Physical, geochemical and mineralogical indicators of aging in Quaternary soils of Central Italy

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Abstract

In this paper, a set of physical, geochemical and mineralogical indicators are proposed for the correlation of soil age. The parameters studied allowed the highlighting of trends in soil aging as well as the relating of these trends to specific soil forming processes. Soil aging was marked by a progressive increase in clay content and a decrease in silt/clay ratio, a slight reduction in the CEC of clay and a striking increase in free iron content. Clay mineralogy transformation over time was marked by a progressive increase in kaolinite and vermiculite, as well as a decrease in illite and chlorite. The most outstanding pedological processes, i.e. crystalline free iron content increase, clay neo-genesis and illuviation, glossic horizon and fragipan formation, were all found to be related to kaolinite content. Element content, namely that of Fe, Cr, Pb, Zn, Ti and K increased from the Holocene to the Upper and Middle Pleistocene soil horizons and, as far as Fe, Cr, Pb and Zn are concerned, up to those attributed to the Lower Pleistocene. Al and Ca content decreased along with time, especially in soils older than Holocene. The trends of silt/clay ratio, CEC of clay and free iron were linear, that is not influenced by changes of weathering conditions during Pleistocene, while vermiculite and kaolinite content, total iron, chromium and lead distinguished the stronger weathering environment occurring during Lower Pleistocene in southern Europe. The tendencies of the remaining indicators revealed intermediate phases of mineral transformation or were influenced by rather fast processes. Besides soil age, the indicators resulted as being affected by clay impoverishment, which occurred within eluvial horizons and bleached streaks of fragipan, reducing and oxidizing conditions, and lithological and chronological discontinuities within profiles.

Keywords: soil physics, geochemistry, clay mineralogy, soil aging, Central Italy

Introduction

Paleosols are widespread throughout Italy and the entire Mediterranean belt. Climatic conditions during the different phases of Quaternary in Italy were favorable to weathering, but soil preservation was limited by the geological activity in the country and by intense land use, which often triggered severe soil erosion.

Dating of Paleosols is important, not only for the reconstruction of Quaternary geology, but also in the understanding of both activity and rate of the processes affecting soil functional qualities, among others, for instance, internal drainage, clay distribution within the profile and element content.

The dating of Paleosols based upon dated materials is very rare because of the scarcity of this kind of information; hence soil correlation is one of the most widespread tools used to estimate Paleosol age. But soil correlation can also be difficult, because Paleosols are often limited in extent, buried or badly preserved, and frequently formed on deposits of heterogeneous parent materials. Therefore the correlation is more reliable when based on the convergence of several kinds of evidence.

In this paper, a set of physical, chemical, geochemical and clay mineralogical soil parameters are proposed for age correlation.

The study elaborated data on soils and paleosols of the Montagnola Senese territory, situated in Central Italy, which had already been investigated to appraise the relationships between Quaternary geomorphological evolution and the occurrence of fragipan and other close-packed horizons (Costantini, 1996), and to characterize soil geochemistry and clay mineralogy (Costantini *et al.,* in press). Of the more than fifty soil profiles studied, ten of them had a common set of physical, chemical, geochemical and clay mineralogy analyses, and were therefore chosen to individuate the most prominent indicators of soil aging.

Materials and Methods

General outlines of the area

The study area is a small ridge located in Central Italy (Tuscany), covering a territory of about 20 km^2. It is made up of several hills, with dominant heights ranging from 400 to 500 meters. The area underwent intense geomorphological evolution during the Pliocene and Quaternary, with alternating periods of erosion and stability. The rising of the ridge led to the erosion of the slopes, but several surfaces remained stable or were stable over a long time (e.g. karst depressions, colluvial areas, terraces). Four main lithological units could be distinguished: i) acid metamorphic rocks, consisting of chloritic and sericitic fine-grained schist, jasper, quartzose micro and macro conglomerate and violet schist breccias (Mesozoic); ii) calcareous rocks, composed of flint limestone, marble, dolomite and cavernous limestone Mesozoic in age, but partially reworked by the Miocene sea; iii) mainly calcareous or iv) mainly siliceous slope and alluvial deposits, the mineralogy of which derives from the mixing of the above mentioned rocks. The average annual rainfall in the area is 1,019 mm, with maximum in October and minimum in July. The average annual temperature is 13.2°C, the warmest month is July and the coldest is January. The soil moisture regime, evaluated by the Newhall Computation (Newhall, 1972) is "udic" with a water holding capacity of 200, 100 and 50 mm, whereas the soil temperature regime, according to Soil Taxonomy (Soil Survey Staff, 1999) is "mesic" ($8<T<15°$ C).

The soils studied

Along with time, the nature of the parent material is the other most important soil forming factor influencing the genesis of soils of the Montagnola Senese area. The present study was focused on the soils derived from acid rocks and mainly siliceous slope and alluvial deposits, while soil genesis on calcareous rocks was studied in other works (Costantini *et al.,* 1992; Mirabella *et al.,* 1992). During the soil survey, some discontinuities were observed and described in various soil profiles. They corresponded in some cases to mere lithological changes in the composition of the parent materials, which were deposited through different episodes in the same age. This is the case of profile 25, 47 and 48, which formed in terraced fluvial sediments belonging to the same geomorphological unit. For soils on slope deposits, on the other hand, the lithological discontinuity may correspond to successive events distanced in time.

As far as soil age determination is concerned, Costantini *et al.* (1996) estimated soil age on the basis of a geomorphological reconstruction, micromorphological evidence, correlation with other studies (Bini *et al.,* 1992; Bronger *et al.,* 1994; Cremaschi *et al.,* 1987; Goldberg *et al.,* 1990; Magaldi, 1979; Previtali, 1985) and one dating coming from the bottom of a profile, ascertained by means of paleonthological findings (Fondi, 1972) to be at least Cromerian (Lower Middle Pleistocene). According to this attribution, the time 0 of the ten chosen soils, that is the time when the rock was exposed to weathering, or when the parent material was deposited, was stated to be Holocene, Upper and Middle Pleistocene, or Lower Pleistocene.

Following Soil Taxonomy (Soil Survey Staff, 1999) the soils were classified as Udorthents, Dystrudepts, Hapludalf, Fragiudalf, Fraglossudalf, Paleudalf and Plinthaqualf, or as Leptosols, Cambisols, Luvisols, Albeluvisols and Plinthosols with the World Reference Base for Soil Resources (FAO *et al.,* 1998).

Field and laboratory methods

Soil description followed the Soil Survey Staff methodology (1993), routine analysis was in compliance with the Italian official methods (SISS, 1985). Plinthite nodules were submitted to the test of Wood and Perkins (1976), with immersion of samples for two hours in water, to check the persistence of aggregates. Cation exchange capacity and exchangeable bases 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. Gasometric determination of $CaCO_3$ was performed on all but the acid horizons. Oxalate-soluble iron was estimated after Schwertmann's method (1964). As to the geochemical analysis, metal extraction was carried out using Aqua Regia and ultra pure concentrate HF. Major and trace element analysis was carried out by Perkin Elmer 5100 AAS at flame (K); and with an AAS equipped with a Zeeman background corrector for Cr, Pb and Zn. ICP/OE was used to analyze Ca, Al, Fe and Ti. All the analytical procedures were tested beforehand with a data quality control program using international soils CRMs, duplicate samples and reagent blanks. DCB-extractable iron was determined after Mehra and Jackson (1969). For the determination of clay mineralogy all samples were saturated with K and Mg by treatment with 1M KCl and 0.5M $MgCl_2$ solutions. The Mg-saturated samples were solvated with ethylene glycol at 60°C for 24 h and heated to 550°C for 2h, while the K-saturated samples were heated to 350°C for 2 h. The clay fraction composition and its semi-quantitative determination were estimated through the area of the peaks obtained by diffraction using a Philips PW 1710 diffractometer. X-ray diffraction identification criteria were based on Biscaye (1965), Bryndley and Brown (1980), Wilson (1987), Dixon and Weed (1989), Barnhisel and Bertsch (1989), Moore and Reynolds (1997). 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 of diagnostic peaks which distinguish every clay mineral. All the indicators were submitted to a nonparametric statistical analysis (Kruskal-Wallis test), to put in evidence significative differences due to the attributed soil age and to highlight possible trends in soil aging. The Pearson test of correlation was applied to relate kaolinite content with that of the other clay minerals.

Results and Discussion

Silt/clay ratio

The ratio between silt and clay content of the fine earth is a first simple indicator of soil aging (Figure 1). In fact, the observed silt decrease and clay enrichment in soils along with their age can be related to clay neogenesis. Other processes however are evident in the graph: the clay impoverishment of eluvial horizons, and consequent clay increase in the illuvial ones (see all profiles with Bt horizons); the similar clay impoverishment occurring within the bleached streaks of fragipan (see profiles 34, 7, 9, 47) but the decrease of the silt/clay ratio inside the reduced parts of the oldest horizons without fragipan (profiles 25 and 48), due to a relative clay concentration.

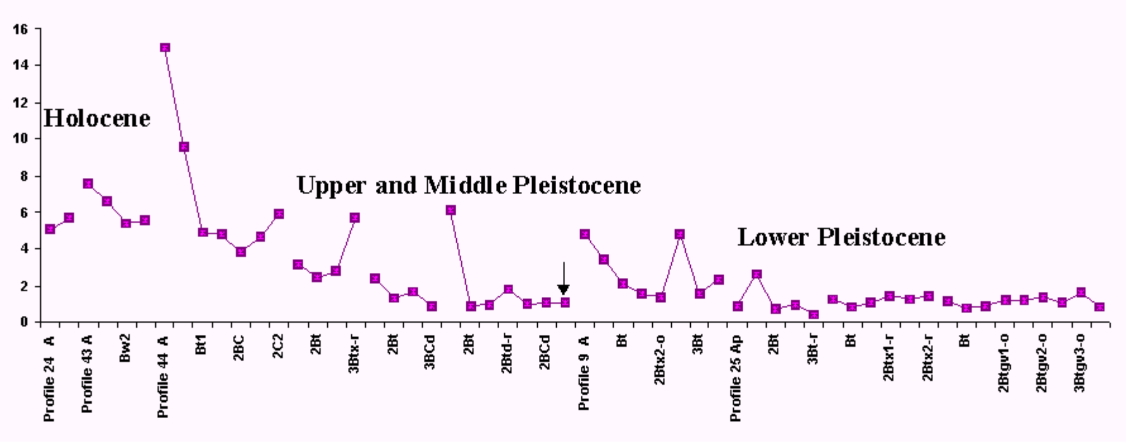

Figure 1 Silt /clay ratio in the studied profiles according to their estimated age. The arrow indicates Cromerian findings.

CEC of clay and clay mineralogy

The CEC of clay showed a certain decrease in the studied profiles according to soil age, indicating a certain clay mineralogy change with time (Table 1).

Among the clay minerals, illite and kaolinite were found in all the examined samples (Table 1). Illite, in particular, is the dominant clay material, in consequence of the physical breakdown of muscovite, which is abundant in the coarse fraction of schist. A slight decrease from Upper and Middle Pleistocene to Lower Pleistocene soil horizons could be observed in all the samples which did not have mixed layers clays.

Chlorite was detected in the Holocene and only in few older soil horizons. It directly derived from the weathering of chloritic schist and its absence in most of the older soils should be associated to its relatively fast transformation in acid environment. Similarly, interstratified illite-HIV and interstratified illite-chlorite were found mainly in Holocene soil horizons.

Table 1 Mean value of soil aging indicators in horizons of different estimated age; effect of age is significant for all properties, except for interstratified clay minerals (Kruskal-Wallis test with $p<0.001$).

Indicator	Holocene soil horizons	Upper and Middle Pleistocene soil horizons	Relative variation (%)	Lower Pleistocene soil horizons	Relative variation (%)
Silt/clay	5.32 (18)[†]	2.46 (18)	-54	1.14 (20)	-54
CEC of clay (cmol kg^{-1})	57 (11)	38 (16)	-33	28 (19)	-26
Illite (%)	61 (18)	69 (18)	13	66 (20)	-4
Chlorite (%)	2.7 (10)	1.3 (3)	-50	absent	-100
HIV (%)	13 (18)	4.9 (17)	-62	5.8 (8)	18
Interstratified illite-HIV (%)	18 (8)	41 (3)	228	absent	-100
Interstratified illite-chlorite (%)	9.3 (4)	absent	-100	absent	-
Vermiculite (%)	3.0 (2)	4.1 (9)	33	6.9 (20)	75
Kaolinite (%)	13 (18)	17 (18)	31	25 (20)	47
Total iron (Fe_t mg kg^{-1})	19983 (18)	26202 (18)	31	39138 (20)	49
Free iron (Fe_d mg kg^{-1})	12256 (9)	19170 (10)	56	30390 (20)	59
Total chromium (mg kg^{-1})	56 (18)	66 (18)	18	108 (19)	64
Total lead (mg kg^{-1})	14 (18)	18 (18)	29	40 (19)	122
Total zinc (mg kg^{-1})	52 (18)	64 (17)	23	71 (19)	11
Total titanium (mg kg^{-1})	1015 (18)	1777 (18)	75	1821 (19)	2
Total potassium (mg kg^{-1})	10312 (18)	14551 (18)	41	14371 (19)	-1
Total aluminium (mg kg^{-1})	20978 (18)	16372 (18)	-22	15900 (19)	-3
Total calcium (mg kg^{-1})	745 (18)	290 (18)	-61	266 (19)	-8

[†] number of horizons

Hydroxy-interlayered vermiculite (HIV) was observed in all Holocene, in almost all Upper and Middle Pleistocene and only in a few Lower Pleistocene soil horizons. It is generally considered an intermediate product of illite and chlorite weathering in acid environment, toward the neogenesis of vermiculite.

Vermiculite content showed a significant tendency to increase when passing from Holocene to Upper and Middle Pleistocene, and to Lower Pleistocene samples. Also the number of soil horizons in which it was present increased according to their attributed age. Vermiculite neogenesis affected mainly illite and chlorite, provided by the mineral components of the parent rock, through the production of a series of intermediate clay minerals, namely HIV and interstratified illite-HIV and 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 was clearly time-dependent (Figure 2) and its trend revealed a continuous enrichment, which was to a certain extend more prominent in the oldest horizons, where it reached 25% of all clay minerals (Table 1).

The neo-formation of kaolinite was not correlated with an impoverishment of any other clay minerals. This would indicate a direct neogenesis from the mineral constituents of the parent material and rock, rather than a transformation of clay mineralogy.

As in the silt/clay ratio, the presence of kaolinite appeared to be influenced by the eluviation process. The passage from the eluvial to the illuvial horizon was almost always marked by a rise in kaolinite percentage. On the other hand, its content within the reduced and more silty streaks of fragipan was not always higher than in the oxidized mass. A clear influence on the kaolinite content came from the lateritization process that occured in the horizons of the oldest soils without fragipan (profiles 25 and 48). The clay enrichment in these cases was marked by a clear increase in kaolinite percentage, as found by Nahon in laterite formation process (1991).

Kaolinite content moreover permitted us to distinguish mere lithological from chronological discontinuities in the profiles (Figure 2). In fact, it was possible to individuate an increasing trend in the horizons belonging to all the soils formed on discontinuous slope deposits, while in soils of the same geomorphological unit (profiles 25, 47 and 48) only the uppermost layers showed a significant lower amount of kaolinite, due to a recent human-induced rejuvenation of the parent material.

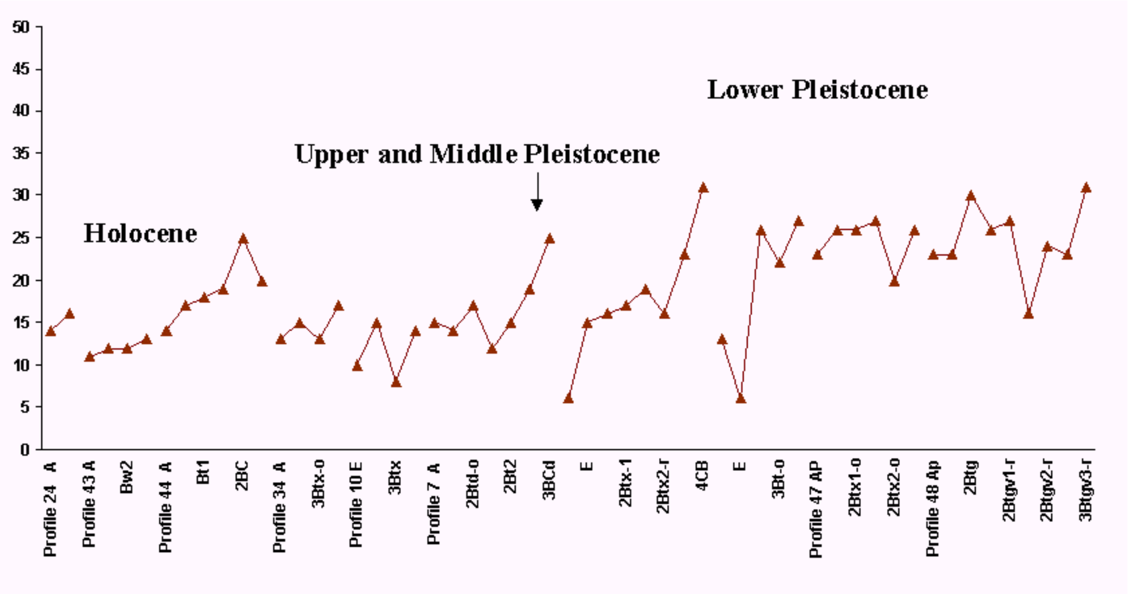

Figure 2 Kaolinite content in the studied profiles according to their estimated age (%). The arrow indicates Cromerian findings.

Iron forms and element content

In the soils of the Montagnola Senese area both total and free iron contents were significantly related to the estimated soil age (Table 1). Amorphous iron content on the other hand (Fe-o) was always very low and did not show any particular trend (Figure 3). Total and free iron resulted as being strongly influenced by reductive processes, in all soil horizons with reduced mottles. The influence of the eluviation process could also be recognized, both in terms of total and free iron increase, as well as the presence of lithological and chronological discontinuities.

Besides iron, the total concentration of other elements, namely chromium, lead, zinc, titanium, potassium, aluminium and calcium differed significantly according to estimated age (Table 1). Cr, Pb and Zn, in particular, showed an accumulation process starting from Holocene and continuing up to Lower Pleistocene, whereas Ti and K content seemed to increase only during the passing from Holocene to Upper and Middle Pleistocene. Aluminium content, abundant in fresh parent material and rock, tended to diminish with time. Finally soil age clearly had an effect on Ca content, possibly due to the parent material providing very little and the incomplete recycling of calcium linked to organic matter.

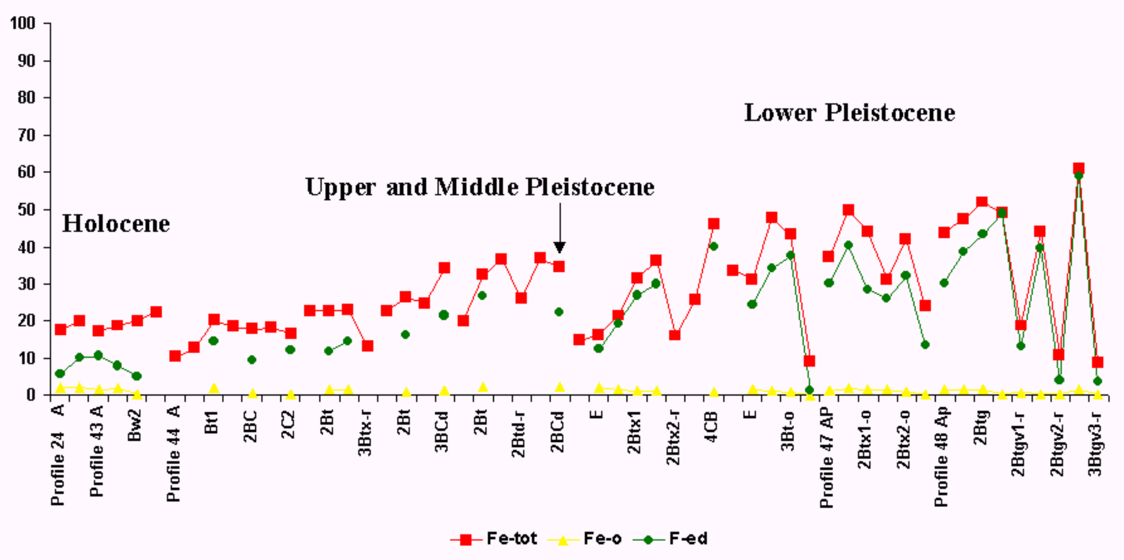

Figure 3 Iron forms (Fe-total = Fetot; Fe-dithionite = Fed; Fe-oxalate = Feo) in the studied profiles according to their estimated age (g.Kg-1); reduced part of horizon excluded. The arrow indicates Cromerian findings.

Conclusions

The relative variation of the mean value of the indicators in the Holocene, Upper and Middle Pleistocene and Lower Pleistocene soil horizons, pointed out different trends in the aging process of the soils studied (Table 1).

The process of neoformation of particles in the dimension of clay was highlighted by a regular decrease in the silt/clay ratio (more pronounced) and CEC of clay (less pronounced) along the three ages. Similarly, free iron release followed a regular rather sharp increase over time. These indicators were not influenced by the changes in weathering conditions occurred during Pleistocene.

Other indicators, namely vermiculite and kaolinite content, total iron, chromium and lead, showed a linear trend with a higher rise in the oldest soil horizons, which evidenced the well known stronger weathering environment taking place during Lower Pleistocene in Southern Europe.

The remaining indicators varied significantly only from Holocene to Upper and Middle Pleistocene soil horizons, probably because they were intermediate phases of mineral transformation or were influenced by rather fast processes.

It must be stressed, however, that all the proposed indicators were affected by other soil processes which played a prominent role in determining their content in different soils, different horizons of the same soil, or different parts of the same horizon. In particular, clay illuviation, bleached streaks and fragipan formation, change in status and mobility of elements due to reduction and oxidation processes, occurrence of lithological and chronological discontinuities.

All these factors and conditions should always be taken into account, and guide the soil sampling, when the proposed indicators are to be used to estimate or correlate the age of soils.

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