

Clay minerals and the development of Quaternary soils in central Italy

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ABSTRACT

Clay mineral analysis is widely used to characterize soil parent material and to relate it to the bedrock. When it is applied to a soil profile, it can give a 'genetic signal' of mineralogical transformations due to soil-forming processes. In this study, ten selected soil profiles in Montagnola Senese, central Italy, were analyzed for genetic signals of soil ageing, eluviation and illuviation, fragipan formation, and other processes. In previous investigations, the parent materials of benchmark soils of the area have been dated to gain an understanding of the Quaternary geomorphological evolution, which spans a time ranging from early Pleistocene to Holocene. The number of profiles selected allowed a statistical analysis of the parameters.

Illite and kaolinite are the most quantitatively important phyllosilicates in the soils studied. The other clay minerals found are vermiculite, hydroxy-interlayered vermiculite (HIV), illite-HIV and illite-chlorite mixed layers, and chlorite. Soil ageing is characterized by a change in clay mineral composition that increases with age. Argilluviation is marked by a preferential accumulation of kaolinite in illuvial horizons, while formation of tongues in fragipans does not cause any significant difference in clay mineral composition between bleached and stained parts of the horizons. Furthermore, bulk density of fragipans is not related to clay mineral content. On the other hand, large bleached masses in more mature soils contain more kaolinite and vermiculite than the surrounding mass. The trends in the contents of clay minerals through the soil horizons confirm the two types of lithological discontinuities that were predicted during the field survey.

Key words: clay minerals, soil-forming processes, Quaternary, central Italy.

RESUMEN

El análisis de minerales arcillosos se usa ampliamente para caracterizar el material parental del suelo y relacionarlo con el lecho rocoso. Cuando se aplica a un perfil de suelo, puede dar una "señal genética" de transformaciones mineralógicas debidas a procesos pedogenéticos. En este estudio, se analizaron diez perfiles de suelos seleccionados en Montagnola Senese, Italia central, buscando señales genéticas del envejecimiento del suelo, eluviación e iluviación, formación de fragipanes y otros procesos. En investigaciones previas, los materiales parentales de los suelos de referencia del área han sido fechados para obtener una mejor comprensión de la evolución geomorfológica del Cuaternario, que abarca el tiempo comprendido entre el Pleistoceno temprano y el Holoceno. El número de perfiles seleccionados permitió un análisis estadístico de los parámetros.

Illita y kaolinita son los filosilicatos cuantitativamente más importantes. Los otros minerales arcillosos encontrados son vermiculita y vermiculita interestratificada con grupos hidroxilo (HIV), illita-

HIV y capas mezcladas de illita-clorita, y clorita. El envejecimiento del suelo se caracteriza por un cambio en la composición de minerales arcillosos, que aumenta con la edad. La argiluvación está marcada por una acumulación preferencial de caolinita en horizontes iluviales, mientras que la formación de lenguas en fragipanes no produce ninguna diferencia significativa en la composición de minerales arcillosos entre las partes lavadas y manchadas de los horizontes. Más aún, la densidad aparente de los fragipanes no está relacionada con el contenido de minerales arcillosos. Por otra parte, las grandes masas lavadas en suelos más maduros contienen más kaolinita y vermiculita que la masa circundante. Las tendencias de los contenidos de minerales arcillosos a través de los horizontes del suelo confirman los dos tipos de discontinuidades litológicas que fueron pronosticadas durante levantamientos de campo.

Palabras clave: minerales arcillosos, procesos formadores de suelo, Cuaternario, Italia central.

INTRODUCTION

Clay mineral analysis has been widely used to characterize soil parent material and to relate it to the bedrock (Bronger *et al.*, 1994), as well as to associate mineralogical transformations with changes in climate and weathering intensity (Bini and Mondini, 1992). The knowledge provided by the clay mineral composition of soils is greatly increased when it is coupled with other studies, such as through geological, geomorphological and soil surveys. Important investigation techniques include detailed profile descriptions, micromorphology, and laboratory analyses, like iron oxides and heavy minerals content (Ajmone-Marsan *et al.*, 1986; Assallay *et al.*, 1998; Kallis *et al.*, 2000).

The soils of the Montagnola Senese territory, in central Italy, have already been studied to appraise the relationships between Quaternary geomorphological evolution and the occurrence of fragipans and other naturally consolidated ('close packed' or 'dense') horizons (Costantini *et al.*, 1996), the influence of parent material on soil genesis (Costantini *et al.*, 1992; Mirabella *et al.*, 1992), soil geochemistry (Costantini *et al.*, 2002a), and ageing indicators (Costantini *et al.*, 2002b). They were also investigated to evaluate their cultural and ecological value (Costantini, 2000; L'Abate and Costantini, 2000).

In this work, the clay mineral composition is related to some soil-forming processes and characteristics, *i.e.*, soil ageing, eluviation and illuviation, fragipan and bleached tongue formation, and origin of discontinuities within a soil profile. These processes are of particular interest, because they characterize paleosols formed in the Quaternary in many places, not only in the Mediterranean environment. The clay mineral composition of a soil, as well as the variations between its horizons and the parts of the same horizon, mark the mineralogical transformations due to soil-forming processes. They are the 'genetic signals' of pedogenic events (Bockheim and Gennadiyev, 2000). Such genetic signals found in the Montagnola Senese soils can be used to correlate and understand soil-forming processes that occurred in other territories in the Quaternary.

MATERIALS AND METHODS

General setting

The study area is located in central Italy (Tuscany) (Figure 1); it constitutes a part of a broad ridge that emerged from the sea during the Miocene and underwent intense geomorphological evolution during the Pliocene and Quaternary periods. Major events of erosion and stability alternated as a consequence of tectonic activity and climatic variations, but direct evidence of glacial processes are lacking (Costantini *et al.*, 1996). The land uplift led to erosion, but parts of the region have remained relatively stable over a long time (*e.g.*, relict karst depressions, terraces, and gentle slopes).

The climate of the area (rainfall from a meteorological station inside the area and temperature of the nearby Siena) is typical of a Mediterranean oceanic type (European Commission, 1999), with maximum rainfall in October and minimum in July, which is also the warmest month, while the coldest month is January (Figure 2). The soil moisture regime is 'udic' (Newhall, 1972), with a 'mesic' soil temperature regime, according to Soil Taxonomy (Soil Survey Staff, 1998).

The geology of the area is complex, however, rocks and sediments can be grouped as follow: (1) metamorphic rocks consisting of fine-grained chlorite-sericite schist, jasper, quartzose conglomerate, and violet schist breccias, all free of carbonates for the major part; (2) calcareous rocks, composed of flint limestone, marble, and dolomite; (3) slope and alluvial deposits derived from the local bedrock. The land use of the area is mainly woodland with dominance of chestnut trees (*Castanea sativa*) on acid metamorphic rocks and acid soils, and evergreen Holm oak (*Quercus ilex*) on shallow soils on limestone. Agricultural lands are limited by the stoniness of the soils on limestone and the steepness of slope; however, almost a third of the area is cultivated with small grain crops and maize, grasslands, vineyards, olive groves, and orchards.

More than 50 profiles have been described and analyzed in past studies. The present study only considers

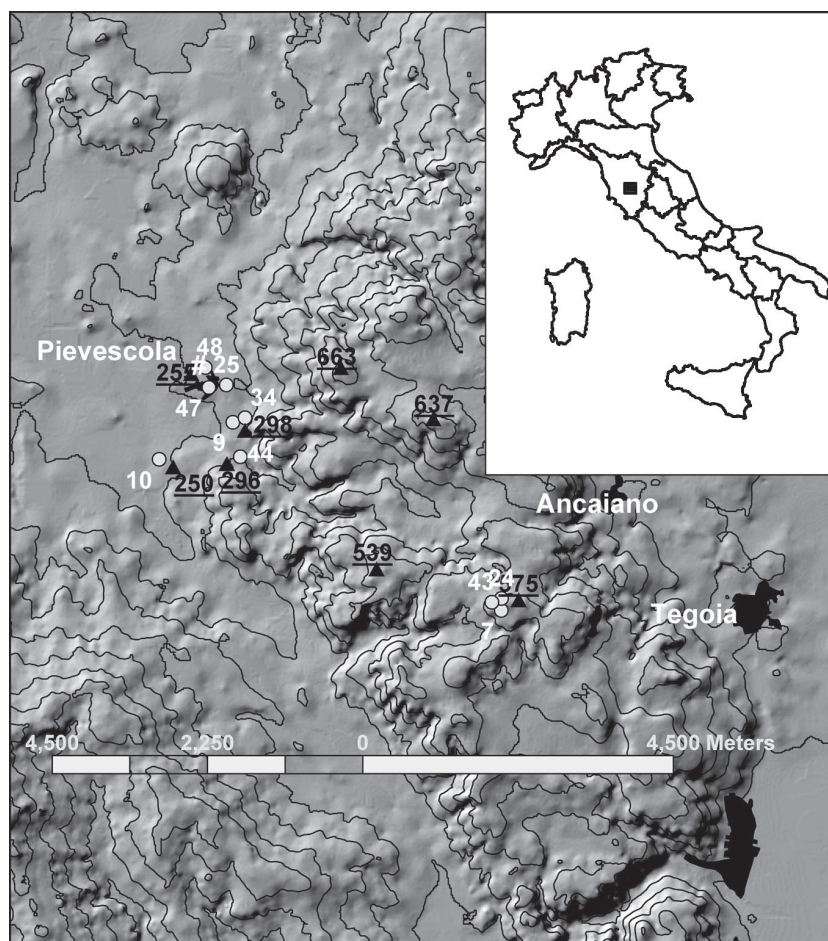


Figure 1. Hillshade map of the study area and location of profiles. Elevations are underlined. Contour interval is 50 m.

ten benchmark soils derived from schist and from slope and alluvial deposits (Table 1). The ten soils are representative of the different typologies found on the following parent materials: (1) rock; (2) thin (typically less than 2 meters), or (3) thick (commonly several meters) slope deposits and karst depression in-fillings; and (4) sediments of the coalesced alluvial fans that form most of the present day terraces. The terrace sediments border the western part of the ridge and in places exceeds 13 meters thickness. Costantini *et al.* (1996) found that the slope deposits and terrace sediments were always weathered.

The age of the parent material of the ten profiles was estimated on the basis of a geological reconstruction (Bartolini *et al.*, 1982), detailed geomorphological and soil surveys, a correlation with the morphological and micromorphological features of similar Italian soils reported in other studies (Magaldi, 1979; Previtali, 1985; Cremaschi and Sevink, 1987; Ajmone-Marsan *et al.*, 1994), and one significant fossil assemblage from the lower part of profile 7, where Fondi (1972) found remains of Cromerian fauna (early–middle Pleistocene) calcified together with the lowest soil horizon. The ages of the soil parent materials were

determined to be (i) Holocene, (ii) late and middle Pleistocene, or (iii) early Pleistocene. The lack of data about the age of each profile precluded more specific age assignments or correlations with deep-sea sediment oxygen isotope records.

Following Soil Taxonomy (Soil Survey Staff, 1998), the soils were classified as Udorthents, Dystrudepts, Hapludalf, Fragiudalf, Fraglossudalf and Paleudalf, or as Leptosols, Cambisols, Luvisols and Plinthosols with the World Reference Base for Soil Resources (FAO, 1998).

The presence of fragipan and other dense horizons is a common characteristic of the older soils of the Montagnola Senese territory formed in carbonate free deposits. They have been called ‘close packed’ by Costantini *et al.* (1996), because they show bulk densities higher than $1.6 \text{ Mg}\cdot\text{m}^{-3}$, up to $1.87 \text{ Mg}\cdot\text{m}^{-3}$ (average $1.69 \text{ Mg}\cdot\text{m}^{-3}$), whereas not dense Bt horizons have a mean bulk density of $1.51 \text{ Mg}\cdot\text{m}^{-3}$ and surficial horizons $1.39 \text{ Mg}\cdot\text{m}^{-3}$.

Different types of close-packed horizons were found (Costantini *et al.*, 1996): (1) True fragipan: one that matches all diagnostic criteria of Soil Taxonomy (Soil Survey Staff, 1998). (2) Glossic close-packed horizon: horizons in which

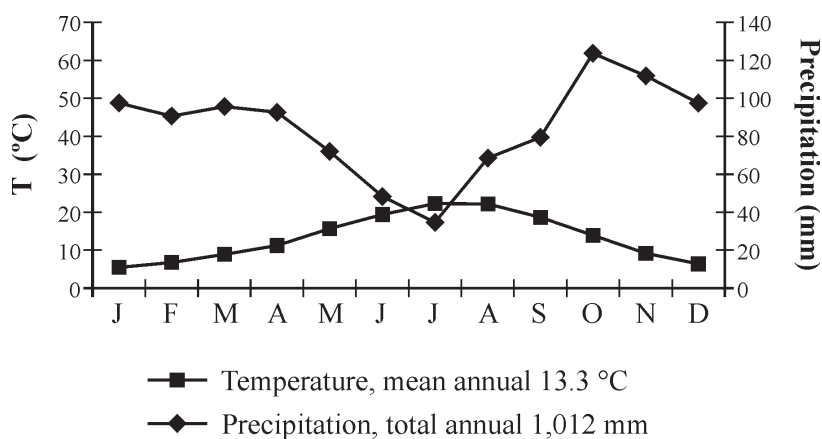


Figure 2. Temperature and precipitation trends of the area.

fragric material does not meet the 60% volume requirements of the fragipan horizon. As a rule, this layer has many bleached streaks and tongues forming a 'glossic' horizon (Soil Survey Staff, 1998), and the remaining mass maintains fragric properties. (3) Densipan: close-packed horizon similar to fragipan except that bleached streaks are rare; clay content is always >35% and structure ranges from moderate coarse prismatic to massive. (4) Pedal dense horizon: close-packed horizon that is not brittle and whose bleached streaks and masses are not coarser than the remaining part of the horizon; the structure is prismatic or angular blocky and clay content is always >35% of the fine earth fraction, it may contain plinthite nodules.

Glossic horizons were always found over fragipans or densipans near the soil surface, where most root development occurs. Unless truncated by erosion, fragipans and densipans are underlying either eluvial E or glossic horizons, or colluvial deposits.

Field and laboratory methods

Soil description followed the methodology of Soil Survey Division Staff (1993); laboratory routine analyses were performed in compliance with the Italian official methods (Ministero delle Politiche Agricole e Forestali, 2000). Plinthite nodules were subjected to the test of Wood and Perkins (1976) with immersion of samples for two hours in water to check the persistence of aggregates. Bulk density was obtained with the core method on replicated samples at field capacity. Cation exchange capacity (CEC) and exchangeable bases were determined by NH_4OAc extraction and spectroscopy; cation exchange capacity of the clay fraction was measured on 14 samples of clay separated by sedimentation or, for the remaining samples, through a correlation with clay content and a correction for the organic matter content.

The clay fraction mineralogy of 57 horizons and parts

of horizons (stained masses and bleached tongues and masses) of the ten selected soils was obtained by X-ray diffraction.

The clay fraction (<2 μm) was separated by gravity sedimentation. Dispersion was facilitated by adding 15 mL of Na-hexametaphosphate, $(\text{NaPO}_3)_6$ (Carnicelli and Mirabella, 1989/1991), and by applying ultrasonic shaking. All the separated clay fraction samples were saturated with K and Mg ions. To get oriented clay minerals, clay samples were placed on glass slides and allowed to dry. In order to isolate the peaks of the minerals, the samples were solvated with ethylene glycol and heated. The Mg-saturated samples were heated to 550° C for 2 h, the K-saturated samples to 350° C for 2 h. Ethylene glycol solvated samples were analyzed to check the presence of expandable minerals.

The clay fraction composition and its semi-quantitative determination were estimated from peak position and peak areas obtained by diffraction using a Philips PW 1710 diffractometer (35 KV, 25 mA, $\lambda=1.5418 \text{ \AA}$) with $\text{Cu-K}\alpha$ radiation at a scanning rate of $1^\circ 2\theta$ per minute. X-ray diffraction identification criteria were based on the indications of Biscaye (1965), Brindley and Brown (1980), Wilson (1987), Dixon and Weed (1989), Barnhisel and Bertsch (1989), and Moore and Reynolds (1997). The clay minerals that made up the examined samples were: illite (the term illite refers here to clay mica, *i.e.*, a nonexpanding 10 \AA mica-like mineral that occurs in the clay size), vermiculite, hydroxy-interlayered vermiculite (HIV), kaolinite, chlorite, interstratified illite-HIV, and interstratified illite-chlorite. Semi-quantitative mineral estimation of the clay minerals was based on the procedure described by Gjems (1967), using the peak area and the correction factors (coefficient of proportionality, C) of diagnostic peaks for each clay mineral.

– Illite: peak area $\cong 10 \text{ \AA}$; C = 1.

– Vermiculite: peak area $\cong 14 \text{ \AA}$; C = 0.34.

– Hydroxy-interlayered vermiculite (HIV): peak area $\cong 14 \text{ \AA}$; C = 0.34.

Table 1. Main characteristics, properties, and classification of the studied profiles according to Soil Taxonomy (Soil Survey Staff, 1998) and the World Reference Base for Soil Resources (FAO, 1998).

Profile	Elevation (m a.s.l.)	FAO (1998)	Soil Survey Staff (1998)	Main characteristics and properties
<i>Soil formed on rock and thin slope deposits</i>				
24	560	Dystric Leptosol	Lithic Udorthent	Acid shallow soil on rock
43	570	Dystric-Skeletal Cambisol	Typic Dystrudept	Brown acid cambic horizon
44	300	Cutani-Chromic Luvisol (Dystric)	Typic Hapludalf	Reddish acid argillic horizon
<i>Soils formed on thick slope deposits and karst depression in-filling (only profile 7)</i>				
34	290	Profondi-Endostagnic Luvisol (Fragi-Chromic)	Typic Fragiudalf	Reddish acid deep argillic horizon, well developed fragipan, stagnic properties
10	245	Chromi-Profondic Luvisol (Fragic)	Fragic Paleudalf	Reddish subacid deep argillic horizon, remnants of fragipan
7	580	Chromi-Profondic Luvisol	Typic Paleudalf	Reddish subacid, deep dense argillic horizon, weak stagnic properties
9	270	Chromi-Profondic Luvisol (Bathifragic)	Fragic Paleudalf	Reddish acid deep argillic horizon, remnants of fragipan
<i>Soils on old alluvial fans</i>				
25	280	Rhodi-Stagnic Luvisol	Aquic Paleudalf	Red not-acid deep dense weak developed argillic horizon, stagnic properties
47	272	Glossalbi-Stagnic Luvisol (Profondic, Chromic, Fragic)	Aquic Fraglossudalf	Red not-acid deep weak developed argillic horizon, glossic horizon, fragipan, stagnic properties
48	275	Eutri-Endostagnic Plinthosol	Plinthaquic Paleudalf	Yellowish not-acid deep dense weak developed argillic horizon, plinthite, stagnic properties

- Kaolinite: peak area $\cong 7 \text{ \AA}$; C = 0.24.
- Chlorite: peak area $\cong 14 \text{ \AA}$; C = 0.34.
- Interstratified illite-HIV (I/V): peak area $\cong 12 \text{ \AA}$, C = 0.40.
- Interstratified illite-chlorite (I/Chl): peak area $\cong 12 \text{ \AA}$; C = 0.40.

The number of profiles selected allowed a statistical analysis of the parameters, to search for significant differences that we assume to be the result of pedological processes. The statistics applied were the t-test for Equality of Means and the Levene's Test for Equality of Variances. The software utilized was SPSS Professional Statistics 6.1 (SPSS, 1994).

RESULTS AND DISCUSSION

Soil ageing

The Mediterranean type of climate is characterized by marked differences between dry and moist seasons. These conditions foster the release of iron from primary Fe-bearing minerals, its oxidation and crystallization in the form of hydroxides and oxy-hydroxides. These minerals, together with other components, in particular organic matter, produce the soil color (Schwertmann, 1985). The degree of rubefaction, that is the soil reddening by pedogenic hematite, tends to increase with age in chronosequences of well drained soils (Torrent, 1995).

The soils studied show brown colors (Munsell 10 YR) in the Holocene horizons (Table 2), while the hue is progressively redder (Munsell 7.5YR–5YR–2.5YR) in the stained part of the horizons, according to the estimated age (Figure 3). In fact, Costantini *et al.* (1996) demonstrated that the increase in total and free iron is the most striking consequence of soil ageing. An opposite trend to soil rubefaction is shown by the CEC of clay, which decreases according to the estimated soil age (Figure 4). The trend of the values suggests a more prominent clay mineralogy transformation passing from the youngest to the Pleistocene soils, and a slower, continuous change in the soils attributed to the Pleistocene.

Illite and kaolinite are the only two species found in all profiles (Table 3). Illite, in particular, is the dominant clay material, a consequence of the physical breakdown of muscovite, which is abundant in schist. A slight decrease in illite from the younger to older horizons can be observed in all the samples that do not have mixed layer clays (Figure 5).

Chlorite was detected in the Holocene deposits and only in a few older soil horizons. Chlorite is directly derived from the weathering of chloritic schist and is absent in most older soils because of its relatively fast rate of transformation in acid soils. Similarly, interstratified illite–HIV and interstratified illite–chlorite were found mainly in Holocene soil horizons.

Hydroxy-interlayered vermiculite (HIV) was observed in most soils, but is rare in early Pleistocene soil horizons.

Table 2. Main properties of the soils studied.

Profile and Horizon	Depth (cm)	Mass color (Munsell, dry)	Structure	Consistence	Mottles color (Munsell, dry)	Sand (%)	Silt (%)	Clay (%)	pH (1:2.5 H ₂ O)	OM (%)	CEC [cmol (+)-kg ⁻¹]	BS	BD (Mg·m ⁻³)
24 A	10	10YR 5/2	GR-st-fm	FR	—	33	56	11	4.6	4.2	14.0	2.6	1.22
24 AC	20	10YR 6/3	SB-we-fi	FR	—	29	63	11	4.2	1.5	12.8	5.8	1.28
43 A	2	10YR 6/3	GR/SB-we-fi	VFR	—	23	68	9	6.5	2.0	—	—	—
43 Bw1	20	10YR 6/4	SB-we-fi	VFR	—	24	66	10	5.0	0.4	5.4	47	1.30
43 Bw2	72	10YR 7/4	SB-we-fm	VFR	10YR 6/2	23	65	12	5.0	0.2	7.2	44	1.32
43 CB	90	10YR 7/4	MA	VFR	—	34	56	10	5.0	0.1	5.7	75	—
44 A	2.5	10YR 6/3	GR-we-fi	FR	—	20	75	5	5.5	3.50	—	—	—
44 E	14.5	10YR 5.5/4	SB-we-fi	FR	—	26	67	7	5.2	1.30	—	—	—
44 Bt1	45	7.5YR 6/6	SB-we-fm	VFR	—	17	69	14	4.8	0.80	6.4	48	—
44 Bt2	58	7.5YR 6/6	SB-mo-fm	VFR	—	19	67	14	4.9	0.20	6.2	52	—
44 2BC	120	10YR 7/6	AB-mo-fi	VFR	—	23	61	16	5.0	0.03	7.1	39	—
44 3BC1	150	7.5YR 7/8	MA	FI	—	15	70	15	4.9	—	—	—	—
44 3BC2	150	7.5YR 7/4	MA	FI	—	17	71	12	5.1	—	—	—	—
34 A	60	7.5YR 4/6	SB-mo-fm	VFR	—	21	61	19	5.2	1.06	—	—	1.24
34 2Bt	95	7.5YR 6/8	PR-mo-fm	FR	—	20	57	23	5.8	0.05	8.7	67	1.67
34 3Btx-o*	170+	7.5YR 6/7	PR-st-vc	VFI	2.5YR 3/6	16	63	22	5.7	0.08	9.0	67	1.79
34 3Btx-r**	170+	10YR 7/2.5	PR-st-vc	VFI	5YR 5/8	20	68	12	5.3	0.16	6.5	93	1.33
10 E	25	7.5YR 6/6	GR-st-fi	VFI	2.5YR 4/6	28	51	21	6.2	1.20	—	—	1.21
10 2Bt	55	7.5YR 5/6	SB/PR-st-me	VFI	7.5YR 5/6	39	35	26	6.5	0.20	9.0	100	1.50
10 3Btx	95	7.5YR 5/6	PR-st-vc	EFI	7.5YR 8/4	25	47	28	7.1	—	7.4	100	1.71
10 3BCd	160+	7.5YR 5/6	MA	EFI	7.5YR 6/7	15	40	45	6.6	—	20.6	68	1.74
7 A	21	10YR 5/4	SB/GR-we-fm	VFR	—	36	55	9	7.5	1.20	—	—	1.50
7 2Bt	50	5YR 5/7	PR-st-fm	FR	7.5YR 5/8	29	34	37	6.5	0.30	14.8	91	1.48
7 2Btd-o	150	7.5YR 5/6	PR-vs-fm	FI	7.5YR 5/8	28	35	37	6.8	0.10	13.5	94	1.66
7 2Btd-r	150	7.5YR 6/6	PR-vs-fm	FI	7.5YR 5/8	33	44	25	7.2	0.20	7.9	90	—
7 2Btd2	225	7.5YR 4.5/6	MA	FI	7.5YR 5/8	30	35	35	6.6	—	12.6	71	1.64
7 2BCd	500	5YR 5/6	MA	FI	7.5YR 5/8	20	41	39	6.4	—	7.8	100	1.58
7 3BCd	700+	5YR 5/6	MA	FI	7.5YR 5/8	27	38	35	7.2	—	22.3	100	—

Table 2. Continued.

Profile and Horizon	Depth (cm)	Mass color (Munsell, dry)	Structure	Consistence	Mottles color (Munsell, dry)	Sand (%)	Silt (%)	Clay (%)	pH (1:2.5 H ₂ O)	OM (%)	CEC [cmol (+)-kg ⁻¹]	BS	BD (Mg·m ⁻³)
9 A	15	10YR 5/4	GR-mo-fm	VFR	—	36	53	11	6.7	2.10	9.0	98	1.23
9 E	45	7.5YR 6/6	SB-wm-fm	FR	—	25	58	17	4.9	0.80	5.0	44	1.56
9 Bt	110	5YR 5/6	SB-st-fm	VFI	7.5YR 8/4	23	52	25	4.6	0.20	9.9	29	1.44
9 2Btx1	155	5YR 5/8	PR-st-vc	VFI	10YR 8/1	19	51	32	5.2	0.31	10.3	45	1.68
9 2Btx2-o	217	5YR 5/8	PR-st-me	VFI	—	21	46	33	4.4	—	13.7	46	1.63
9 2Btx2-r	217	10YR 8/1	PR-st-me	VFI	—	19	67	14	4.8	—	9.0	55	—
9 3Bt	264	5YR 5/8	PR-we-me	VFI	5YR 5/6	28	44	28	5.0	—	11.6	35	—
9 4CB	280+	5YR 5/6	MA	FI	—	27	51	22	5.9	—	13.1	90	—
25 Ap	30	5YR 4/6	SB-st-mc	FI	—	30	33	37	6.8	1.00	—	—	1.50
25 E	60	5YR 4/6	SB-st-fm	FI	—	20	58	22	7.1	0.70	15.0	99	1.55
25 2Bt	170	2.5YR 5/8	PR-st-mc	VFI	5YR 6/2	13	36	51	7.2	0.05	16.6	100	1.60
25 3Bt-o	250+	2.5YR 4/6	PR-mo-fm	EFI	5YR 6/2	12	43	45	6.6	—	11.8	79	1.70
25 3Bt-r	250+	5YR 7/1	PR-mo-fm	EFI	5YR 6/2	15	26	60	7.7	—	16.7	93	—
47 Ap	33	7.5YR 5/6	SB-mo-fm	FR	—	25	42	33	7.3	1.40	—	—	1.49
47 Bt	60	7.5YR 5/6	PR-st-fi	FR	10YR7/2	17	38	45	7.0	0.50	10.5	93	1.63
					10R 3/6								
47 2Btx1-o	140	2.5YR 5/6	PR-st-mc	FI	7.5YR 5/5	15	44	41	6.8	0.05	10.2	93	1.69
47 2Btx1-r	140	5YR 7/1	PR-st-mc	FI	—	18	48	34	7.3	0.50	9.0	96	—
47 2Btx2-o	240+	2.5YR 4/6	PR-st-vc	VFI	7.5YR 5/5	22	43	35	6.3	0.01	7.6	86	1.87
47 2Btx2-r	240+	5YR 7/1	PR-st-vc	VFI	—	19	47	33	7.2	0.30	10.1	100	—
48 Ap	40	10YR 5/6	SB-we-fm	FR	—	23	41	36	6.4	1.30	11.1	91	1.63
48 Bt	55	10YR 6/8	AB/PR-mo-fi	FI	5YR 6/8	10	39	49	5.2	0.69	11.8	73	1.51
					5YR 7/1								
					2.5YR 4.5/7								
48 2Btg	78	7.5YR 5/6	PR/MA-we-me	FI	5YR 7/1	10	42	48	5.4	0.50	11.8	76	1.62
					10R 4/8								
48 2Btgv1-o	190	7.5YR 5/8	PR-st-mc	VFI	5YR 7/1	23	42	35	7.3	0.50	9.2	100	—
48 2Btgv1-r	190	5YR 7/1	PR-st-mc	VFI	5YR 6/8	13	47	40	6.9	0.40	12.7	100	—
48 2Btgv2-o	220	7.5YR 6/8	PR-st-mc	VFI	5YR 7/1	26	43	31	8.2	0.04	10.3	100	—
48 2Btgv2-r	220	5YR 7/1	PR-st-mc	VFI	5YR 6/8	15	44	41	7.6	0.40	9.5	100	—
48 3Btgv3-o	310+	2.5YR 3/6	PR-st-mc	EFI	5YR 7/1	58	26	16	8.1	0.05	6.8	100	—
48 3Btgv3-r	310+	5YR 7/1	PR-st-mc	EFI	5YR 6/8	36	29	35	7.9	0.01	9.6	100	—

* = stained mass; ** = bleached tongues and isolated masses. OM: Organic matter; CEC: cation exchange capacity; BS: base saturation; BD: bulk density.
 Structure: MA: massive; GR: granular; PR: prismatic; AB: angular blocky; SB: subangular blocky; we: weak; mo: moderate; st: strong; vs: very strong; fi: fine; fm: fine and medium; me: medium; vc: very coarse.
 Consistence: VFR: very friable; FR: friable; FI: firm; VFI: very firm; EFI: extremely firm.



Figure 3. Photographs of soil profiles. From upper left to bottom right. The scale is in decimeters. a) Acid shallow soil on rock (Lithic Udorthent). b) Soil formed on thin slope deposits, with an acid cambic horizon (Typic Dystrudept). c) Soil formed on thin slope deposits, with a reddish acid shallow argillic horizon (Typic Hapludalf). d) Soil formed on thick slope deposits, showing a reddish acid argillic horizon, a fragipan, and stagnic properties (Typic Fragiudalf). e) Soil formed on thick in-fillings. It shows a reddish subacid, thick, dense argillic horizon, (Typic Paleudalf). f) Soil formed on the sediments of the terraced fluvial fans. It has a red not-acid, thick, dense, weak developed argillic horizon, and stagnic properties (Aquic Paleudalf). g) Soil formed on the sediments of the terraced fluvial fans. It is possible to recognize a yellowish not-acid, deep, dense, weak developed argillic horizon, with plinthite nodules, and stagnic properties (Typic Plinthaqualf).

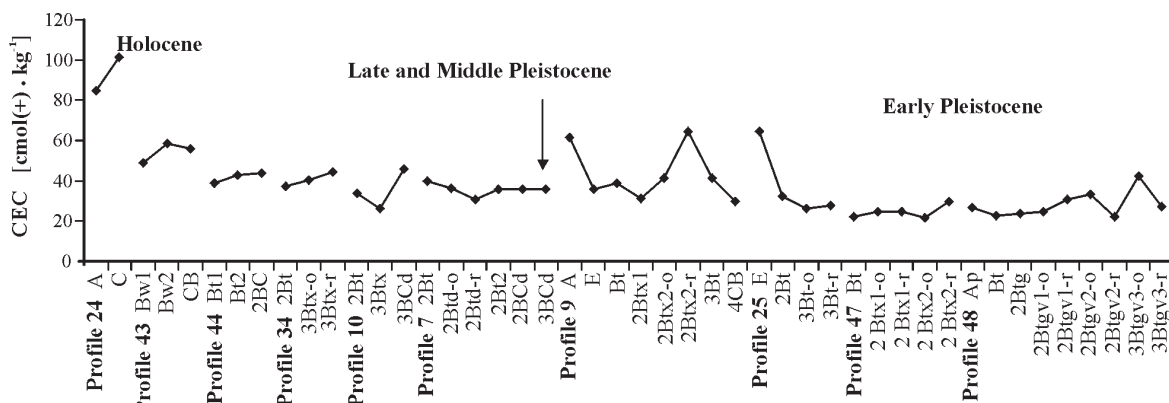


Figure 4. Cation Exchange Capacity (CEC) of the clay fraction. Profiles are arranged by estimated age. Arrow points to horizon where Cromerian fossils were found.

On the other hand, vermiculite content shows a significant tendency to increase with age. Furthermore the number of soil horizons in which it is present increases according to their attributed age. As also found by other authors (Barnhisel and Bertsch, 1989), vermiculite neogenesis in acid environments is largely derived from illite and chlorite, which are common components of the parent rock. The process involves the formation of a series of intermediate clay minerals, namely HIV and interstratified illite–HIV, as well as illite–chlorite.

Kaolinite is the second most important clay mineral in the soils studied, having been found in all horizons and layers. The kaolinite content is clearly time-dependent (Figure 6) and its trend reveals a continuous enrichment. In the oldest horizons it reaches 25% of the clay fraction. The increase in kaolinite content do not appears to be correlated with the impoverishment of any other clay mineral. We believe this indicates a direct neogenesis from the mineral constituents of the parent material and rock, rather than a transformation of a clay mineral.

Clay eluviation and illuviation (argilluviation)

In many Mediterranean soils, the process of iron release and accumulation accompanies clay eluviation and illuviation (Fedoroff, 1994). Most of the soils studied have eluvial and illuvial horizons. The Holocene soils have a moderate amount of clay cutans, but they are more abundant and complex in the late and middle Pleistocene soils, whereas they are commonly much less distinct in the early Pleistocene horizons.

Clay content and bulk density are significantly higher in the illuvial horizons than in the eluvial horizons immediately above (Table 4). Sand is significantly lower, as well as the CEC of clay in the illuvial horizons. The lower CEC of clay is due to the kaolinite content, which is significantly higher in the illuvial horizons. Contrarily, the

illite content is higher in the eluvial horizons. This indicates that there is a preferential transport of kaolinite during the argilluviation process.

Bleached tongues and masses in fragipans and other dense horizons

Many soils of the Montagnola Senese territory have redoximorphic features. The Pleistocene soils, in particular, have horizons that are more or less close packed, not well drained, and show manganese and iron depletion and concentration features. The redoximorphic features are particularly evident in the Pleistocene soils formed in carbonate free deposits and they can take various forms: bleached tongues, interfingerings, and masses.

The physical and mineralogical properties of bleached materials in the soils of the Montagnola Senese region can vary considerably. They depend on whether they take the form of interfingering and tongues, which are associated with fragipans, or large mottles and masses, which characterize the horizons of soils without fragipans belonging to early Pleistocene age (Table 5).

In fragipan horizons, bleached material is richer in silt and poorer in clay than the surrounding stained mass, although the clay mineralogy is similar in each part. On the other hand, iron depletion features of dark red and plinthic dense horizons are significantly more clayey and richer in kaolinite and vermiculite than the surrounding matrix. This suggests that the bleached parts of these horizons are zones of more intense weathering. Nahon (1991) found a similar result while studying laterite formation.

Clay minerals in fragipans and other dense horizons

A fragipan is a horizon where the contacts among the skeletal grains are close enough to make the mass ‘hard’

Table 3. Clay mineral content (%) of the soils studied.

Profile and horizon	Illite	Kaolinite	HIV	Vermiculite	Chlorite	I/HIV	I/Chl
24 A	80	14	4	–	2	–	–
24 C	42	16	15	–	2	25	–
43 A	57	11	9	–	1	17	5
43 Bw1	39	12	15	–	3	18	13
43 Bw2	44	12	13	–	2	18	11
43 CB	51	13	14	–	1	13	8
44 A	64	14	22	–	–	–	–
44 E	35	17	37	–	2	9	–
44 Bt1	32	18	35	–	4	11	–
44 Bt2	21	19	19	–	5	36	–
44 2BC	34	25	6	–	–	35	–
44 3BC1	28	20	3	–	–	49	–
44 3BC2	32	28	2	–	–	38	–
34 A	67	13	15	–	5	–	–
34 2Bt	75	15	9	–	1	–	–
34 3Btx-o	79	13	6	–	2	–	–
34 3Btx-r	64	17	18	–	1	–	–
10 E	88	10	2	–	–	–	–
10 2Bt	82	15	3	–	–	–	–
10 3Btx	89	8	3	–	–	–	–
10 3BCd	80	14	6	–	–	–	–
7 A	80	15	5	–	–	–	–
7 2Bt	81	14	2	3	–	–	–
7 2Btd-o	78	17	3	2	–	–	–
7 2Btd-r	80	12	5	3	–	–	–
7 2Bt2	79	15	4	2	–	–	–
7 2BCd	75	19	–	6	–	–	–
7 3BCd	72	25	–	5	–	–	–
7 3BCd2	88	28	–	2	–	–	–
9 A	88	6	6	–	–	–	–
9 E	71	15	14	–	–	–	–
9 Bt	70	16	10	4	–	–	–
9 2Btx1	73	17	4	6	–	–	–
9 2Btx2-o	69	19	4	8	–	–	–
9 2Btx2-r	78	16	4	2	–	–	–
9 3Bt	70	23	2	5	–	–	–
9 4CB	65	31	–	4	–	–	–
25 Ap	84	13	3	–	–	–	–
25 E	90	6	2	2	–	–	–
25 2Bt	71	26	1	2	–	–	–
25 3Bt-o	76	22	–	2	–	–	–
25 3Bt-r	65	27	–	8	–	–	–

and brittle when dry, but not cemented enough to resist the swelling pressures when ‘rehydrated’. Clay minerals control the critical swelling pressures that cause the swelling and loss of strength. Although not all fragipans are dense or ‘close packed’, those found in the Montagnola Senese territory always have a bulk density $>1.6 \text{ Mg}\cdot\text{m}^{-3}$. No correlations have been found between bulk density of close-packed horizons and their iron or silica content (Costantini

et al., 1996).

Several processes can cause the typical close packing of fragipans: the presence of permafrost, cycles of desiccation and precipitation of SiO_2 -rich amorphous aluminosilicate, increase of free iron oxides and silica, shear, and adding overburden weight such as a glacial cover. In the case of the Montagnola Senese soils, the genesis of fragipans has been attributed to a process, called

Table 3. Continued.

Profile and horizon	Illite	Kaolinite	HIV	Vermiculite	Chlorite	I/HIV	I/Chl
47 Ap	70	23	4	3	—	—	—
47 Bt	66	26	5	3	—	—	—
47 2Btx1-o	66	26	6	2	—	—	—
47 2Btx1-r	61	27	7	5	—	—	—
47 2Btx2-o	61	20	14	5	—	—	—
47 2Btx2-r	64	26	6	4	—	—	—
48 Ap	67	23	3	7	—	—	—
48 Bt	63	23	—	14	—	—	—
48 2Btg	56	30	—	14	—	—	—
48 2Btgv1-o	60	26	—	14	—	—	—
48 2Btgv1-r	63	27	—	10	—	—	—
48 2Btgv2-o	79	16	—	5	—	—	—
48 2Btgv2-r	64	24	—	12	—	—	—
48 3Btgv3-o	70	23	—	7	—	—	—
48 3Btgv3-r	58	31	—	11	—	—	—
Mean	66	19	9	6	2	24	9

Note. HIV: hydroxy-interlayered vermiculite; Chl: chlorite.

'hydroconsolidation' (Bryant, 1989). The dewatering of sediments produces an arrangement of particles that fill all space and eliminates all voids larger than the particles. This close packing reduces porosity, isolates the macropores, restricts water and air circulation, and usually inhibits root penetration.

Some authors stated that the characteristic high bulk density of fragipan is directly related to the kaolinite content, up to the threshold of 25% of the total clay minerals (Assallay *et al.*, 1998). However, if we match the bulk density of fragipans with their kaolinite or any other clay mineral content, we cannot recognize any significant relationship. This also holds true for the other dense horizons (Figure

7). This result further supports the hypothesis that physical processes are mainly responsible for the formation of the dense horizons of the Montagnola Senese region. Their different morphologies depend on clay percentage, as well as on the stage of degradation process caused by root penetration and redox processes in the firm soil layers.

Clay minerals and discontinuities within the soil profile

During the soil survey, discontinuities were observed and described in many soil profiles. They corresponded to

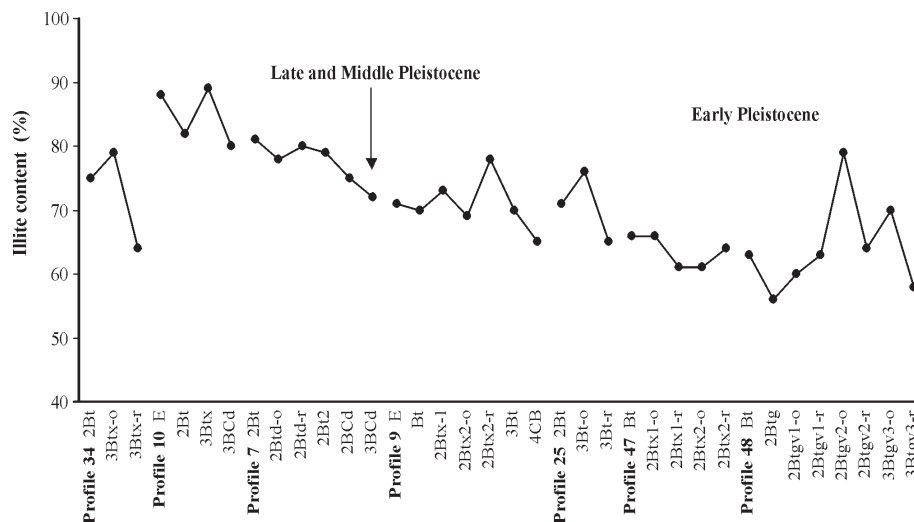


Figure 5. Illite content in horizons E, B and C from profiles without mixed layers. Arrow points to horizon where Cromerian fossils were found.

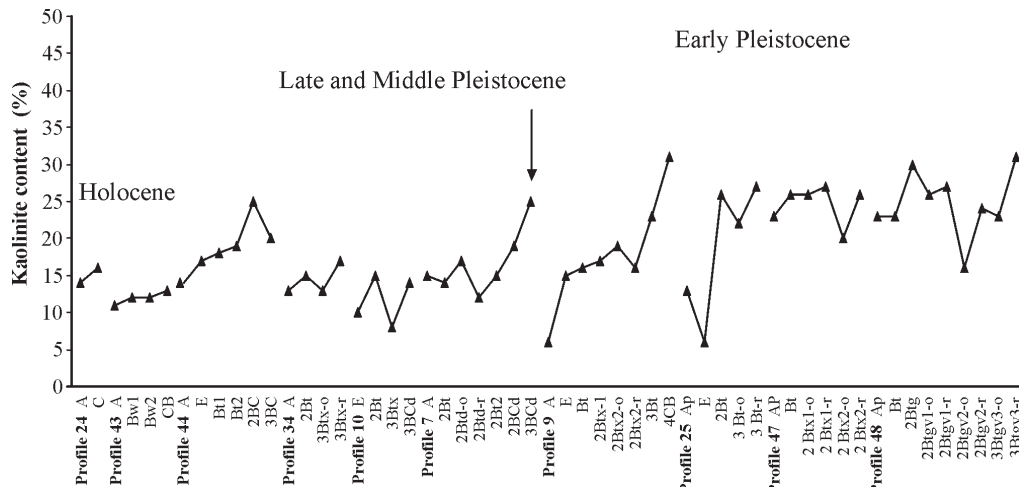


Figure 6. Kaolinite content in profiles arranged by estimated age of parent material. Arrow points to horizon where Cromerian fossils were found.

variation in particle size and presence of stone lines, but were also confirmed by a micromorphological investigation (Costantini *et al.*, 1996). In the case of soils formed on old alluvial fans of Pievescola, they were believed to represent lithologic changes in the composition of similar parent materials, deposited during subsequent episodes within an interval (type 1 discontinuity). For the remaining soils, located on slopes, lithologic discontinuities might correspond to events separated in time, or to deposition of differently weathered materials (type 2 discontinuity). Clay mineral composition can be used to distinguish type 1 from type 2 discontinuities in profiles. Profile 47 and profile 44 are chosen as an example.

Profile 47 is from the geomorphological unit of Pievescola (Figure 1). During the field survey, a discontinuity was identified on the basis of a change in color and field texture, which separate the Bt and 2Btx1 horizons in this profile. The particle size analysis shows an increase in silt and a decrease in clay from the Bt to the 2Btx1 (Table 2). However, as no changes occur in clay mineral composition, (Figure 8) we attribute the discontinuity to a change in the depositional characteristics of fluvial sediments. This relationship does not suggest a hiatus or type 2 discontinuity.

Profile 44 belongs to the class of soils formed on slopes (Figure 1). Two discontinuities were found during

the field survey on the basis of a change in color and in particle size characteristics. The material horizon numbers were assigned on the basis of these criteria, placing the discontinuities between the Bt2 and the 2BC horizons and between the 2BC and the 3BC1 horizons (Table 2). The disappearance of chlorite corresponds with the first discontinuity as well as a sharp increase in kaolinite and a decrease of HIV (Figure 9). Starting from the 2BC horizon, illite, kaolinite and illite–HIV mixed layers show a change in their trends. Therefore, the materials above and below the discontinuities have a different degree of weathering, indicating a change in the source of sediments and possibly a hiatus between the depositional events.

In addition, clay mineralogy provides evidence for another discontinuity, which was not appreciated in the field. The high illite content of the A horizon testifies to a recent addition of fresh material covering the surface. This unconformity is also attested by the appearance of illite–HIV mixed layers and chlorite.

Clay minerals and age of soil horizons

Within the age framework established above, the clay mineral study suggests that age of the main soil groups of

Table 4. Results of comparison of means tests between main properties and clay minerals of eluvial and subjacent illuvial horizons of all the eight soils studied having a Bt. For each parameter, means significantly differ when followed by different letters. Statistical test are at $P \leq 0.05$ (capital letters) or at $P \leq 0.10$ (lower case).

	Clay (g·kg ⁻¹)	Sand (g·kg ⁻¹)	Bulk density (Mg·m ⁻³)	CEC of clay [cmol(+)-kg ⁻¹]	Illite (%)	Kaolinite (%)
<i>Eluvial horizons</i>						
Mean	205 A	255 a	1.44 b	43 A	71	15 B
<i>Subjacent illuvial horizons</i>						
Mean	338 B	221 b	1.53 a	33 B	68	19 A

Table 5. Results of comparison of means tests between main properties and clay minerals in fragipan and in Bt, Btg, and Btgv horizons of profiles 25, 47 and 48. For each parameter, means significantly differ when followed by different letters. Statistical test are at $P \leq 0.05$ (capitals) or at $P \leq 0.10$ (lower case).

	Clay (g·kg ⁻¹)	Silt (g·kg ⁻¹)	Silt/Clay	Illite (%)	Kaolinite (%)	Vermiculite (%)
<i>Fragipan</i>						
Stained parts of horizons						
Mean	336	461 b	1.5 b	71	19	4.3
Number of cases	5	5	5	5	5	4
<i>Bleached parts of horizons</i>						
Mean	236	549 a	3.0 a	69	20	3.5
Number of cases	5	5	5	5	5	4
<i>Bt, Btg, and Btgv horizons of profiles 25, 47 and 48</i>						
Stained parts of horizons						
Mean	338 b	401	1.2	69	22 B	5.8 b
Number of cases	6	6	6	6	6	6
Bleached parts of horizons						
Mean	405 a	401	1.1	62	27 A	8.3 a
Number of cases	6	6	6	6	6	6

horizons can be estimated. With this aim, soil horizons were grouped into eight assemblages that are homogeneous for the main pedological process (Figure 10). These assemblages are: (1) superficial A and Ap horizons; (2) eluvial E horizons; (3) structured and more or less argilluviated subsurface horizons (Bw-Bt); (4) fragipans and glossic horizons with fragic properties (Btx); (5) densipans (Btd and BCd); (6) pedal dense horizons (Btgv-Bt dense); (7) weathered bedrock (BC-CB-C); (8) unweathered bedrock (R).

Holocene clay was assumed to be relatively rich in chlorite, HIV, interstratified illite–HIV, and interstratified illite–chlorite. Late and middle Pleistocene clay showed a relative increase of about one third in vermiculite and

kaolinite percentage. Early Pleistocene clay was characterized by a stronger increase of the kaolinite and vermiculite contents, as well as by the absence of chlorite and interstratified minerals.

CONCLUSIONS

The clay mineral composition of soils of the Montagnola Senese marks the main soil-forming processes occurring during the Quaternary age in this part of the Mediterranean region. The number of profiles, which allowed a statistical analysis of the parameters, supported the comprehension of the relationships between the

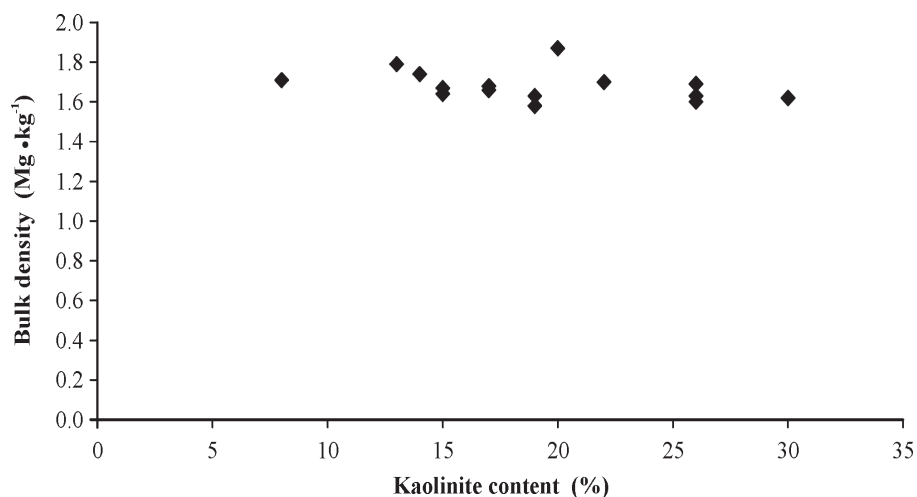


Figure 7. Bulk density (Mg·m⁻³) vs. kaolinite content (%) in fragipan and dense horizons (bleached part excluded).

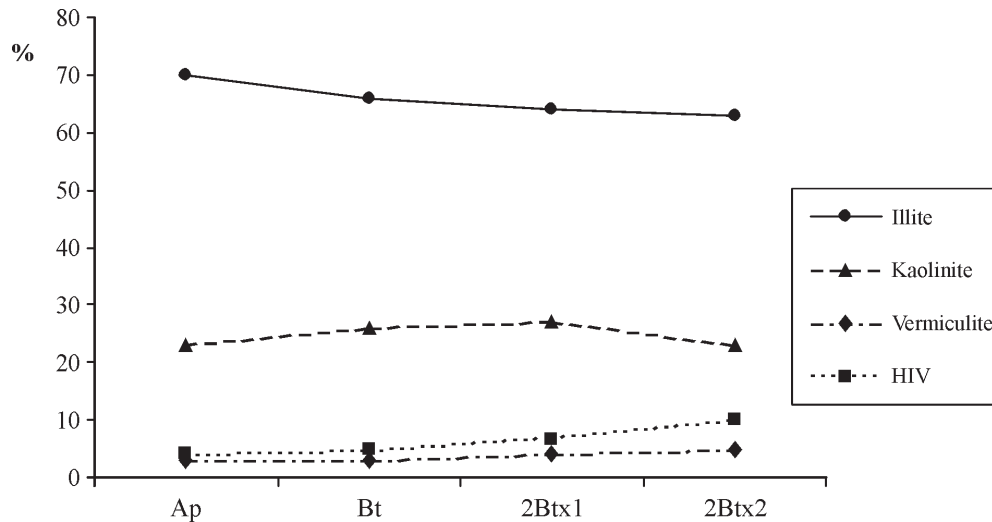


Figure 8. Composition of the clay fraction in horizons of profile 47. HIV: hydroxy-interlayered vermiculite.

parameters studied and the pedological processes.

Soil ageing causes a change in the clay mineral composition producing trends through the horizons, which become more enhanced from the most recent to those where the parent material was attributed to the late and middle Pleistocene. Changes continue to occur in older horizons and are prominent for kaolinite and vermiculite. In general, kaolinite content increases as a consequence of direct neogenesis from the mineral constituents of the parent rock. Vermiculite increases through the transformation of illite and chlorite into a series of intermediate HIV and mixed layers. In the ten profiles examined in central Italy,

argilluviation is marked by a preferential accumulation of kaolinite in the illuvial horizon.

Bleached streak formation has a different genetic signal in fragipan compared to the horizons formed in the oldest parent materials. In fragipan soils of this study, no significant differences were found in clay mineral composition between bleached and stained parts of individual horizons. In Bt, Btg and Btg_v horizons of soils on the old alluvial fan of Pievescola, bleached streaks have more kaolinite and vermiculite than the surrounding matrix. In contrast to what has been found by other authors, the bulk density of fragipans and other dense horizons from

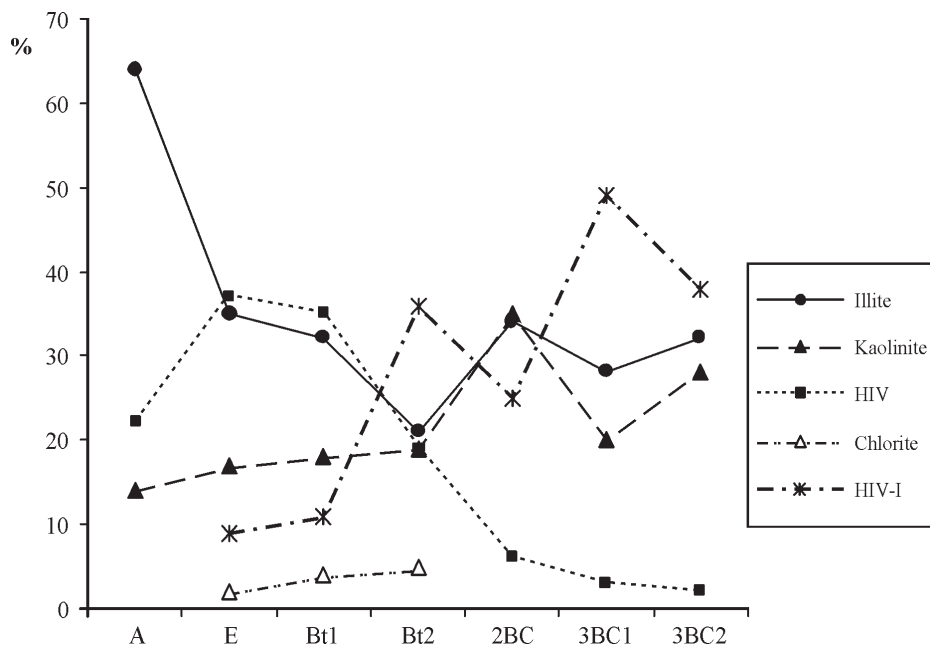


Figure 9. Composition of the clay fraction in horizons of profile 44. HIV: hydroxy-interlayered vermiculite.

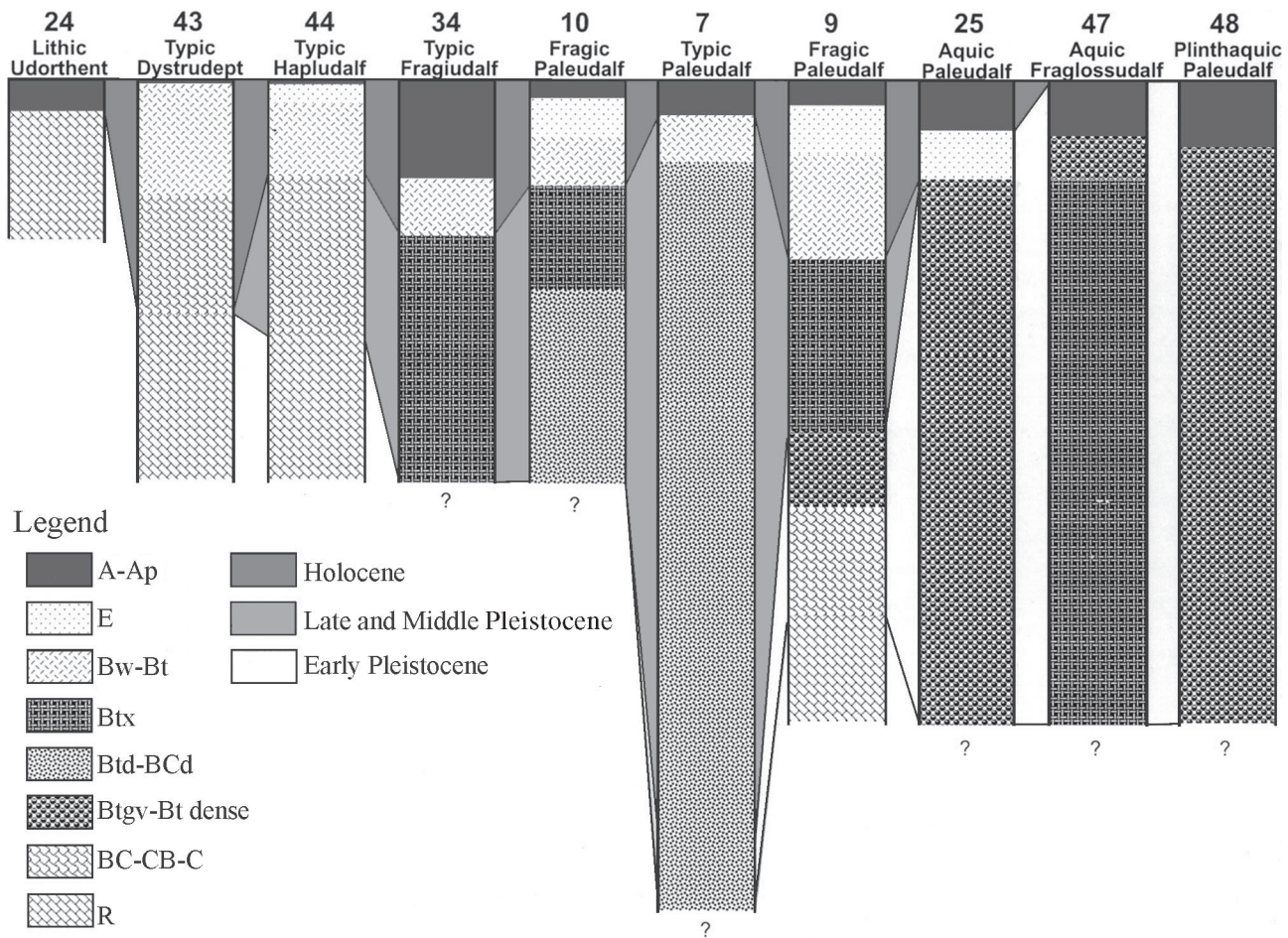


Figure 10. Estimated age of the parent materials of the soil horizons.

Montagnola Senese soils ($BD > 1.6 \text{ Mg}\cdot\text{m}^{-3}$) are related neither to kaolinite nor to any other clay mineral content.

The clay mineral contents through soil profiles gives useful signals to distinguish between type 1 and 2 discontinuities. Type 1 is a normal lithological discontinuity that occurs during a shift in the sediment type during an event. Type 2 is a discontinuity associated with a missing interval, which usually represents a break in sedimentation followed by soil formation or erosion. Finally, the correlation of clay mineral composition, added to the other already acquired information on the age of soils and surfaces, permits to estimate the age of the clay material constituting each horizon of the ten studied profiles.

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REFERENCES

- Ajmone-Marsan, F., Zanini, E., Franchini, M., 1986, Iron oxides and clay minerals within profiles as indicators of soil age in Northern Italy: *Geoderma*, 37, 45–55.
- Ajmone-Marsan, F., Pagliari, M., Pini, R., 1994, Identification and properties of fragipan soils in the Piemonte region of Italy: *Soil Science Society of America Journal*, 58, 891–900.
- Assallay, A.M., Jefferson, I., Rogers, C.D.F., Smalley, I.J., 1998, Fragipan formation in loess soil: development of the Bryant hydroconsolidation hypothesis: *Geoderma*, 83, 1–16.
- Barnhisel, R.I., Bertsch, P.M., 1989, Chlorites and Hydroxy-Interlayered Vermiculite and Smectite, in Dixon, J.B., Weed, S.B. (eds.), *Minerals in Soil Environments*: Madison, Wisconsin, USA, Soil Science Society of America, 729–788.
- Bartolini, C., Bernini, M., Carloni, G.C., Costantini, A., Federici, P.R., Gasperi, G., Lazzarotto, A., Marchetti, G., Mazzanti, R., Papani, G., Pranzini, G., Rau, A., Sandrelli, F., Vercesi, P.L., Castaldini, D., Francavilla, F., 1982, Carta neotettonica dell'Appennino Settentrionale, Note illustrative: *Bollettino della Società Geologica Italiana*, 101, 523–549.
- Bini, C., Mondini, C., 1992, Clay mineralogy of paleosols at archaeological sites in mediterranean environment, Italy: *Mineralogica et Petrographica Acta*, XXXV-A, 245–252.
- Biscaye, P.E., 1965, Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans:

- Geological Society of America Bulletin, 76, 803–832.
- Bockheim, J.G., Gennadiyev, A.N., 2000, The role of soil-forming processes in the definition of taxa in Soil Taxonomy and the World Soil Reference Base: *Geoderma*, 95, 53–72.
- Brindley, G.W., Brown, G., 1980, Crystal structures of clay minerals and their X-ray identification: London, Mineralogical Society, 495 p.
- Bronger, A., Bruhn-Lobin, N., Heinkele, T., 1994, Micromorphology of paleosols - genetic and paleoenvironmental deductions: case studies from central China, south India, NW Morocco and the Great Plains of the USA, in Ringrose-Voase, A.J., Humphreys, G.S. (eds.), *Soil Micromorphology; Studies in Management and Genesis*, Proceedings of the IX International Working Meeting on Soil Micromorphology, Townsville, Australia, July 1992: Elsevier, *Developments in Soil Science*, 22, 187–206.
- Bryant, R.B., 1989, Physical processes of fragipan formation, in Smeck, N.E., Ciolkosz, E.J. (eds.), *Fragipans: their Occurrence, Classification and Genesis*: Soil Science Society of America Journal, 24, 141–149.
- Carnicelli, S., Mirabella, A., 1989/1991, Effetto del tipo di dispersione sulla determinazione dei minerali argillosi nel suolo: *Annali dell'Istituto Sperimentale Studio e Difesa Suolo*, XX, 153–160.
- Costantini, E.A.C., 2000, The recognition of soils as part of our cultural heritage, in Gisotti, G., Zarlenga, F. (eds.), *The Second International Symposium on the conservation of our geological heritage*, Rom, 20–22 May, 1996: Rom, Italy, *Memorie Descrittive della Carta Geologica d'Italia*, LIV, Istituto Poligrafico e Zecca dello Stato, 175–180.
- Costantini, E.A.C., Lulli, L., Bidini, D., Napoli, R., Castellani, F., 1992, Karst landforms and soils of the Poggio del Comune relief (Central Italy), in Chardon, M., Sweeting, M., Pfeffer, K.H. (eds.), *Proceedings of the karst-symposium, 2nd International Conference on Geomorphology*, Blaubeuren, 1989: Tubingen, Geographisches Institut der Universität Tubingen, *Tubinger Geographische Studien*, 109, 83–130.
- Costantini, E.A.C., Napoli, R., Bragato, G., 1996, Properties and geographic relevance of fragipan and other close-packed horizons in a non-glaciated mediterranean region: *Geografia Fisica e Dinamica Quaternaria*, 19 (1), 29–45.
- Costantini, E.A.C., Angelone, M., Napoli, R., 2002a, Soil geochemistry and pedological processes; The case study of the quaternary soils of the Montagnola Senese (Central Italy): *Il Quaternario, Italian Journal of Quaternary Sciences*, 15(1), 111–120.
- Costantini, E.A.C., Angelone, M., Damiani, D., 2002b, Physical, Geochemical and Mineralogical Indicators of Aging, in Bronger, A., Kanyawongha, P., *Quaternary Soils of Central Italy*. Transactions of the 17 World Congress of Soil Science: Bangkok, Thailand, International Union of Soil Sciences (IUSS), *Symposium 49, Full Paper 599*, (CD-ROM), 9 p.
- CreMASchi, M., Sevink, J., 1987, Micromorphology of paleosols chronosequences on gravelly sediments in Northern and Central Italy, in Fedoroff, N., Bresson, L.M., Courty, M.A. (eds.), *Soil Micromorphology*, Proceedings of the VIIth International Working Meeting of Soil Micromorphology: Paris, Association Française pour l'étude du Sol, 577–582.
- Dixon, J.B., Weed, S.B., 1989, Mineral in soil environments: USA, Wisconsin, Madison, Soil Science Society of America, 1264 p.
- European Commission, 1999, Georeferenced Soil Database of Europe, Manual of Procedures, version 1.0: Luxembourg, European Commission, European Soil Bureau, Research Report 5, EUR 18092 EN, 184 p.
- Fedoroff, N., 1994, Clay illuviation in Red Mediterranean soils: *Catena*, 28, 171–189.
- Food and Agricultural Organization (FAO), 1998, World Reference Base for Soil Resources: Rome, Italy, Food and Agricultural Organization of the United Nations (FAO), International Society of Soil Science (ISSS), International Soil Reference and Information Centre (ISRIC), *World Soil Resources Reports*, 84, 91 p.
- Fondi, R., 1972, Fauna cromeriana della Montagnola Senese: *Paleontologia Italiana*, 68, 1–27.
- Gjems, O., 1967, Studies on clay minerals and clay-mineral formation in soil profiles in Scandinavia–Norwegian Forest: Vollebakk, Norway, *Meddelelser fra det norske skogforsoksvesen* (Reports of the Norwegian Forest Research Institute), 21, 303–345.
- Kallis, P., Bleich, K.E., Stahr, K., 2000, Micromorphological and geochemical characterization of Tertiary 'freshwater carbonates' locally preserved north of the edge of the Miocene Molasse Basin (SW Germany): *Catena*, 41, 19–42.
- L'Abate, G., Costantini, E.A.C., 2000, I suoli e la valorizzazione delle risorse naturali e culturali del territorio. Un prototipo di sistema esperto applicato in Alta Val d'Elsa: *Elsanatura*, 1, 8–22.
- Magaldi, D., 1979, Paleosuoli e stratigrafia del Quaternario continentale: *Ateneo Parmense, Acta Naturalia*, 15, 159–161.
- Ministero delle Politiche Agricole e Forestali, 2000, *Metodi di analisi chimica del suolo*: Milano, Italy, Franco Angeli Editore.
- Mirabella, A., Costantini, E.A.C., Carnicelli, S., 1992, Genesis of a polycyclic Terra Rossa (Chromic Cambisol on Rhodic Nitisol) at the Poggio del Comune in Central Italy: *Zeitschrift für Pflanzenernährung und Bodenkunde*, 155, 407–413.
- Moore, D.M., Reynolds, R.C. Jr., 1997, X-Ray diffraction and the identification and analysis of clay minerals: Oxford University Press, 378 p.
- Nahon, D.B., Self-organization in chemical lateritic weathering: *Geoderma*, 51, 5–13.
- Newhall, F., 1972, Calculation of soil moisture regimes from the climatic record: USA, Nebraska, Lincoln, United States Department of Agriculture, Soil Conservation Service, Revision 4, Mimeographed, 17 p.
- Previtali, F., 1985, I paleosuoli dell'area pedemontana lombarda: *Genio Rurale*, 3-4, 21–28.
- Schwertmann, U., 1985, The effect of pedogenic environments on iron oxide minerals, in Stewart, B.A., *Advances in Soil Science*, v. 1: New York, Springer Verlag, 171–200.
- Soil Survey Division Staff, 1993, *Soil Survey Manual*: Washington D.C., United States Department of Agriculture, Soil Conservation Service, Handbook, 18, 437 p.
- Soil Survey Staff, 1998, *Keys to Soil Taxonomy*: Blacksburg, Virginia, SMSS Technical Monograph, 19, Pocahontas Press, 541 p.
- SPSS, 1994, *SPSS Professional Statistics 6.1*: Chicago, SPSS Inc., 385 p.
- Torrent, J., 1995, Genesis and properties of the soils of the Mediterranean regions: Italy, Università di Napoli, *Diploma Sc. Chimico-Agrarie*, 111 p.
- Wilson, M.J., 1987, X-ray Powder Diffraction Methods, in Wilson, M.J. (ed.), *A Handbook of Determinative Methods in Clay Mineralogy*: London, Blackie(Glasgow), 26–98.
- Wood, B.W., Perkins, H.F., 1976, A field method for verifying plinthite in Southern Coastal Plain soils: *Soil Science*, 122, 240–241.

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