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Pedogenesis of plinthite during early Pliocene in the Mediterranean environment
Case study of a buried paleosol at Podere Renieri, central Italy

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Abstract

A complex buried paleosol at Podere Renieri at Montalcino (central Italy) formed during a series of continental episodes within an interval of Pliocene marine sediments from about 4.1 to 4.8 My BP. The aim of this work was to document the kind of pedogenesis which occurred throughout this time and, in particular, the plinthite formation. Plinthite (soft and hard) is poor in organic carbon, neutral or subalkaline, dominated by illite, and enriched in iron and chromium. The main differences between soft and hard plinthite are attributed to soil structure, which is absent in hard plinthite, and to the abundance of iron depleted zones, which are much larger in soft plinthite. Variations in mineralogy, chemistry and genesis of soft and hard plinthite can be ascribed to the specific environment of plinthite formation, close to the Pliocene sea. Pedogenetic evidence indicates that plinthite evolved in a hot and humid paleoclimate, showing a progressive increase in seasonality, and that low-grade plinthite formation occurred in a time span of a few hundred thousand years. Soils with low-grade plinthite have agronomic value in their suitability for the production of high quality Brunello di Montalcino wine.

Keywords: Pliocene; Plinthite; Illite; Paleoclimate; Brunello di Montalcino

1. Introduction

There is a general consensus about the dominance of warm-climate pedogenesis in the Mediterranean region during the early Pliocene, which was significantly warmer and more humid than at present, although very few paleosols are documented in the literature. Gaucher (1981) states that during the Tertiary much of the world was dominated by a climate favourable to laterization, this being especially true close to the equator. In particular, the “climatic optimum” for laterization took place during the Miocene, while during the Pliocene climatic conditions progressively changed towards a slower rate of laterization, until the Pleistocene, when climate change induced the erosion of many lateritic soils. Also Günster and Skowronek (2001) concluded that iron accumulation was the most striking product of pedogenesis during the Tertiary in Mediterranean countries.

The buried complex paleosol at Podere Renieri at Montalcino (Fig. 1) in central Italy illustrates an example of pedogenesis that occurred during early Pliocene in the middle of the Mediterranean basin. The paleosol represents a series of continental episodes between Pliocene marine sediments that range from about 4.1 to 4.8 My BP, based on the biostratigraphic record.

The paleosol has pedological, geological and paleoenvironmental relevance for regional and continental correlation. The horizons containing plinthite, those with iron accumulation and segregations, are of particular interest, because they show different stages of hardening and plinthite formation. Plinthic soils are widespread around Montalcino, and are largely cultivated with vineyards, which produce the world famous wine “Brunello di Montalcino”. The aim of this work was to document the kind of pedogenesis which occurred over a time span of about 700,000 yr during the early Pliocene. Special attention was given to the characteristics of soft and hard plinthite.

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2. Area description

2.1. Geology, soils and land use

The area of Podere Renieri is situated near the town of Montalcino, in the province of Siena, and overlies Neogene deposits of the Siena basin, close to the Murlo–Montalcino ridge (Fig. 2). The Neogene deposits record a variety of depositional systems that have resulted from a complex interplay between regional tectonic and eustatism (Aldinucci and Sandrelli, 2004). After the Alpine tectonic event, late Miocene block-faulting gave rise to tectonic depressions limited by emerging topographic highs that are expressed in the present-day topography. During the Miocene, the Siena Basin was filled with lacustrine sediments, which later subsided into a marine depositional setting, up to the late middle Pliocene marine regression that led to the emersion of the whole basin. Today, the Mediterranean sea is about 65 km west of the study area.

In the study area, the lowermost Pliocene sediments were deposited at the beginning of the early Pliocene (early Pliocene ranges from about 5.4 to 3.6 Ma BP), corresponding to the *Sphaeroidinellopsis seminulina l.s.* zone — lower part of the *Globorotalia margaritae* zone (about 4.8 Ma) (Bossio et al., 1992) (Fig. 3a). After a continental episode, (Fig. 3b and c), marine sediments with molluscs and planktonic foraminifers, referable to the *Globorotalia puncticulata*–*Globorotalia margaritae* zone (about 4.1 Ma) were deposited (Fig. 3d). The regional marine regression affected Tuscany during the middle Pliocene and culminated with the emersion of the basin at the beginning of the late Pliocene (Fig. 3e).

In the Podere Renieri area the surface soils are developed in marine Pliocene sediments and classify as Chromic Calcixerert, according to Soil Taxonomy (Soil Survey Staff, 1998), or Calcic Vertisol in the WRB system (IUSS-ISRIC-FAO, 1998). In the cultivated fields surrounding the studied section, the parent materials are mostly continental deposits and the soil types vary from Aquic, Plinthic, Typic Haploxeralfs and Palexeralfs, or Stagnic, Profondic, Chromic Luvisols.

Present land use at Podere Renieri, as well as in the whole Montalcino territory, correlates well with geology and soils. Most of the soils on pre-Miocene deposits are forested, while cereals dominate the Vertisols formed on the Pliocene sediments. The local economy is agricultural and vineyards occupy about 8% of the total land surface. These vineyards produce the world famous wine "Brunello di Montalcino", which assures the prosperity of the population. Some vineyard soils have been reshaped by bulldozing of native soils formed in Pliocene continental deposits, which contain plinthite.

2.2. Climate and paleoclimate

The latitude at Podere Renieri is 43°N and the elevation 303 m asl. The present climate is Mediterranean suboceanic (Costantini et al., 2004), the mean annual temperature is 14 °C, the mean summer and winter temperatures are 22.9 and 6.2 °C respectively, the hottest month is August (30 °C) and the coldest January (5.8 °C), mean annual precipitation is 643 mm, the rainiest month is November (112.3 mm), the driest months are June and July (37.8 and 15.5 mm). Soil moisture regime according to Soil Taxonomy is dry xeric 24% of the years, xeric 28%, ustic 48%; soil temperature regime is thermic.

The climate during the early–middle part of Pliocene was characterized by hot and steady temperatures, which became more variable during the middle–late Pliocene, and then became colder during the early Pleistocene (Haywood et al., 1999). According to Abreu et al. (1998) the north-western parts of the Mediterranean basin have been strongly affected by climatic fluctuations since the Pliocene, with variations in the

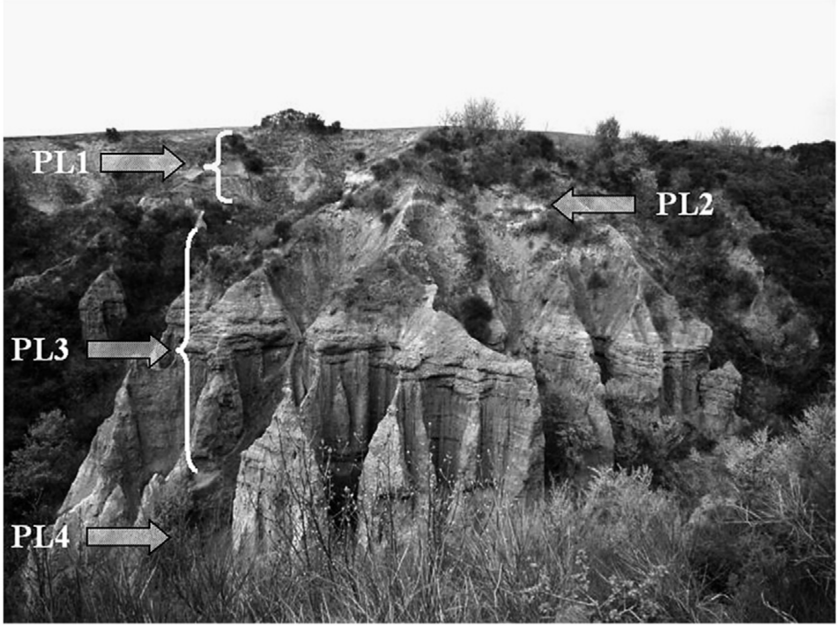


Fig. 1. Pedostratigraphic levels at Podere Renieri paleosol at Montalcino, Siena, Italy. The explanations are in the text.

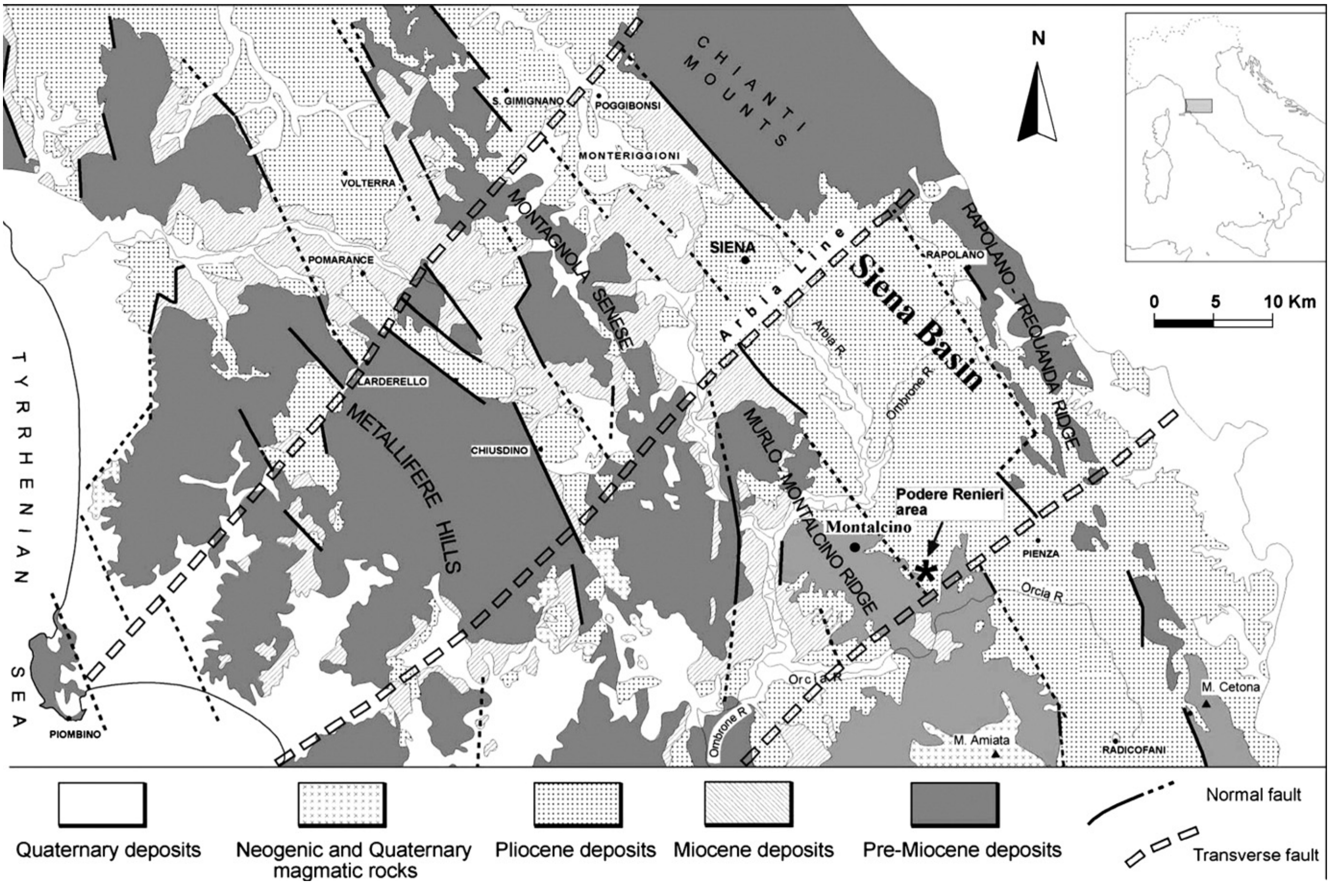


Fig. 2. Southern Tuscany Neogene basins.

rainfall rhythm and temperature. Günster and Skowronek (2001) concluded that climate has been subtropical Mediterranean since the early Pliocene.

Oceanic plankton, as well as animal and vegetal species distribution, indicate a considerably hotter climate in the Pliocene than at the present time according to Palombo (1994). In fact, during early–middle Pliocene, the species distributions were comparable to those now living several hundred kilometers to the south. Chandler et al. (1994) estimated that at mid-latitudes during early–middle Pliocene the mean annual temperatures were from 1 to 5 °C higher than today's.

On the other hand, Barron et al. (1999) of the PRISM project (Pliocene Research, Interpretation, and Synoptic Mapping) of the U.S. Geological Survey, calculated mean air temperatures of about 12–15 °C and 28 °C for February and August, the coldest and hottest months, for an area at 43°N latitude and 10°E longitude along the coast of the Tyrrhenian Sea, which is situated very close to Podere Renieri.

A certain seasonality of temperatures was also postulated by Palombo (1994), who stated that in the northern Italian Apennines, during the early Pliocene, subtropical conditions prevailed, but temperature fluctuations increased, starting from about 4.6 Ma BP. Rainfall amount is more difficult to estimate, however. The model of Haywood et al. (1999) predicts, for our latitudes, values of 400 to 1000 mm higher than the present day values.

The bulk of paleoclimate evidence leads us to hypothesise that during the early Pliocene the mean annual temperature ranged from 17 to 21 °C and the annual rainfall was more than 1000 mm, or even 1500 mm, with less seasonality of temperatures than today, because of the warmer winters. Gaucher (1981) claimed the climatic conditions inducing laterization today correspond to a mean annual temperature higher than 20 °C and an annual rainfall of more than 1200 mm. Therefore we can assume that in the study area climatic conditions were close to those needed for plinthite formation. A similar humid subtropical climate is now present in regions like southern China, south-east USA, and south east Australia, where soils with plinthite are widespread (Driessen et al., 2001).

3. Methods

An outcrop near the farm of Podere Renieri, 32 km SE of Siena, was described in terms of lithology and structure following Ricci Lucchi (1992). The sedimentological features were described following methods of Walker (1984).

A geomorphological map of the study area was produced following the national methodology for detailed geomorphological survey and using the symbols of the Geomorphological Map of Italy 1:50,000, a guide produced by the Italian Geological Survey (Serv. Geol. Naz., 1994), which highlights the morphological evidence of the recent and current processes.

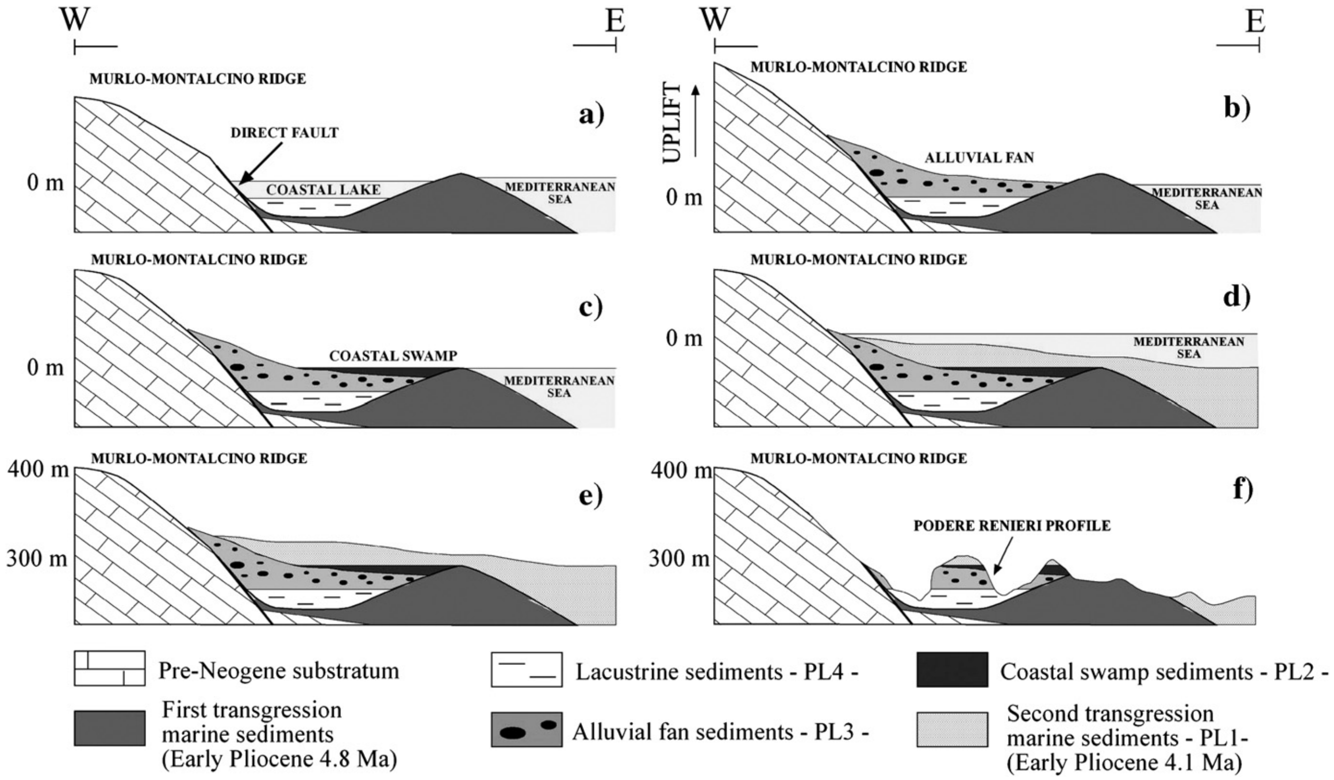


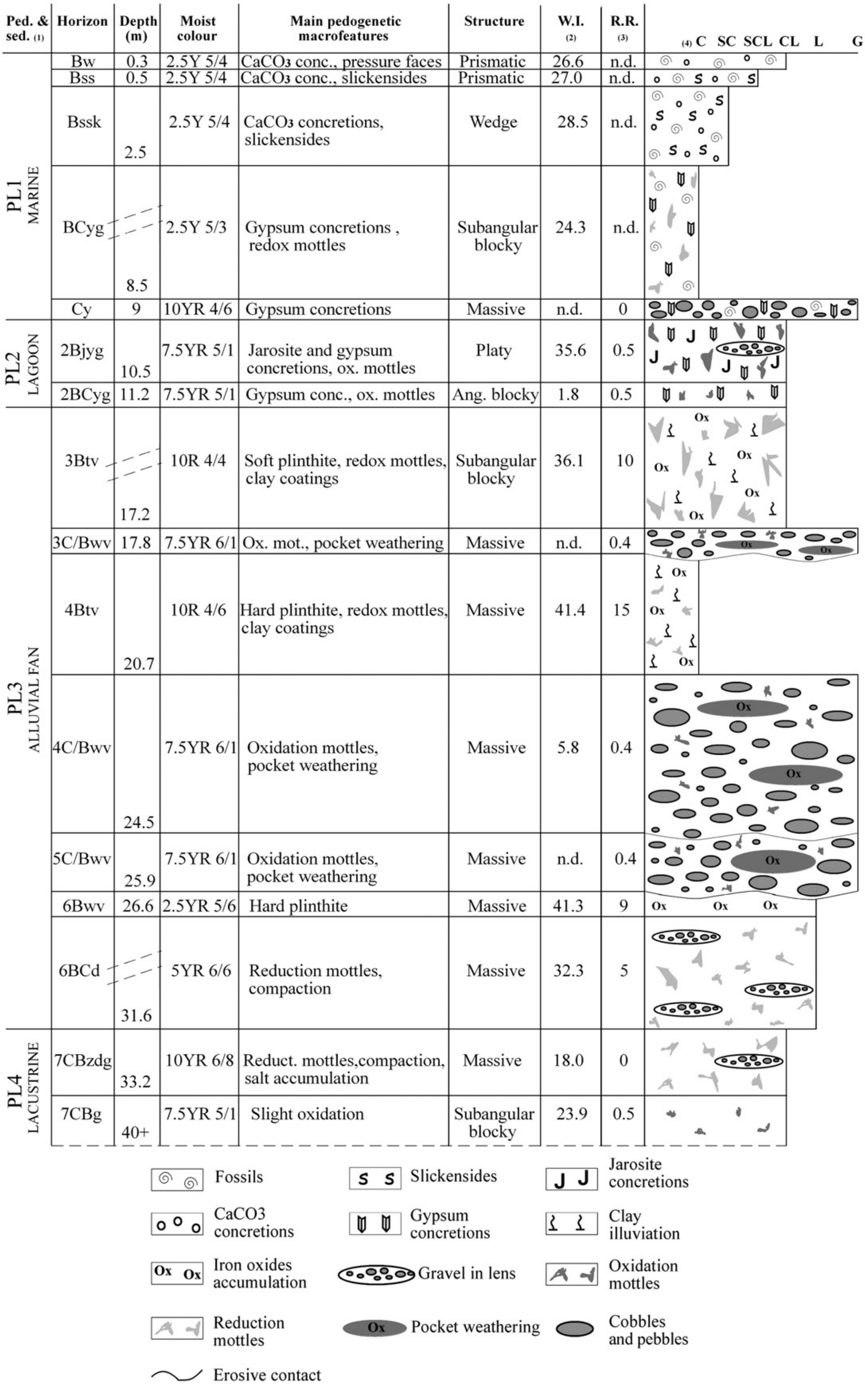
Fig. 3. Paleoenvironmental reconstruction: (a) formation of lacustrine environment about 4.8 Ma BP; (b) transgression of alluvial fan; (c) formation of coastal swamp; (d) transgression of Mediterranean sea, about 4.1 Ma BP; (e) regression of sea and (f) incision of the deposits (from late Pliocene to present).

3.1. Soil description

The Podere Renieri section is more than 40 m thick and complex. Soil horizons were described in the field according to standard procedures of the Field Book for Describing and Sampling Soils, version 1.1 (Schoeneberger et al., 1998). Plinthite was verified by testing soil samples in water following Wood and Perkins (1976) and Daniels et al. (1978). Pedostratigraphic interpretations were drawn from previous sedimentological studies and our pedological studies in the area. The pedostratigraphic column was made using a new descriptive modality, developed from those of Carnicelli et al. (2003) and Terhorst and Ottner (2003). The soil horizons were described in terms of colour, main pedogenetic macrofeatures, structure, weathering index, redness rating, particle size, and eventually named with a genetic designation. Erosional contacts, gravel, fossils, clay cutans, redoximorphic features, occurrence of natrojarosite, gypsum and calcium carbonate concentrations, slickensides and pockets of weathered materials were also reported in the pedostratigraphic section.

3.2. Laboratory methods

Particle size analysis followed the pipette method of the national standards (Metodi di analisi fisica del suolo, MiPAF, 1997). Water dispersible clay was measured according to the soil survey laboratory methods manual (NCCS-NRCS-USDA, 1996). Fine earth pH and electroconductivity were measured on a 1:2.5 (for pH) and 1:5 (for EC) water suspension. The $CaCO_3$ content of the <2 mm fraction was determined by a Dietrich–Fruehling calcimeter. Organic carbon was determined on air-dry samples using the traditional Walkley–Black method (MiPAF, 2000). Cation exchange capacity and exchangeable cations were determined by leaching air–dry soil samples with $BaCl_2$–triethanolamine ($BaCl_2$–TEA) at pH 8.2. The total content of Si, Al, Fe, Ca, Mg, Na, K, Mn, Ti, S, Cr, Zn, Ni, Cu, Co, and Pb was measured by an elemental analysis. The <2 mm soil fraction was pulverized in a chalcedony jar and samples were submitted to X-ray fluorescence. Free iron extraction was done following the Holmgren (1967) method, using 10 g of fine earth with an addition of 60 ml of dithionite–citrate–bicarbonate extracting solution. The resulting iron dithionite (Fed) content was measured by atomic absorption spectrophotometer (FAAS). As for ammonium oxalate extraction, 50 ml of 0.2 M ammonium oxalate acid solution adjusted to pH 3 was added to 10 g of soil, and the suspension was shaken for 4 h in the dark. The iron oxalate (Feo) was measured by atomic absorption spectrophotometer (FAAS). Clay mineralogy was studied by X-ray diffraction. Samples of clay were separated by stirring and ultrasound irradiation, as described by Mirabella (2000), standard sieving and sedimentation. The clay minerals were analyzed using oriented mounts with the following treatments: K-saturated heated to 25, 250, 350, and 550 °C, Mg-saturated at 25 °C and Mg and glycerol saturated and heated to 60 °C. The diffractograms were scanned and an estimation of the quantitative values of the clay minerals was obtained in according to the Gjems (1967) methodology. X-ray diffraction was also used to characterize primary minerals in unweathered



Ped. & sed. (1)	Horizon	Depth (m)	Moist colour	Main pedogenetic macrofeatures	Structure	W.I. (2)	R.R. (3)
PL1 MARINE	Bw	0.3	2.5Y 5/4	$CaCO_3$ conc., pressure faces	Prismatic	26.6	n.d.
	Bss	0.5	2.5Y 5/4	$CaCO_3$ conc., slickensides	Prismatic	27.0	n.d.
	Bssk	2.5	2.5Y 5/4	$CaCO_3$ concretions, slickensides	Wedge	28.5	n.d.
	BCyg	8.5	2.5Y 5/3	Gypsum concretions , redox mottles	Subangular blocky	24.3	n.d.
	Cy	9	10YR 4/6	Gypsum concretions	Massive	n.d.	0
PL2 LAGOON	2Bjyg	10.5	7.5YR 5/1	Jarosite and gypsum concretions, ox. mottles	Platy	35.6	0.5
	2BCyg	11.2	7.5YR 5/1	Gypsum conc., ox. mottles	Ang. blocky	1.8	0.5
PL3 ALLUVIAL FAN	3Btv	17.2	10R 4/4	Soft plinthite, redox mottles, clay coatings	Subangular blocky	36.1	10
	3C/Bwv	17.8	7.5YR 6/1	Ox. mot., pocket weathering	Massive	n.d.	0.4
	4Btv	20.7	10R 4/6	Hard plinthite, redox mottles, clay coatings	Massive	41.4	15
	4C/Bwv	24.5	7.5YR 6/1	Oxidation mottles, pocket weathering	Massive	5.8	0.4
	5C/Bwv	25.9	7.5YR 6/1	Oxidation mottles, pocket weathering	Massive	n.d.	0.4
	6Bwv	26.6	2.5YR 5/6	Hard plinthite	Massive	41.3	9
	6BCd	31.6	5YR 6/6	Reduction mottles, compaction	Massive	32.3	5
PL4 LACUSTRINE	7CBzdg	33.2	10YR 6/8	Reduct. mottles,compaction, salt accumulation	Massive	18.0	0
	7CBg	40+	7.5YR 5/1	Slight oxidation	Subangular blocky	23.9	0.5

Fig. 4. Pedostratigraphic section. (1): Pedostratigraphic levels and sedimentary environment. (2): Weathering index [((Fed − Feo) / Fet) × 100], Arduino et al. (1984). (3): Redness rating [((10 − H) × C) / V], Torrent et al. (1983). (4) C: clay, SC: silty-clay, SCL: silty-clay loam, CL: clay-loam, L: loam, G: gravelly.

Table 1
Field description of the Podere Renieri section

Pedostr. level	Horizon	Depth (m)	Boundary(1)	Color (moist)(2)			Structure(3)	Cons.(4)	Skeleton(5)	Concentrations(6)	Ped & void(7) surface features
				Matrix	Principal mottles	Secondary mottles					
PL1	A	0.06	GS	2.5Y 4/3	-	-	GR 2 m	S	0.5% fg sr SED ww	SFB	-
	Bw	0.3	CW	2.5Y 5/4	-	-	SBK 2 f	S	0.5% fg sr SED ww	CAM f 1, SFB	PRF f F PF
	Bss	0.5	CS	2.5Y 5/4	-	-	PR 1 f	SH	0.5% fg sr SED ww	CAN f 1, SFB	SS f F PF
	Bssk	2.5	CI	2.5Y 5/4	-	-	weg 1 m	SH	0.5% fg sr SED ww	CAN c 2, SFB	SS f F PF
	BCyg	8.5	GS	2.5Y 5/3	2.5Y 5/1 (m4)	-	sbk 1 m	MH	0.5% fg sr SED ww	GYX f 2, SFB	-
	Cy	9	CS	10YR 4/6	-	-	-	-	60% cg sr SED ww	GYX c 2	-
PL2	2Bjyg	10.5	GS	7.5YR 5/1	7.5YR 5/8 (c3)	7.5YR 3/1 (f3)	PL 2 co	SH	4% mg sr SED mw	GYX c 2, JAR m 2	-
	2BCyg	11.1	GI	7.5YR 5/1	10YR 5/6 (c3)	-	ABK 1 m	SH	4% mg sr SED mw	GYX c 3	-
PL3	3Btv	17.2	CS	10R 4/4	7.5YR 6/1 (m4)	-	SBK 2 co	VH	5% mg sr SED mw	-	FEF c D RF,SP
	3C/Bwv	17.8	CW	7.5YR 6/1	2.5YR 4/6 (c5)	-	M	EH	50% cg-co sr SED ww	-	FEF f D RF
	4Btv	20.7	CI	10R 4/6	7.5YR 6/1 (c2)	-	M	EH	10% cg-co sr SED sw	-	-
	4C/Bwv	24.5	AI	7.5YR 6/1	2.5YR 4/6 (c5)	-	M	EH	70% co sr SED ww	-	-
	5C/Bwv	25.9	AI	7.5YR 6/1	2.5YR 4/6 (c5)	-	M	EH	70% co sr SED ww	-	-
	6Bwv	26.6	GW	2.5YR 5/6	-	-	M	EH	4% mg sr SED mw	-	-
	6BCd	31.6	GS	5YR 6/6	5YR 6/1 (m4)	-	M	EH	10% mg sr SED mw	-	-
PL4	7CBzdg	33.2	CS	10YR 6/8	7.5YR 7/1 (c3)	7.5YR 5/8 (f3)	M	EH	10% mg sr SED mw	FDS	-
	7CBg	40+	-	7.5YR 5/1	7.5YR 5/6 (c3)	-	SBK 1 m	MH	5% mg sr SED ww	-	-

Main horizons with plinthite are shadowed.

(1)AI: Abrupt irregular, CS: clear smooth, CW: clear wavy, CI: clear irregular, GS: gradual smooth, GW: gradual wavy, GI: gradual irregular. (2)f: few, c: common, m: many; 2: medium, 3: coarse, 4: very coarse; 5: extremely coarse. (3)GR: granular, ABK: angular blocky, SBK: subangular blocky, PL: platy, WEG: wedge, PR: prismatic, M: massive; 1: weak, 2: moderate, 3: strong; f: fine, m: medium, co: coarse. (4)Cons.: consistence; S: soft, SH: slightly hard, MH: moderately hard, VH: very hard, EH: extremely hard. (5)fg: fine gravel (2–5 mm), mg: medium grave(l 5–20 mm), cg: coarse gravel (20–75 mm), co: cobbles (75–250 mm), st: stones (>250 mm); sr: subrounded; SED: sedimentary rocks; ww: slightly weathered, mw: moderate weathered, sw: strong weathered. (6)SFB: shell fragments, CAM: carbonates masses; CAN: carbonate nodules, GYX: gypsum crystals, JAR: jarosite concretions, FDS: finely disseminated salts; f: few, c: common; 1: fine, 2: medium, 3: coarse. (7) PFR: pressure faces, SS: slickensides, FEF: ferriargillans; f: few, c: common; F: faint, D: distinct; PF: on faces of peds, RF: on grains, SP: on surface of pores.

rock fragments. Six undisturbed soil samples were taken to prepare 80 × 50 mm thin sections for petrographic observation. Thin section descriptions followed the manual of Bullock et al. (1985). Soluble salt content was measured in horizons with high electrical conductivity. 100 g of deionized water were added to 10 g of fine earth. The suspension was stirred and the supernatant dried in an oven. The percentage of crystallized salts was calculated. The nature of the salts was determined by X-ray analysis.

4. Results and discussion

4.1. Characteristics of the sediments

The sedimentological characteristics of the section are divisible into the three intervals, which have been described by the local geologists (Bossio et al., 1992; Aldinucci and Sandrelli, 2004).

4.1.1. Interval A

Marine deposits that begin at the base with coarse-grained pebbly sand unconformably overlie pre-Miocene deposits (Fig. 3a). These sands change upwards to marine sandy clays. The transgressive trend is marked by the change of the foraminifera association, from *S. seminulina* zone to lower part of *G. margaritae* zone.

4.1.2. Interval B

A continental sequence consisting of massive, grey sandy clays, characterised by the occurrence of root traces, ostracods and characeae oogons, indicative of a shallow lacustrine setting (Fig. 3b). Sandy clays grade upwards to conglomerates, sandy to clayey silts and pebbly sands, with coarser deposits, particularly developed in the middle part of the section. The conglomerates lack any evidence of sorting and range from matrix-supported to clast-supported. They are massive or inversely graded, and show erosive bases with decimeter-thick undulations (Fig. 4). Clasts, ranging from a few millimeters to several decimeters in size, have the same lithology, which includes quartzose and calcareous sandstone and breccia. These come from nearby Ligurian Units of the pre-Miocene and explain the homogeneity of the deposits. The clasts are moderately to strongly weathered, which is incompatible with transport and redeposition. Thus these conditions imply an in situ pedogenesis. The sedimentological features in the conglomerates show evidence of deposition by debris-flows or hyperconcentrated flow conditions, reflecting high-magnitude events in the proximal part of an alluvial fan, indicating rapid runoff after sudden heavy rains. Sand and silt deposits, interbedded within conglomerates, represent the diluted tail of these highly concentrated flows.

4.1.3. Interval C

Lagoonal-marine deposits that represents a marine transgression onto the underlying continental deposits (Fig. 3c and d). This interval begins with dark grey silty clays with natrojarosite [(K, Na)$Fe_3(SO_4)_2(OH)_6$] concretions and gypsum crystals, which can be related to diagenetic alteration of pyrite. These features, as well as the absence of fossils, indicate a very shallow water environment with very little oxygen, such as a lagoon or a coastal swamp. These sediments pass upwards into conglomerates and marine clays, with abundant fossils like *Ostrea*, *Venus*, *Dentalium* and bored clasts (lithophaga traces), indicative of a shallow marine setting. At the top of the section, planktonic foraminifera, referred to as the *G. puncticulata–G. margaritae* zone, become abundant and indicate an outer neritic environment.

4.2. Pedostratigraphy

The whole section, more than 40 m thick, was subdivided into 19 soil horizons (Table 1, Fig. 4). We recognized seven main lithological discontinuities, and avoided differentiating soil boundaries between the main body of fining-upward sequences and basal zones with pebbles (Fig. 5). In the pedostratigraphic column, the suffix letter “b” was omitted from the horizon designation, as we were dealing with a sequence of buried paleosols. The surface A horizon was also omitted, because it was too thin to be represented in the drawing.

All soil horizons were grouped in four pedostratigraphic levels (PLs). A pedostratigraphic level was intended as a set of horizons formed from parent materials having the same origin and age.

The uppermost pedostratigraphic level (PL1: marine) groups cambic, vertic and calcic horizons, with slickensides and hard and soft calcium carbonate concretions, formed in marine deposits. At the base of the level, and for the whole thickness of the underlying level, many lenticular shaped gypsum crystal

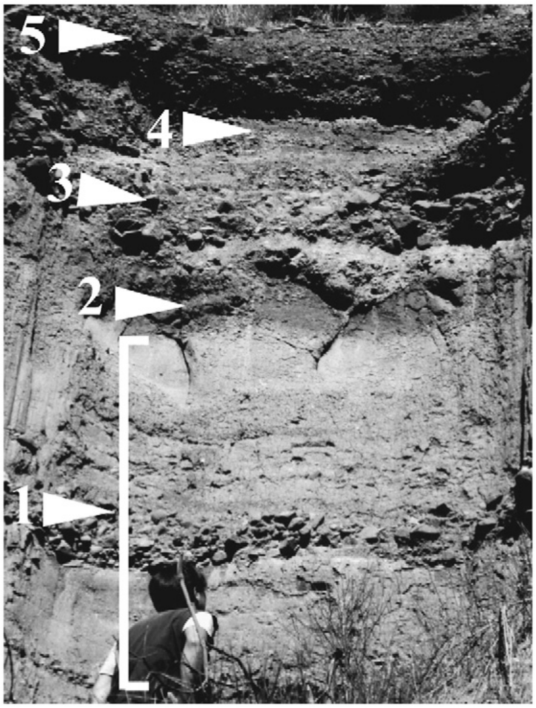


Fig. 5. Photo of the PL 3. From the bottom: (1) 6BCd horizon with gravel lenses, (2) 6Bwv horizon with gradual wavy boundary, (3) 5C/Bwv with (4) a wide pocket of weathered material and (5) 4C/Bwv gravelly horizon.

Table 2
Textural data

Pedostr. level	Horizon	Sand	Silt			Clay	Textural class	Silt/Clay	W.D.C.(2)	W.D.C.
		(%)	Coarse	Fine	Total	(%)			(%)	Clay (%)
				(%)						
PL1	A	26.1	13.1	31.7	44.8	29.1	Clay loam	1.5	n.d.	n.d.
	Bw	20.2	16.0	28.4	44.4	25.4	Clay loam	1.7	n.d.	n.d.
	Bss	18.5	9.4	32.6	42.0	39.5	Silty clay loam	1.1	n.d.	n.d.
	Bssk	17.2	7.8	32.8	40.6	42.1	Silty clay	1.0	29.0	68.9
	BCyg	15.9	7.5	30.0	37.5	46.6	Clay	0.8	n.d.	n.d.
PL2	2Bjyg	28.6	10.1	28.5	38.6	32.8	Clay loam	1.2	6.0	18.4
	2BCyg	40.8	7.6	21.4	29.0	30.2	Clay loam	1.0	n.d.	n.d.
PL3	3Btv	33.8	9.2	21.7	30.9	35.3	Clay loam	0.9	34.7	98.3
	4Btv	25.9	7.9	21.6	29.5	44.6	Clay	0.7	2.6	5.9
	4C/Bwv (1)	35.2	13.9	26.4	40.3	24.5	Loam	1.6	n.d.	n.d.
	6Bwv	26.6	15.6	34.3	49.9	23.5	Loam	2.1	n.d.	n.d.
	6BCd	39.6	13.8	24.1	37.9	22.5	Loam	1.7	n.d.	n.d.
PL4	7CBzdg	18.1	10.5	36.1	46.6	35.3	Clay loam	1.3	n.d.	n.d.
	7CBg	19.1	14.4	36.1	50.5	30.4	Clay loam	1.7	n.d.	n.d.

Main horizons with plinthite are shadowed.
(1)Gray parts of Bwv. (2)Water dispersible clay.

aggregates were found. A sulfuric horizon with natrojarosite concentrations characterizes the second PL (PL2: lagoon), where parent material is coastal swamp deposits.

The most prominent pedogenesis, giving the paleosol its distinctive dark red colour and plinthite morphology, distinguishes the thick third PL (PL3: alluvial fan). Within the PL3, the horizons with plinthite morphology are argic or cambic, more or less hydromorphic and hardened. They alternate with light grey conglomerates, constituted by moderately to strongly weathered clasts, with pockets of red fine material. Hard plinthite nodules are part of big firm aggregates, without any solution of continuity between hard plinthite and the rest of the mass. The last PL (PL4: lacustrine) groups cambic horizons, whether massive or weakly structured, having hydromorphic features and salt accumulation, and which are more or less compacted.

4.3. Main physical and chemical characteristics of pedostratigraphic levels

The PL1 has a clay content which tends to increase with depth, while sand and silt/clay ratio decrease, probably as a result of surficial selective erosional and colluvial processes (Table 2). Most clay is water dispersible, which indicates a high potential for dispersion and movement throughout the soil. As expected in a relatively young soil formed from marine sediments, organic matter is low, pH is subalkaline, calcium carbonate and CEC are elevated, and the exchange complex is saturated (Table 3). The lower BCyg horizon, however, shows transitional characteristics toward the underlying pedostratigraphic level. In fact, calcium carbonate and CEC are rather low, the exchange complex has a significant amount of sodium and magnesium, and the electrical conductivity significantly increases.

The PL2 is divided into two horizons, one of which is a sulfuric horizon with natrojarosite, acid and only partially saturated by magnesium and sodium. CEC of both horizons is remarkably lower than in the PL1, and electrical conductivity higher. The soil on PL2 has wetland soil characteristics and would not have experience much change by burial of the marine sediments. The changes only occurred when the land rose and exposed the sediments to oxidizing condition. This would demonstrate that the soils of the underlying PLs have not been affected by water percolating from the surface, because of the extremely low permeability of the overlying clayey horizons.

Horizons of the PL3 have different particle size, but they are all poor in organic carbon, neutral or subalkaline and, except for the lowermost horizon, they have a very low or negligible calcium carbonate content and are saturated, or nearly saturated, mainly by magnesium and sodium. The electrical conductivity is lower than the horizons of the other PLs, nevertheless the values show the presence of a certain quantity of dissolved salts, which can promote soil slaking.

The two horizons of the lowermost PL4 are both clay loam and contain calcium carbonate giving them subalkaline or alkaline conditions. They are richer in organic carbon than the overlying horizons and are saturated with calcium and sodium. Horizon 7CBzdg, in particular, has a high electrical conductivity, caused by soluble salts, which are 3% of the weight of the fine earth fraction. X-ray analysis showed that the salts are NaCl and $NaNO_3$, and the presence of sodium nitrate, in particular, indicates that the ground water was connected to a nearby lacustrine environment.

4.4. Iron forms and indices of weathering

While total iron content (Fet) is rather variable, dithionite extractable iron (free iron: Fed), oxalate iron (amorphous iron:

Table 3
Main chemical and physical properties of the soil horizons

Pedostr. level	Horizons	pH	EC (dS/m)	$CaCO_3$ (%)	OC (%)	CEC soil (cmol Kg^{-1})	CEC clay$^{(1)}$ (cmol Kg^{-1})	Exchangeable bases (cmol Kg^{-1})				BS$^{(2)}$ (%)	ESP$^{(3)}$	Fe (g/Kg)$^{(4)}$			Weathering indices		
								Ca	Mg	K	Na			Fet	Fed	Feo	Feo/Fed	$\frac{\text{Fed-Feo}}{\text{Fet}}$	Fed/clay (%)
PL1	A	8.0	n.d.	0.7	n.d.	1.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.21	n.d.	n.d.	n.d.	n.d.	n.d.
	Bw	8.0	2.0	0.9	0.0	1.0	3.3	25.7	1.4	0.3	0.2	100	0.9	57.90	16.40	1.00	0.06	0.27	6.5
	Bss	8.5	2.2	22.7	1.2	25.1	49.6	25.5	1.8	0.3	0.3	100	1.1	58.60	16.80	1.00	0.06	0.27	4.3
	Bssk	8.5	2.3	27.2	0.9	25.4	50.7	22.5	3.7	0.2	0.5	100	2.0	55.50	16.50	0.70	0.04	0.28	3.9
	BCyg	8.3	3.5	7.8	0.6	7.3	10.2	10.8	4.2	0.3	3.8	100	19.8	62.60	18.60	3.40	0.18	0.24	4.0
PL2	2Bjyg	4.0	4.4	< 0.5	0.5	10.5	24.6	0.6	6.1	0.3	1.2	78	14.5	62.60	24.50	2.20	0.09	0.36	7.5
	2BCyg	8.3	4.5	3.8	0.5	6.9	14.9	1.0	5.6	0.3	1.3	100	16.5	68.20	24.50	23.30	0.95	0.02	8.2
PL3	3Btv	7.8	2.7	0.5	0.4	9.7	22.6	0.4	7.4	0.4	1.2	95	12.7	63.90	22.50	1.70	0.08	0.33	6.4
	3Btv-r-*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	77.00	28.20	0.40	0.01	0.36	n.d.
	4Btv	7.4	2.9	< 0.5	0.5	12.4	22.5	0.5	8.1	0.6	3.3	100	26.2	75.30	32.40	1.20	0.04	0.41	7.3
	4C/Bwv**	7.5	3.3	< 0.5	0.3	9.8	33.8	0.3	7.9	0.5	3.4	100	28.2	44.70	5.10	2.50	0.49	0.06	2.1
	6Bwv	7.3	2.5	1.9	0.4	10.6	37.8	0.5	8.3	0.6	1.9	100	17.2	44.00	29.40	1.40	0.05	0.64	12.5
	6BCd	7.9	2.3	10.3	0.5	10.1	35.1	25.3	3.1	0.4	2.1	100	6.8	67.80	22.60	0.70	0.03	0.32	10.0
PL4	7CBzdg	8.6	7.2	14.2	0.6	13.8	31.6	12.4	4.8	0.7	6.8	100	27.6	118.80	22.20	0.80	0.04	0.18	6.3
	7CBg	8.0	4.1	10.8	0.7	9.7	21.7	21.1	2.3	0.4	2.2	100	8.5	50.20	12.80	0.80	0.06	0.24	4.2

Main horizons with plinthite are shadowed.

*Red matrix without gray mottles; **gray parts of Bwv. (1) CEC clay: $[(\text{CEC soil})-(4.5\times \text{OC\%})]\times 100/\%\text{clay}$. (2) BS: base saturation. (3) Exchangeable sodium percentage. (4) Fet: total iron, Fed: dithionite extractable iron, Feo: oxalate extractable iron.

Table 4
Elemental composition of the soil horizons

Pedostr. level	Horizon	SiO_2 (g/kg)	Al_2O_3 (g/kg)	Fe total (g/kg)	CaO (g/kg)	MgO (g/kg)	Na_2O (g/kg)	K_2O (g/kg)	MnO (g/kg)	TiO_2 (g/kg)	S (g/kg)	Cr (ppm)	Zn (ppm)	Ni (ppm)	Cu (ppm)	Co (ppm)	Pb (ppm)	L.O.I. (%)
PL1	A	432.9	115.8	53.6	97	17.3	3.8	19.2	1	6.1	1.0	104	88	55	22	12	23	25.0
	Bw	461.6	133.1	57.9	114.8	18.9	4	18.9	0.9	6.5	0.3	109	79	61	20	11	16	18.1
	Bss	460.1	136.5	58.6	116.3	19.3	4.1	19.2	0.8	6.6	0.7	111	78	59	18	10	16	17.6
	Bssk	443.5	128.9	55.5	134.6	19.4	4.2	17.9	0.7	6.2	0.2	101	71	57	17	10	14	18.7
	BCyg	513.2	181.4	62.6	73.9	27.1	9.1	27.1	0.5	7.4	15.0	104	92	60	20	10	12	8.1
PL2	2Bjyg	624	165.8	62.6	4.8	15.8	12.7	27.2	4.9	9.6	n.d.	135	182	136	60	32	34	7.1
	NJ (1)	60	23.5	388.6	3.4	3.5	26.7	11	0.1	2.9	151.2	119	14	2	87	3	21	32.8
	2BCyg	577.5	173.7	68.2	24.8	19.2	14.3	27.8	6.6	8.1	n.d.	146	70	46	44	11	31	7.9
PL3	3Btv	629.1	181.5	63.9	8.7	13.3	12.1	28.4	0.3	9.3	n.d.	140	125	74	45	20	33	5.2
	3Btv -r- (2)	627.7	177.9	77	1.8	13.8	11.7	27.7	0.6	9.5	n.d.	123	120	69	65	20	34	5.1
	3Btv -g-(3)	669	189.6	26.6	1.2	14.6	12.8	28.5	0.1	9.7	n.d.	121	93	65	30	14	20	4.7
	4Btv	615.5	177.4	75.3	2.1	15.3	16.6	29.1	0.1	10.2	n.d.	157	78	48	29	16	33	5.7
	4C/Bwv (4)	606.2	190.3	44.7	1.4	22.2	40.3	33.7	0.9	10.1	0.4	92	119	83	45	30	31	4.5
	6Bwv	514.6	169.4	44	9	20.7	83.4	35.2	0.4	13.4	1.1	104	181	61	33	36	29	4.9
	6BCd	515.5	174.5	67.8	76.5	18.5	15.2	30.6	2.1	8.4	n.d.	117	82	54	17	14	32	9.9
PL4	7CBzdg	329	160	118.8	117	28.7	49.9	28.5	2.2	11.4	11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8.2
	7CBg	514.2	172.6	50.2	79.1	19.3	16.1	27.1	1.2	8.6	n.d.	115	86	53	21	14	32	11.1

Main horizons with plinthite are shadowed.

(1) Natrojarosite concretions [$(K,Na)Fe_3(SO_4)_2(OH)_6$] in the sulfuric horizon 2Bjyg; (2)red matrix, (3)grey matrix, (4)grey parts of Bwv horizon.

Table 5
Clay mineralogy of the soil horizons

Pedostr. level	Horizon	Illite (%)	Kaolinite (%)	Vermiculite (%)	Chlorite (%)	Mixed layer (%)
PL1	Bssk	15	27	35	2	21
	BCyg	70	11	18	2	0
PL2	2Bjyg	77	7	4	1	11
PL3	3Btv	81	15	2	1	1
	4Btv	91	7	1	0	1
	4C/Bwv[(1)]	89	9	1	1	0
	6Bwv	91	3	1	0	5
	6BCd	84	9	2	5	0
PL4	7CBzdg	82	11	1	5	1
	7CBg	79	16	0	5	0
	8Cr[(2)]	54	23	21	2	0

Main horizons with plinthite are shadowed.
[(1)]: Gray parts of Bwv. [(2)]: Underlying marine deposits, not outcropping in the section.

Feo) and weathering indices give indications about the different stages of weathering of the parent material (Table 3). As indicated by the low values of Feo/Fed ratio, the high (Fed–Feo)/Fet and Fe/clay percentage ratios, the most altered parent materials are those of the horizons of PL3. Within this level, however, grey parts of 4C/Bwv horizon have indices of weathering that reflect intense reduction and consequent free iron removal.

Both horizons of PL2 have high values of Fed/clay, and 2Bjyg has values of Feo/Fed and (Fed-Feo)/Fet similar to those of the underlying horizons of the PL3. On the other hand, the 2BCyg horizon shows very high values of Feo, probably because of the presence of natrojarosite. Finally, all the indices of weathering indicate that the parent materials of the horizons of PL1 and PL4 are less altered than PL2 and 3.

4.5. Elemental composition

Descriptive analysis of major and trace elements concentration in the studied horizons is reported in Table 4. In spite of the lithological discontinuities, it is fairly evident that the average concentration of heavy metals is higher in the horizons with a more pronounced pedogenesis. In particular, Fe, TiO_2, Cr, Ni, Co and Zn contents are greater in the horizons with plinthite and in the sulfuric 2Bjyg horizon. Moreover, natrojarosite concretions are particularly rich in Fe, S and Na, while the 7CBzdg horizon, with salt accumulation, is also the richest in CaO, MgO and Fe.

The horizons with plinthite show on average a higher SiO_2 and Al_2O_3 content than the other horizons, while on the other hand, there is striking decrease of CaO and MnO. As a consequence of the reduction and oxidation process, the grey areas of these horizons have a lower content of Fe and other heavy metals (Cr, Zn, Co, Ni, Pb, Cu) than the red areas, while they have a larger amount of SiO_2 and Al_2O_3. Horizon 3Btv, which has been more affected by waterlogging, and consequently has the largest proportion of grey spots, also shows the highest amount of silica plus alumina (810.6 g/kg). Similarly, K_2O and Na_2O contents are higher in the grey parts than in the matrix of all the horizons with plinthite.

4.6. Clay mineralogy

Clay minerals (Table 5, Fig. 6) highlight a distinct differentiation between the covering and basal marine clays and horizons of the continental PLs. Although belonging to the

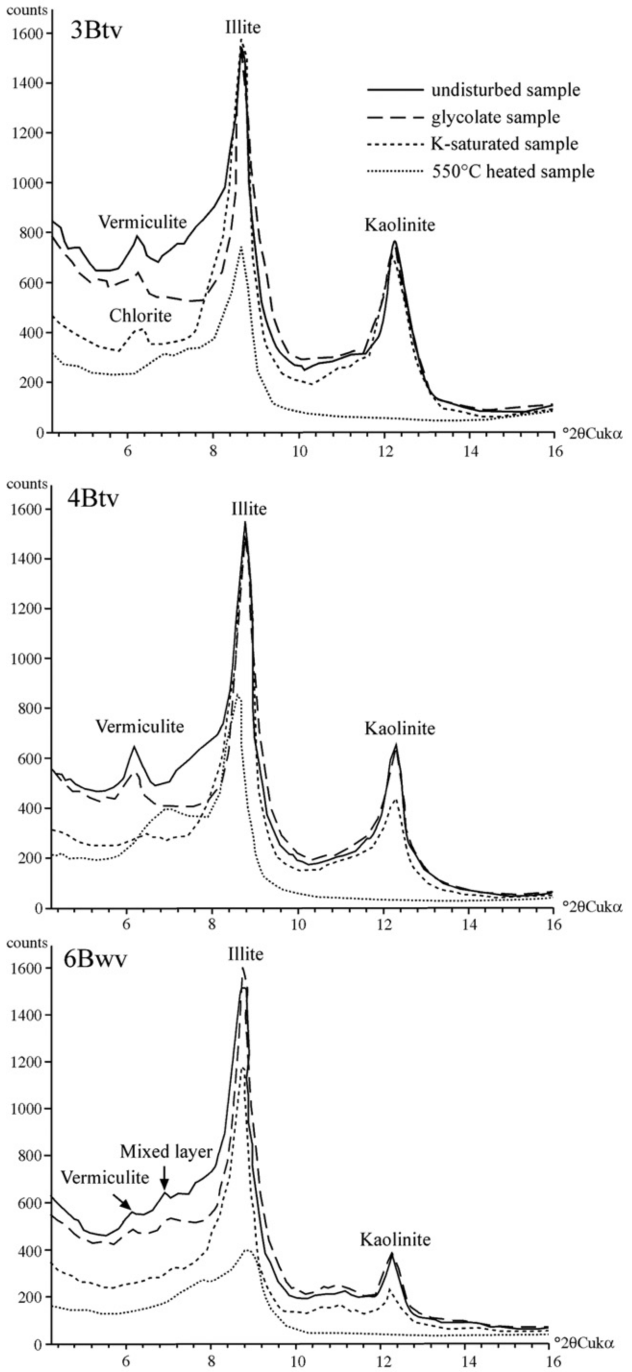


Fig. 6. Diffractograms of the clay fraction from horizons with plinthite.

Table 6
Micromorphological description of horizons with plinthite

Horizon			3Btv	4Btv	6Bwv
			sbk	ma	ma
Microstructure[a]					
Voids	Vughs (%)		4	1	1
	Channels (%)		4	1	1
	Chambres (%)		1	–	–
Coarse fraction	Mineral (nature)		Quartz	Quartz	Quartz
	Rocks (nature)[b]		sed	sed	sed
	Shape[c]		sbr	sbr	sbr
	Quartz weathering[d]		1 (E)	1 (E), 2 (A)	1 (E)
	Rock weathering[d]		2 (D)	2 (D)	2 (D)
Groundmass	*c*/*f* ratio		1/1	1/1.5	1/1
	Relative distribution (porphyric)		Single spaced	Single spaced	Single spaced
	b-fabric[e]	Undifferentiated		d	d
		Stipple speckled	s	o	
		Mosaic speckled	o		
		Granostriated	s		
		Porostriated	d	s	
		Parallel striated	o		
Depletion pedofeatures	Mottles (gray and yellow)		++++	++	+
Amorphous pedofeatures[f]	Ferruginous hypocoatings		++	++	+
	Ferruginous concretions			+	+
Textural pedofeatures[f]	Infillings	Silt (reddish-brown)	+		
		Dusty clay (gray, orange and reddish)	++	+	
		silt-clay (gray, orange and reddish)	++	+	+
	Coatings (dusty clay)	Laminated (reddish, orange and yellow)	++	+	
		Non-laminated (reddish, orange, yellow and gray)	+	+	
		Convolute	++		

[a] sbk: Subangular blocky, ma: massive.
[b] sed: Sedimentary rocks (sandstone, siltstone).
[c] sbr: Sub-rounded.
[d] Class (pattern) according to Bullock et al. (1985).
[e] d: Dominant, s: subordinate, o: occasional.
[f] +: Rare (<2%), ++: occasional (2–5%), +++: many (5–10%), ++++: abundant and very abundant (10–30%).

PL1, the BCyg horizon, as already mentioned, actually shows transitional properties with the underlying PL. Continental clays have illite (clay mica) values from 79 to 91%, compared to only 15 or 54% in the marine clays. Kaolinite and vermiculite range from 3 to 16% and from 0 to 4% in continental clays, respectively, whereas they reach 27% and 35% in the marine sediments.

Within PL3, we can appreciate the effects of pedogenesis by comparing horizons which formed in the same parent material, but are at a different stage of weathering, that is 4Btv and grey matrix of the underlying 4C/Btwv, as well as 6Bwv and underlying 6BCd. The most noteworthy are the increases in illite content in 4Btv and 6Bwv and corresponding decreases in kaolinite. Minor changes are related to the disappearance of chlorite, and concomitant mixed layers formation.

4.7. Micromorphology of horizons with plinthite.

Rock fragments and coarse mineral grains throughout the profile appear weathered and testify an "in situ" weathering of parent materials (Table 6). Mineralogical composition of least weathered parts of the clasts is dominated by quartz and mica as shown by micromorphological and X-ray diffraction examination. The main pedogenetic processes in plinthite formation is accumulation of iron oxides, which produces a dark red colour, and iron reduction and depletion, which produce bleached zones.

Iron accumulates in the material as hypo-coatings around grains. Small (500–1000 μm) ferruginous concretions, with irregular shapes and diffuse boundaries, are present in horizons 4Btv and 6Bwv and demonstrate an "in situ" formation. Iron depleted zones are more abundant in horizon 3Btv. They commonly correspond with areas of clay accumulation and non-laminated clay infillings. In the 3Btv horizon, three main successive generations of textural pedofeatures can be distinguished: the older one is represented by occasional, thick (300–1000 μm) silty-clay non-laminated infillings, which are more abundant in the grey iron depleted zones; the second one is characterized by occasional, medium–thick (100–800 μm) dusty clay infillings and coatings, coarsely parallel or convoluted laminae, which can occur both in the grey and red areas (Fig. 7a, b); the younger one is represented by rare medium (100–300 μm) reddish-brown silt infillings in channels of biological origin. Clay coatings show some signs of aging, like fragmentation and disorientation, leading to dull extinction bands under crossed polarized nicols. The underlying 4Btv horizon with hard plinthite (Fig. 7c) has only two principal textural pedofeatures: the first one is rare, medium–thick (100–

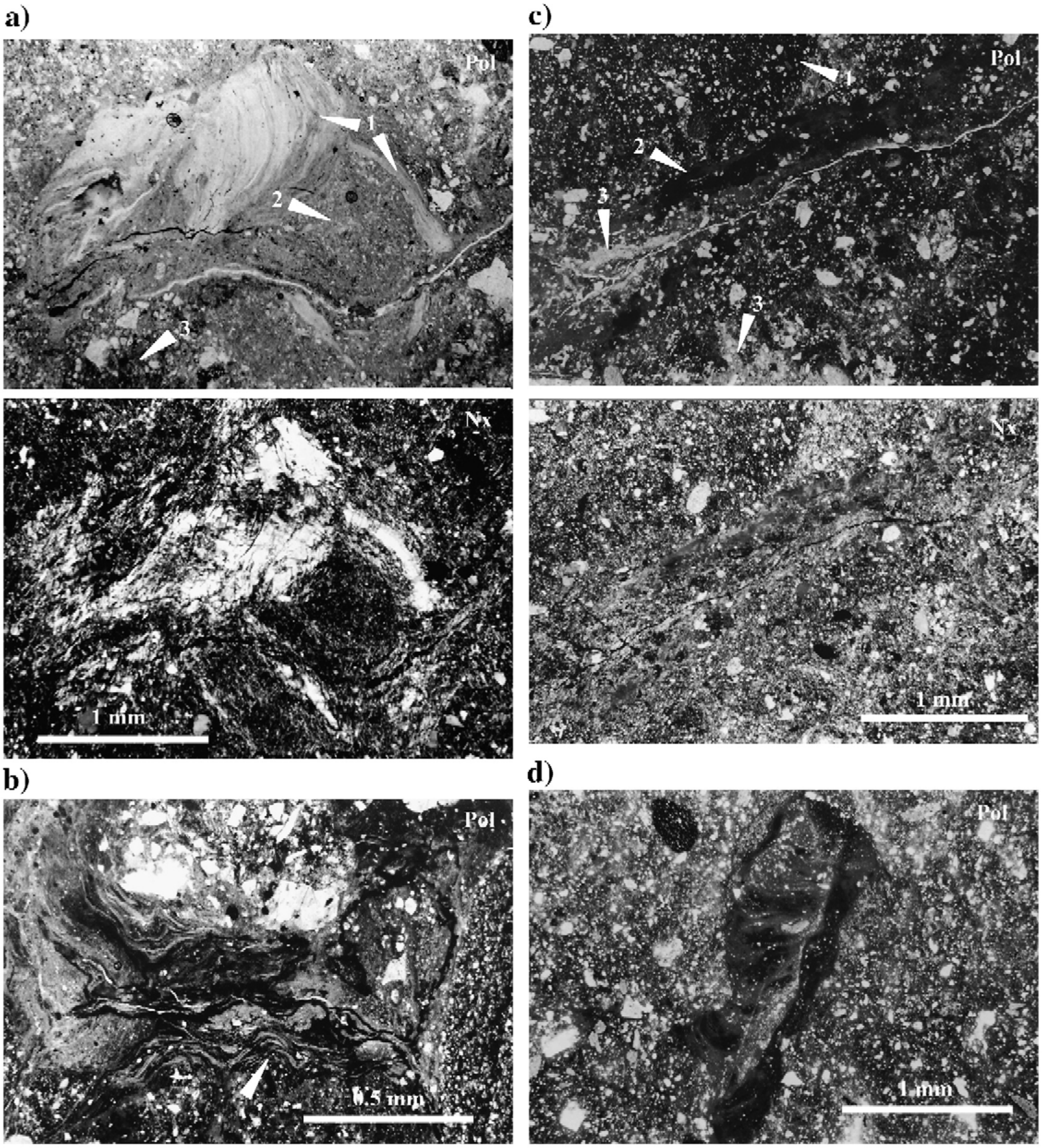


Fig. 7. a. Micromorphology of 3Btv horizon. Grey dusty clay infillings, coarse laminated (1), predating grey silty-clay infillings, non-laminated (2). In the lower part of the picture there is a reddish mottle (3). Upper — plain light; lower— polarized light. b. 3Btv horizon. Grey and yellow dusty clay coatings, coarse and convoluted laminae (arrow). c. 4Btv horizon. (1): Iron oxides accumulation in the matrix; (2): reddish dusty clay coatings, non-laminated; (3): grey, iron depletion mottles. d. 6Bwv horizon. Reddish silty-clay infilling.

500 μm) silty-clay non-laminated infillings, superposed by rare, medium (100–300 μm) dusty clay poorly laminated coatings. In the lowest 6Bwv horizon, textural pedofeatures are only rare and medium-thick (100–500 μm) silty-clay non-laminated infillings (Fig. 7d).

5. Discussion

5.1. Interplay between geomorphological evolution and soil genesis

The Podere Renieri section contains a sequence of inter-stratified paleosol profiles. Their genesis can be best explained by taking as a reference the succession of geomorphological events which occurred from early Pliocene to Quaternary, which was interpreted from the bulk of sedimentological, geomorphological, soil surveys and laboratory analysis, matched with the literature (Ambrosetti et al., 1978; Bartolini et al., 1982) (Fig. 3).

a) PL4: the lacustrine sediments were deposited on the first marine transgressive clays. Following the lake environment, an incipient pedogenesis developed the horizons 7CBg and 7CBzdg.
b) PL3: during early Pliocene, a normal fault raised the Murlo–Montalcino ridge. The erosion of the uplifted rocks created a system of coalescent alluvial fans. The sedimentation was cyclical, as we recognized at least four main debris flows,

which formed conglomerates. The debris flows were followed by longer periods of quiet and finer (sand, silt and clay) deposition. In between the debris flows, the pedogenetic conditions permitted a strong iron release from parent material and accumulation in soil. A water table fluctuated within the soil, causing the characteristic grey and red mottling produced by iron reduction and oxidation. The groundwater must have been contaminated by seawater, as it was rather rich in salts. The influence of the water table, and the consequent mottling, were more accentuated within the very permeable conglomerates, and progressively towards the upper horizons of the PL, giving evidence of an increasing impairment of the drainage. The conglomerates are mostly greyish, rather than reddish, as we expected them to be, although pebbles are slightly or moderately weathered, because the iron released by weathering has been reduced and removed, giving evidence that conglomerates acted as preferential pathways for the sea water to contaminate groundwater. Thus, the periodic cycle of deposition and pedogenesis interplayed with a progressive rising of the sea level.

c) PL2: in this time of early Pliocene the sea rose again and an environment with brackish water, little oxygenated, was created. Sedimentation was characterized by pyrite microcrystalline precipitation and clay and silt alternated with lenses of gravel and sand. Pedogenesis transformed the whole deposit and generated an acid sulphate soil (horizon 2Bjyg).
d) PL1: a second marine transgression submerged and buried the whole area and the underlying pedogenized deposits.
e) During late–middle Pliocene the whole basin emerged and the deposited clays began to form soil.
f) Quaternary was a time of intense erosion, which did not allow advanced pedogenesis of the clays. River incision, however, permitted the buried soils to outcrop in many parts of the area (Fig. 8). The soil sections are still continuously rejuvenated today by water and mass erosion, as evidenced

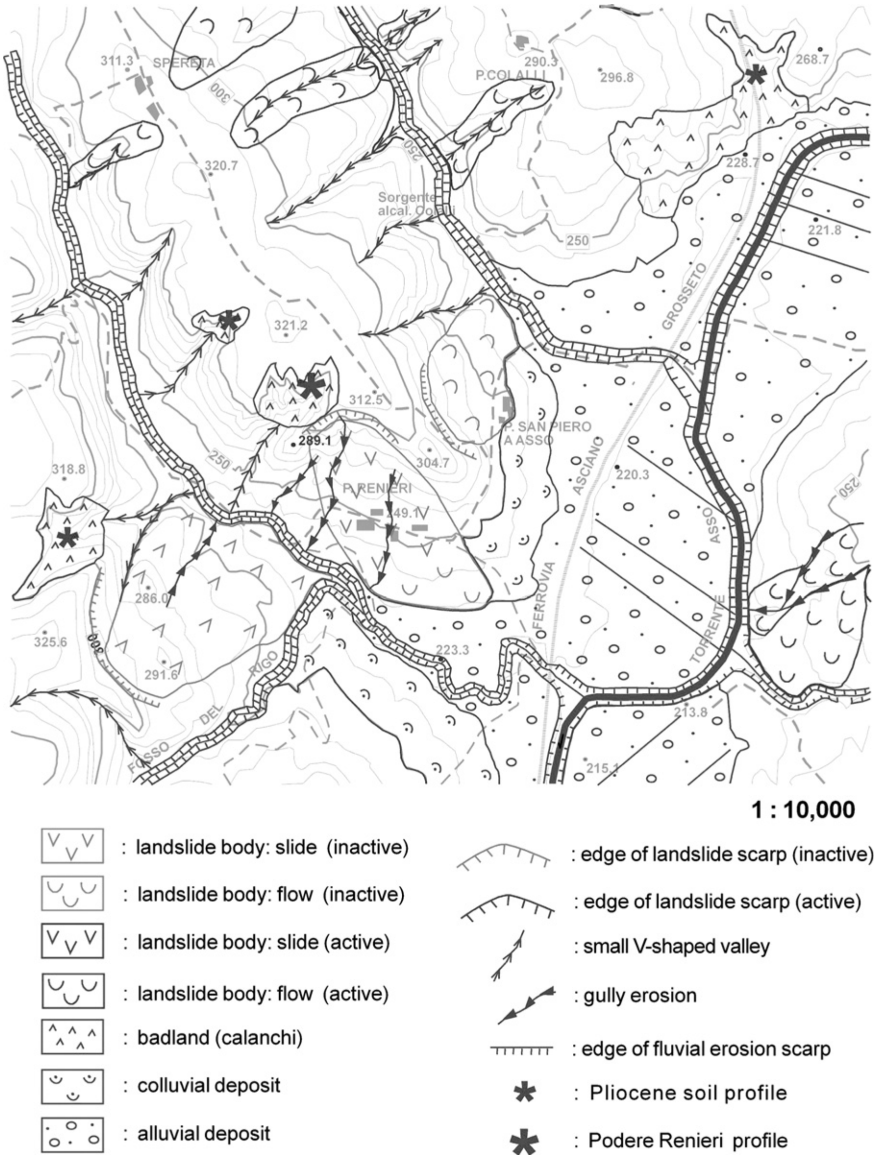


Fig. 8. Geomorphological sketch of the Podere Renieri area.

in the geomorphological map, therefore the paleosols are not transformed by the present pedogenesis.

5.2. Clay mineralogy of the Podere Renieri paleosol complex

The clay mineralogy of the horizons formed in continental sediments is mainly illitic, with a low percentage of kaolinite. As the literature reports, this clay mineralogy is very unusual for soils with plinthite (Macedo and Bryant, 1987; Dos Anjos et al., 1995), moderately and strongly weathered tropical soils (Osher and Buol, 1998; Krasilnikov et al., 2005) or for red soils in the Mediterranean areas (Torrent et al., 1980; Costantini and Damiani, 2004). In general, these soils all have a much higher kaolinite content that is always greater than illite. In Soil Taxonomy and WRB classifications too, plinthite is defined as a mixture of kaolinitic clay with quartz and other minerals. Kaolinite is one of the typical products of weathering in plinthite and red soil formation.

We assume that illite is detrital and its stability was favoured by a particular chemical condition at the time of soil formation, that is, high potassium and base content and low water activity. In fact, according to Grim (1953), a potassium rich rock or sediment can provide the soil with such an elevated amount of potassium that illite will persist in the system after other primary minerals break-down, even under strong weathering conditions. In actual fact, potassium content of the horizons formed in PLs 2 to 4 averages 30 g/kg of K_2O (Table 4), a value which is much larger than the marine clays of PL1, as well as the other Pliocene marine clays of the Siena Basin, which span from 19 to 23 g/kg (Benvegnù et al., 1993), and also greater than the Quaternary paleosols of the Siena Basin, which average 13–14 g/kg (Costantini et al., 2002). The main factor, however, seems to be the low water activity during the pedogenesis, because of the presence of a water table connected to the very close Mediterranean sea (Fig. 3). As argued by Fletcher (1993), a low water activity can support illite preservation.

5.3. Soft and hard plinthite

5.3.1. Definitions

According to both Soil Taxonomy and WRB, plinthite is an iron-rich, humus-poor mixture of clay with quartz and other minerals, which changes irreversibly to an ironstone hardpan or to irregular aggregates on exposure to repeated wetting and drying, especially if it is also exposed to heat from the sun. Plinthite may or may not form a continuous phase within an epipedon, a cambic, an argillic, an oxic, or a C horizon. It forms by segregation of iron in a horizon that is saturated with water for some time during the year. Plinthite can be distinguished from iron concentrations which are not plinthite when the latter do not irreversibly harden. Even though, plinthite does not harden irreversibly as a result of a single cycle of drying and rewetting. Plinthite can be separated from irreversibly hardened petroplinthite (ironstone) because petroplinthite cannot be dispersed in water containing a dispersing agent.

According to Soil Taxonomy, plinthite occurrence is diagnostic for subgroup classification when it occupies more than 5% of the horizon volume, while a plinthic horizon in the WRB system must have at least 25% plinthite. WRB, moreover, specifies that the plinthic horizon must have 2.5% (by weight) or more citrate–dithionite extractable iron in the fine earth fraction, especially in the upper part of the horizon, or 10% in the mottles or concretions; a ratio between acid oxalate (pH 3) extractable iron and citrate–dithionite extractable iron of less than 0.10; less than 0.6% (by weight) organic carbon; and thickness of 15 cm or more.

Although “soft” and “hard” plinthite are terms which are often utilized, there are no precise definitions for them. Soil Taxonomy says that plinthite must be soft enough to be cut with a spade. Daniels et al. (1978) suggested that plinthite should be firm to very firm when moistened and very hard to extremely hard when dry. Similar materials that will not irreversibly harden are friable to firm when moistened and hard to slightly hard when dry. Driessen et al. (2001) reported that soft plinthite occurs in less well-drained positions of the landscape and are indigenous to the rain forest zone, while its hardening is initiated by the removal of vegetation and consequence exposure to the open air.

5.3.2. Problems with plinthite recognition

In spite of the fact that plinthite is well known and has been extensively studied, its recognition is still open to a certain degree of interpretation. In fact, plinthite is supposed to harden irreversibly, but the time needed for its hardening is not specified, although both Soil Taxonomy and WRB classification systems suggest it should be long. Wilding et al. (1983), in particular, wrote that many classification problems arise because of a lack of standard regarding the time necessary for induration to occur. On the other hand, in a recent work carried out in Ghana, Asiamah (2002) described soft plinthite in different geomorphological conditions, which had hardened in less than 14 months. The hardening took place with only one cycle of wetting and drying, as a consequence of vegetation removal, strong dehydration and iron concentration.

To overcome the problem of plinthite recognition as a function of hardening, Daniels et al. (1978), as well as Wood and Perkins (1976), proposed the use of the “slaking in water” test, a test of sample resistance when submerged in water. Wood and Perkins suggested a single 2-hour submersion, while Daniels et al. (1978) recommended two soakings; soaking of the bulk sample for 8 h, followed by another 2 h for samples <3 cm in size. The non slaked material will be retained on a 2 mm sieve. To assess cementation in plinthite nodules Schoeneberger et al. (1998) recommended using a sample of about 3 cm in size, submerging it water for a minimum of 1 h to test, and performing a manual rupture resistance evaluation.

In conclusion, plinthite recognition is difficult, because plinthite has been allowed to range across a continuous series of iron oxide enriched materials that hardens to different degrees, in different time frames and under different conditions. The variables involved are soil mineralogy, characteristics of the site, climate, vegetation cover, land use, underlying lithology (Fitzpatrick, 1980), morphological position and hydrology (Ollier and Galloway, 1990).

Fig. 9. “Hard” plinthite, 4Btv horizon, grey mottles in the reddish matrix.

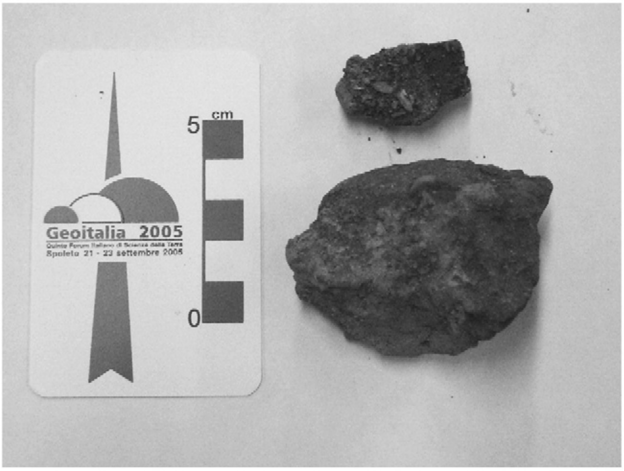


Fig. 10. Hard plinthite concretions of the 4Btv horizon, after 2 h of water submersion (Wood and Perkins test).

5.3.3. Podere Renieri plinthite

The consistence of horizons with “soft” and “hard” plinthite in the Podere Renieri paleosol complex (Fig. 9) is similar to that reported by Daniels and co-authors for plinthite and petroplinthite, respectively, but only one of the two horizons with “hard” plinthite (horizon 4Btv) clearly passed the water submersion tests of Wood and Perkins (1976), Daniels et al. (1978) and Schoeneberger et al. (1998), that is, it had concretions that did not slake in water (Table 7, Fig. 10). Therefore we can not confirm the relationship between soil consistency and resistance to slaking in water.

Besides consistency, the main macromorphological differences between the two kinds of horizons are related to structure, which is massive in hard plinthite (4Btv, 6Bwv) and moderate coarse subangular blocky in soft plinthite (3Btv), and to iron depletion mottles, which are more abundant in soft plinthite (Table 1). Matrix colour is similar in both soft and hard plinthite, although 4Btv has the highest redness rating.

At Podere Renieri, horizons with both soft and hard plinthite are saturated and have neutral or subalkaline pH, while most authors report buried plinthite in acid or subacid and desaturated horizons (Torrent et al., 1980; Magaldi and Bidini, 1991; Dos Anjos et al., 1995). As already quoted in Section 5.1, we can explain the chemistry of these horizons by the vicinity of the sea.

Soft and hard plinthite show similar values of pH, EC, carbonate and organic matter content (Table 3). CEC is slightly lower in soft plinthite than in hard plinthite, as a consequence of clay mineralogy, which is more kaolinitic and less illitic in the softer forms (Table 5). As for exchangeable bases, both horizons with hard plinthite show a larger amount of sodium than the horizon with soft plinthite, and a higher exchangeable sodium percentage.

Particle size distribution varies from loam to clay loam and clay. It thus does not differentiate the two kinds of plinthite. However, the 3Btv horizon, with soft plinthite, contains much more water dispersible clay, namely 98.3% of the total clay, than the 4Btv horizon with hard plinthite, which has only 5.9% (Table 2). That means that clay particles in hard plinthite are

Table 7
Rupture resistance evaluation of the horizons with plinthite and results of Wood and Perkins (1976) and Daniels et al. (1978) tests

Horizon	Type of plinthite	Consistence				Test for plinthite presence[b]	
		Rupture resistance class for block-shaped specimens[a]					
		Moderately and very dry	Slightly dry and wetter	Air dried, water submerged		Wood and Perkins (1976)	Daniels et al. (1978)
				Total mass	Concretions		
3Btv	Soft plinthite	Very hard	Very firm	Loose	Absent	0	0
4Btv	Hard plinthite	Extremely hard	Extremely firm	Loose	Very hard[c]	7	3
6Bwv	Hard plinthite	Extremely hard	Extremely firm	Loose	Absent	1	0

[a] According to Schoeneberger et al. (1998).

[b] Percentage of plinthite.

[c] 5% of concretions on the total mass.

almost all aggregated in a permanent form, probably by iron oxides. Analysis of iron forms seems to confirm this hypothesis (Table 3). In fact, dithionite extractable iron in horizons 4Btv and 6Bwv is 32.4 and 29.4 g kg^{-1} respectively, while it is 22.5 g kg^{-1} in horizon 3Btv and 28.2 g kg^{-1} in its red stained mottles. The Feo/Fed ratio is much lower in hard plinthite (0.04 and 0.05) than in soft plinthite (0.08), showing a higher crystallinity of iron oxides in the former, while it is 0.49 in the less weathered parent material (4C/Bwv horizon) and reaches 0.01 in red masses of the 3Btv. The higher values of the Fed/clay ratio indicate a more advanced iron segregation in hard plinthite than in soft plinthite. With reference to the requirements for a plinthic horizon in the WRB classification system, both horizons with hard plinthite meet the criteria for Fed content and Feo/Fed ratio, while only the red parts of soft plinthite have a Fed content higher than the threshold of 25 g/kg.

The comparison of the iron values in the forms of soft and hard plinthite with those obtained by other authors for Quaternary paleosols outcropping in the same geological basin (Costantini et al., 1996b), in Tuscany (Magaldi and Bidini, 1991) and in Northern Italy (Arduino et al., 1984) can give us a better estimation of the time of plinthite formation. (Fed–Feo)/Fet, which is generally considered the most reliable weathering index, is always lower in the Podere Renieri horizons than in soils attributed to early Pleistocene. In particular, soft plinthite has (Fed–Feo)/Fet values ranging from 0.33 to 0.36 compared to the hard plinthite forms that have values of 0.41 to 0.64. The values are comparable to those reported in the referenced works on relict middle and late Pleistocene soils, but they are always lower than 0.7, which is the minimum for non-buried soils attributed to early or early–middle Pleistocene. If we assume that climatic conditions during early Pliocene were much more favourable for iron release and recrystallization than in middle and late Pleistocene, we can infer that this process must have lasted for a considerably shorter time, probably for only 100,000 or 200,000 yr, or even less, and then ceased after burial.

Horizons with soft and hard plinthite are hardly differentiated by the elemental analysis (Table 4), due to a substantial homogeneity of the source of parent material. Apart from the Cr, which follows Fe content and is higher in the 4Btv horizon with plinthite concretions, the main differences are related to Na, Mg, K and TiO_2 contents, which increase from 3Btv to 4Btv and 6Bwv, and to SiO_2 and Al_2O_3, which decrease in similar fashion, probably because of a greater influence of salt water and a higher proportion of coarse gravels and cobbles.

Micromorphology analysis confirms the differences in soil structure and iron depletion features between soft and hard plinthite observed during the field survey (Table 6). The presence of ferruginous hypocoatings and concretions is also in accordance with field observations and the test of Wood and Perkins (1976). Other relevant differences between the horizons with soft and hard plinthite are related to: (1) the percentage of void space, which is larger in soft plinthite, (2) the degree of weathering of the coarse fraction, which is more advanced in hard plinthite, and (3) the b-fabric of the groundmass, which is much more articulated and complex in soft plinthite.

Key information comes from the clay coatings. Horizon 3Btv shows many more clay coatings and infillings than 4Btv and 6Bwv. Only the coatings of 3Btv are deformed and folded. This would imply that the burial of PL3 has not compacted and deformed the horizons with hard plinthite, and that the stronger consistency of the horizons with hard plinthite is not caused by a greater compaction by the overlying sediments. The deformation of the coatings in the 3Btv horizon, on the other hand, can be explained by the reaction of a more plastic mass to the overlying load, and to the landslides which have been wasting this locality (Fig. 8).

From the 6Bwv up through the 3Btv, there is a marked progressive increase in the number of infilling and coating generations, as well as a tendency to be more laminated. The first generation of textural features are silty-clay non-laminated infillings, which can be correlated across this interval. Non-laminated infillings point to a process of non-seasonal illuviation. The second generation of textural features are dusty clay coatings, absent in 6Bwv. Coatings in 3Btv clearly indicate a seasonality, but are only weakly expressed in 4Btv. A change in the nature of the clay skins is interpreted as a change in seasonality, which indicates a change in climate.

A more marked seasonal differentiation of the climate in the final part of the alluvial fan construction would be in agreement with the paleoclimate reconstructions of Palombo (1994) and Günster and Skowronek (2001), who postulated a trend of greater contrast between dry and wet seasons towards the end of the early Pliocene, and the beginning of a Mediterranean-like climate.

6. Conclusions

The buried paleosol complex at Podere Renieri documents the trend of climate change and pedogenesis that occurred during the early Pliocene in central Italy, along the cost of the Mediterranean sea. The macro and micro pedological features, the analytical data, together with the sedimentological and geomorphological evidence, have permitted the reconstruction of events which modified this land during early Pliocene, since its emersion from the sea until the successive re-submersion. The main pedogenetic features match well with a pedogenesis influenced by a hot and humid climate, similar to that attributed to this region during early Pliocene by some paleoclimatic and paleopedological models. Palombo (1994), in particular, assumes a trend towards an increase in the temperature seasonality during early Pliocene for the northern Italy area. The microfeatures of the horizons with plinthite at Podere Renieri demonstrate that, in the middle of early Pliocene, evidence of rain seasonality begins to show for a Mediterranean type of climate along the west coast of Italy.

The most distinctive soil horizons at Podere Renieri are those with plinthite that ranges from soft to hard. Their genesis and characteristics were significantly influenced by the geomorphological position of the paleosol during early Pliocene, an alluvial fan close to the coast. The horizons were therefore affected by the sea level changes occurring during that time, which caused the peculiar chemistry and mineralogy. Illite content is much higher than the expected kaolinite in the plinthic horizons, because of a high potassium and other base content of the soil water solution, and a low water activity. In addition, plinthic horizons are not acid, as expected, and the exchange complex is saturated.

In spite of the particular environment and chemistry of the soil water solution, plinthite formed in the classical way, that is, iron was released and accumulated in a pedo-environment with an oscillating water table, through reduction and oxidation, and consequent concentration in more or less hardened masses.

The different characteristics of soft and hard plinthite can be attributed to a more or less prolonged waterlogging and to climatic change. Soft instead of hard plinthite formed in the horizons with most prominent iron reduction and depletion, when the increased seasonality of the climate favoured the formation of coarse aggregates.

The horizons with soft plinthite do not have water resistant iron impregnated masses. The horizons with hard plinthite show only a small amount of water resistant concretions. Therefore they should be more properly called “low-grade plinthite”. Free iron content is always rather low, if compared to relict paleosols of Pleistocene age of the same region. Assuming that climatic conditions during early Pliocene were much more intense than in the Pleistocene, hence the time needed for plinthite formation appears to have been a rather short period, which may have lasted no more than 100,000 or 200,000 yr.

Finally, it is worth emphasizing that the presence of plinthite in some soils of the Montalcino region has a significant agronomic value for vineyards. The hardness of plinthic horizons limits the growth of the roots and reduces the risk of an excessive vegetation of the vines, while enhancing the quality of the grapes for making wine (Costantini et al., 1996a). In combination with the low nutrient status, the plinthic soil materials of the Podere Renieri area have iron and other elements needed for producing high quality wine. Therefore, contrary to the low quality soil characteristics for plant growth in general, plinthic soils are quality soils for vineyards, particularly the low grade plinthite of the Brunello di Montalcino wine region.

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