c \text{ ha}^{-1}$ in profiles 1 and 3. Since the

Table 9
Acid neutralising capacity (ANC) of the soil profiles

profile	thickn. (cm)	bulk dens. (g cm ⁻³)	element concentration in mol kg ⁻¹						ANC ^a (mol _c kg ⁻¹)	ΔANC ^b (kmol _c ha ⁻¹)
			Na ₂ O	K ₂ O	CaO	MgO	FeO	Fe ₂ O ₃		
1	AEh	3	0.79	0.03	0.12	0.18	0.09	0.13	6.02	1425
	Bw1	18	1.31	0.03	0.16	0.01	0.03	0.20	7.04	14220
	Bw2	13	1.31	0.04	0.26	tr	0.04	0.27	9.36	6614
	C	27	n.d	0.04	0.43	tr	0.01	0.36	13.2	—
									Σ profile 1:	22260
2	AEh	2	0.97	0.03	0.10	0.07	0.07	0.09	4.46	1087
	Bw1	13	1.22	0.03	0.13	0.01	0.03	0.15	5.79	6772
	Bw2	13	1.46	0.04	0.16	tr	0.02	0.19	6.86	6075
	C	35	1.53	0.07	0.28	tr	0.02	0.27	10.06	—
									Σ profile 2:	13935
3	AEh	1	0.98	0.04	0.08	0.09	0.05	0.08	3.60	690
	Bw1	24	1.09	0.04	0.12	0.02	0.03	0.15	5.31	14340
	Bw2	23	1.24	0.07	0.17	0.02	0.04	0.20	8.20	7375
	C	12	n.d	0.05	0.21	0.02	0.02	0.31	10.8	—
									Σ profile 3:	22400

^a ANC = 6(Al₂O₃) + 2(CaO) + 2(MgO) + 2(K₂O) + 2(Na₂O) + 6(Fe₂O₃) + 2(FeO) in mol kg⁻¹. Concentrations of MnO and P₂O₅ are negligible.

^b ΔANC: change in ANC due to weathering, based on the composition of the C horizon.

Table 10

Acid production caused by mineralization of litter

litter input ^a	in kmol ha ⁻¹ yr ⁻¹										kmol _c ha ⁻¹ yr ⁻¹
	K	Na	Ca	Mg	Fe	Mn	Al	N	P	S	cations + N – P – 2 * S
deciduous	0.40	0.08	1.64	0.66	0.04	0.17	0.09	4.60	0.10	0.18	9.95
sclerophyllous	0.69	0.05	1.89	0.47	0.03	0.21	0.07	3.36	0.07	0.19	9.05
pine	0.28	0.05	1.00	0.29	0.05	0.02	0.11	3.08	0.04	0.21	6.00

^a Derived from Van Wesemael (1993a).

input of atmospheric acidity on the forest floor (sum of free acidity and NH_4^+) is relatively small (1.1 kmol_c ha⁻¹ in Tuscany; Barbolani et al., 1988; unpublished data), the spatial de-coupling of mineralisation (in the mature ectorganic layer) and root uptake (in the endorganic horizon) is the most important source of acidity for the mineral soil (Table 10). In a steady state condition, the input of elements through litter fall is equal to the uptake of elements by roots. Provided that the de-coupling of mineralisation and root uptake is complete, the input of acids into the mineral soil is equal to the sum of cations and nitrogen (exchanged for H^+ during root uptake) subtracted with sulphur and phosphorus (exchanged for an equivalent amount of OH^- during root uptake). The acidity produced and entering into the mineral soil ranges from 6 to 10 kmol_c ha⁻¹ yr⁻¹ for the major vegetation types (Table 10). The dominant form of inorganic nitrogen is NH_4^+ (Van Wesemael, 1993b). Nitrification and subsequent root uptake does not influence the net acidification in the mineral soil, and leaching of nitrate produces an extra equivalent amount of acids (Van Breemen et al., 1983). The foregoing implies that the time required for the impoverishment, observed in the solum, is about 2000 to 4000 years (Tables 9 and 10), ignoring the acidifying effects of processes such as export of timber and litter as well as net accumulation of bases in the vegetation and ectorganic layer after large-scale clearing or forest fires. This calculated age is very realistic for relatively young soils.

The calculations clearly support the earlier conclusion, that dissolution of clay under acid conditions (pH 4.0–4.5) is an important process in these soils, resulting in transformation of K-mica into vermiculite and smectite, and in a significant impoverishment. Aluminium and iron freed by weathering are partly trapped in 2:1 minerals as hydroxy-interlayers. The mobility of Al and Fe apparently is determined by organic complexation. The impoverishment must be largely due to lateral subsurface flow causing the removal of basic cations and Al and Fe as organo–metal complexes. Strong indications for this process are: the absence of cheluviation features, the strong positive correlation between Al, Fe and DOC and the small metal organic acid ratios in soil waters, the results of the selective extracts and the lesser hydroxy-interlayering in the topsoil.

6. Conclusions

Soil forming processes in the investigated mediterranean forests, where litter decomposition rates are slow, are dominated by clay hydrolysis under acid conditions (pH

4.0–4.5) and to a lesser extent complexation of iron and aluminium by organic matter. The morphological characteristics of the soil profiles are: a moder type humus profile and a greyish Ah horizon without illuviation features in the B horizon. The proposed mode of pedogenesis is restricted to acid parent materials in mediterranean climates with enough precipitation to ensure a leaching soil moisture regime, provided that lateral removal of soluble weathering products is feasible. This process deviates from the current concept of fersiallitisation, in which neoformation of 2:1 clay minerals and formation of free iron clay complex under neutral conditions prevails.

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