Aeolian inputs and dolostone dissolution involved in soil formation in Alpine karst landscapes (Corna Bianca, Italian Alps)

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ABSTRACT

Very different soil types occur across a few tens of meters on dolostone, in a never glaciated karst landscape in the Lombard Pre-Alps (Selvino, Italy). This substrate is locally enriched in well-crystallized sand-grained quartz. The quartz content is responsible for the localized genesis of Podzols. Other soil types observed in the area include strongly rubified (Terra Rossa) horizons (paleosols), preserved in the most protected dolostone cracks. Non-rubified Luvisols and Cambisols were observed in karst dry valleys and dolines while Rendzic Leptosols/Phaeozems were common on the steepest slopes. Such a variety of soils was explained assuming different parent materials (dolostone, silica-rich dolostone, with different amounts of aeolian inputs, ascertained using textural properties, mineralogy, micromorphology, total element composition, mass balance calculations, rare earth elements, and stable elements. Many soils were highly polycyclic, with different layers associated to different parent materials and characterized by different pedogenic processes evidencing different ages. We were thus able to distinguish the horizons mainly developed from the dissolution of the dolostone from those formed in Pleistocene loess. The geochemistry of all surface soil horizons, including Podzols and Rendzic Leptosols/Phaeozems, apparently formed from pure or quartz-rich dolostone dissolution, has been influenced by recent aeolian additions (likely Saharan dust), with deeply modified effects according to different pedogenetic processes acting locally. Saharan dust, in fact, significantly

increased metal and rare earth elements contents compared to the substrate, also in the youngest and least weathered soil types.

Keywords: Clay mineralogy, Loess, Micromorphology, Podzol, Rare Earth Elements, Saharan dust, Terra Rossa

Abbreviations

PL: Pleistocene loess

SD: Saharan dust

Dol: dolostone

DolSi: quartz-rich dolostone

LGM: Last Glacial Maximum

1 - Introduction

One of the main issues in soil sciences is the detection and quantification of the actual parent material of the soils, which are often formed from the weathering of the substrate with frequent, but difficult to quantify, aeolian addition (e.g., Loba et al., 2019; Waroszeqski et al., 2019; Kowalska et al., 2022). This is particularly true in karst terrains, where soil formation has always attracted a lot of interest concerning the origin of the material. Terra Rossa soils are probably the most studied soil type in karst terrains. Three main theories have been produced, namely the residual theory (e.g. de Lapparent, 1930; Thornbury, 1954), the detrital-aeolian input theory (Yaalon 1997), the isovolumetric replacement theory (Merino and Banerjee, 2008; Lucke et al., 2012). Polygenesis is however considered a common feature of these soils (e.g., Durn et al., 2023).

The residual theory for karst soil formation considers soils developed in karst areas, mostly in closed sinkholes and in doline bottoms, as the product of carbonate rock dissolution and the resulting autochthonous concentration of insoluble minerals originally included in the parent rock (e.g. Kubiena, 1953). Slope redistribution of such residual materials cannot of course be excluded, nevertheless the main limit in this theory is shown by the commonly observed great thickness of soils, which would require the dissolution of “incredible” thicknesses of parent rock, considering that most karst landscapes are developed in rather pure limestone/dolostone; for example, in the Northern Limestone Alps, Küfmann (2003) measured soils too thick to be derived from limestone dissolution, in terrains covered by ice until the end of the LGM. In that case, more than 7 m of rock should have been solubilized to release sufficient material to create 25 cm thick Bw horizons, revealing that the dissolution of limestones/dolostones can only give materials for a small fraction of the resulting soils. In fact, a widespread aeolian silty layer covering much of the landscape has been detected in the Northern Alps, deposited at the end of the LGM (Gild et al., 2018).

According to the detrital theory, Terra Rossa soils (and karst soils in general) are mainly the product of the accumulation of alluvial, volcanic and/or aeolian deposits. Aeolian inputs are particularly important for many authors (e.g. Yaalon, 1997, according to whom more than 50% of Mediterranean red soil materials are derived from Saharan inputs). There are however shortcomings also in this theory (Merino and Danerjee, 2008): it does not consider the existence of “floaters”, which are isolated residual blocks of limestone surrounded by soil material, and the proven simultaneous formation of soils/bauxite layers and karst depressions. Both these facts would require soil formation associated with substrate dissolution.

The third theory thus comes into consideration: the authigenic replacement of limestone by red clay at the Terra Rossa-substrate interface (Merino and Danarjee, 2008). According to this theory, the authigenic red clay minerals form from Al, Fe, and Si ions, derived from the acid dissolution of clay-sized dust particles deposited on the soil surface, then brought in suspension by soil water. The larger (silt-sized) aeolian particles would however remain in the soil to be weathered.

Thus, aeolian inputs are a prerequisite for two of the considered karst soil formation theories.

Podzols are very unusual in karst landscapes, but they historically attracted a lot of interest. Their formation has often been related to the input of external materials on carbonate substrates, such as glacial till or volcanic ash (Smirnova and Gennadiev, 2011; King and Brewster, 1976; Duffy, 2011). Many authors are more inclined to consider the formation of Podzols on carbonate rocks as possible only after the complete dissolution of carbonates and the accumulation of insoluble residues (e.g. Carrol and Hathaway 1954; Smith et al 1983). For example, a dissolution succession from limestone/dolostone to Podzols, passing through the stages of Calcaric Regosols ("Kalkrohboden"), Rendzic Leptosols (“Rendzinas”), Eutric and Dystric Cambisols, has been historically considered characteristic in the European Alps (e.g. Braun-Blanquet and Jenny, 1926). No recent examples of such sequence are however available in the literature.

Thus, the origin of soils in karst areas remains ambiguous. In this manuscript, we characterize soils in a pedologically highly diverse karst plateau in the Italian Alps (Corna Bianca, Selvino, Bergamo Province, Fig. 1), where many different soil types coexist over short distances (Podzols, Rendzic Leptosols/Phaeozems, Cambisols, Luvisols, and truncated horizons belonging to Terra-Rossa soils including Rhodic Luvisols and Lixisols, according to IUSS Working Group WRB, 2022). Starting from the variability, the peculiarity and the proximity of the detected soil types, we face the hypothesis of external contributions to the soil development in mountain karst environments, able to influence the genesis over time of unusual or rare soils as well. In order to unravel the origin of such diverse soils and their actual parent material and formation processes (rock dissolution, Saharan dust - SD and Pleistocene loess - PL), we used soil micromorphology, mineralogy, elemental composition and rare earth elements. Given the particular texture and composition of some of the studied soils, we also attempt at quantifying the inputs of dust during the Holocene in southern Alpine soils..

2 - Materials and methods

2.1 Study area description

The study area is the Corna Bianca karst plateau located near the Salmezza village (Selvino, Bergamo province, Central Italian Pre-Alps, Fig. 1), between ca. 1160 and 1228 m a.s.l.. The average annual temperature is around 8°C, while the annual precipitation is around 1600 mm (data derived from nearby weather stations located in Selvino municipality, unpublished), with the highest rainfall measured during summer and autumn months. Snow covers the soil surface discontinuously between late November and March.

The lithological substrate is dolostone (Dol) belonging to the "Dolomia Principale" ("Hauptdolomit") formation, which was deposited as a wide carbonate platform during the Lower-Middle Norian (Upper Triassic). It is composed of grey and whitish dolostones, in layers and banks (Bersezio et al., 2012), intensely fractured by tectonic stresses. The Dol on the Corna Bianca Plateau is strongly recrystallized and includes serpulid channels and microbial bioconstructions (Berra and Jadoul, 1996) and is characterized by localized silicified arenodolostones (DolSi) and precipitations of microcrystalline, sand-sized quartz.

The Corna Bianca Plateau has never been glaciated during the Quaternary (Ravazzi et al., 2007), and it was affected by karst processes (dolomite dissolution, doline development), periglacial processes during glacial periods, and loess deposition, as it has been observed in many similar prealpine plateaus in the southern Alpine margin (e.g., Castiglioni et al., 1990; Magaldi and Sauro, 1982; Costantini et al., 2018). The topography is thus highly varied, in relation to long-lasting karst processes, which created closed depressions (dolines), dry valleys, highly dissected slopes with very different slope angles and aspects, separated by rocky outcrops and tors.

The vegetation is influenced by complex interactions between soil, climate, topography and land management. In the study area these interactions result in a mosaic of different vegetation types, often occupying very little surfaces. Acid soils with low nutrient contents are favorable to stress-tolerant grasses and shrubs such as *Nardus stricta* and *Calluna vulgaris*, while shallow soils with high Ca-saturation are favorable to basophiles such as *Sesleria caerulea* and *Erica carnea*. Mesophile species for ecological factors like light and moisture occur elsewhere. Hay meadows are strictly conditioned to traditional, low-intensity agricultural practices like regular cutting and manure management. Forested area are the relicts of the original vegetation, confined to the less favorable surfaces and exposures; they are represented by beech forest in mesic sites and hop-hornbeam woods in xerothermic ones, often managed as semi-abandoned coppices. Birch is often present with young specimens expanding on abandoned pastures along with hazels and other bushes.

The presence of podzolic soils on the Corna Bianca Plateau has already been recognized (ERSAL, 1992), and the site is classified as pedosite, containing good examples of low-altitude Podzols (Costantini et al., 2000).

2.2 Soil survey, sampling and analysis

Based on the known location of well-developed podzols on the dolomitic plateau near Salmezza (Panarello, 2001), we performed 52 soundings with auger, to quickly detect the soil type distribution, with a particularly high density of observations where the soil variability was known to be the highest (Fig. 1). Based on the results of this first campaign, we opened, described, and sampled 10 soil profiles, representative of the main soil types and topographies (Table 1). Some profiles were located on steep slopes (> 25°, P5, P9), some on gentle slopes (<15°, P1, P2, P3, P4, P6, P10), one in a karst valley bottom (P7), one in a doline bottom (P8). P10 was assumed to be a PL profile, thanks to its yellowish-brown colour, coarse blocky structure and silty texture, very similar to many well-known loess layers in Northern Italy (e.g., Negri et al., 2021). The soils were described according to FAO (2006) and classified according to IUSS Working Group WRB (2022). At least 500 g of soil material were sampled from every genetic horizon, and undisturbed 100 cm^3 cores were collected where possible (three cores per horizon), to measure the bulk density (BD). The BD of the substrates was measured as well: a few unweathered rock fragments were weighed, and their volume was calculated by immerging them on a weighing scale after impermeabilization with a thin wax layer.

The main chemical and physical properties (pH, Organic C, total carbonates, exchangeable bases, Fe and Al extracted in ammonium oxalate – Feo and Alo - and Fe in dithionite –Fed-, texture) were measured according to standard methods (van Reeuwijk, 2001, Supplementary Materials). Texture was measured with the pipette method, considering five fractions: clay (<0.0002 mm), fine silt (0.0002-0.02 mm), coarse silt (0.02-0.05 mm), very fine sand (0.05-0.1 mm) and coarse to fine sand (0.1-2 mm).
Oriented and undisturbed bulk soil samples were collected from the most representative horizons in the profiles in metal boxes and impregnated with resin to prepare 60 x 45 mm thin sections. The thin sections were observed using a polarizing microscope (Leitz Wetzlar HM-POL) and described following Stoops (2003) and Verrecchia and Trombino (2021),.

2.3 Soil and parent material mineralogy

The mineralogical investigations were carried out using a PANalytical X'Pert Pro PW 3040/60 X-ray diffractometer (40 kV and 20 mA, CuKα radiation, graphite monochromator). The bulk mineralogy of Dol, DolSi and of the main genetic horizons was evaluated on backfilled, randomly oriented powder mounts between 3° and 80° 2θ. The soil clay fraction (<2 µm) was separated by sedimentation, flocculated with $MgCl_2$, washed until free of Cl-, and freeze-dried. Scans were made from 3° to 35° 2 θ at a speed of 1° 2θ min-1, on air dried Mg-saturated (AD), ethylene glycol solvated (EG), and heated (330° and 550° C) oriented mounds.
The identification of clay minerals was done by comparing peak position and intensity in all XRD spectra. Briefly, kaolinite was identified by the presence of a 0.7 nm peak in the AD diffraction pattern that disappeared after heating to 550°C; illite by a 1.0 nm peak in the AD

diffraction pattern; chlorite by the persistence of a 1.4 nm peak after heating. Vermiculite was assessed by comparing the 1.4 nm diffraction peak in EG and heated spectra, smectite by the appearance of a peak or shoulder at 1.6-1.7 nm after EG treatment. The presence of hydroxyl-interlayered vermiculite (HIV) and/or hydroxyl-interlayered smectites (HIS) was ascertained, and their thermal stability assessed, by comparing the heated at 330° and 550° C. Interstratified minerals were recognized by the presence of a diffraction peak or band exhibiting a behavior intermediate between that of the single components. Gibbsite was detected by its main peak at 4.8 nm. Associated minerals (quartz, talc, and feldspars) were identified in the AD diffraction pattern by peak positions according to the data reported by Brown (1980). A semi-quantitative evaluation of mineral abundance was performed using the Mineral Intensity Factors method reported by Islam and Lotse (1986) that considers peak areas. For the analysis, the background was subtracted, and the peak positions, intensities and areas were calculated using the second derivative option of the X'Pert High Score software (Degen et al., 2014).

The presence of crystalline Fe and Al (hydr)oxides was checked on backfilled, randomly oriented mounds of the separated clay fraction. The presence of amorphous Al-compounds (Imogolite-type materials, ITM) was verified measuring pH values after suspension in 1M NaF, 1:2.5 soil: solution for 2 minutes (pHNaF). Values above 9 in acidic or neutral soil samples indicate their presence, with increasing pHNaF values well correlated with ITM contents (Burt 2004).

2.4 Elemental analysis and Rare Earth Elements

Major and rare earth elements (REE) of the main genetic horizons and of some Dol and DolSi rock fragments were analysed by ICP-MS after $LiBO_2/Li_2B_4O_7$ fusion (Bureau Veritas lab, Vancouver, CA), and were later corrected for the loss on ignition (LOI). Major elements (as oxides) and BD data were used to calculate mass balance equations according to Brimhall and Dietrich (1987) and Egli and Fitze (2001). We calculated the volumetric strain (volume change during weathering/pedogenesis) according to:

$$\varepsilon_{i,w}=(\rho_p*C_{i,p})/(\rho_w*C_{i,w})-1 \qquad \text{(eq. 1)}$$

Where:

ρ_p: bulk density of the parent material (2.8 and 2.7 g cm^{-3} for Dol and DolSi, respectively);

ρw: bulk density of the soil horizon;

$C_{i,p}$: concentration of the stable element *i* in the parent material *p*;

$C_{i,w}$: concentration of the stable element *i* in the weathered material *w*.

We also calculated the open-system mass transfer function $\tau_{j,w}$, which represents the mass fraction of the element j added to or removed from each horizon relative to the mass originally in the parent material. It was calculated according to:

$$\tau_{j,w} \; j,w = (C_{j,w} \; j,w * C_{i,p} / C_{j,p} * C_{j,w} \; i,w) - 1 \quad \text{(eq. 2)}$$

where:

$\tau_{j,w}$: function of mass transport in the open system of *j* element, in the weathered material *w*;

$C_{j,w}$: concentration of the *j* element in the weathered material *w*;

$C_{j,p}$: concentration of the *j* element in the parent material;

The mass balance equations were calculated for the different horizons considering various possible parent materials (Dol or DolSi, PL and SD). Zr was the considered stable element in the mass balance calculations.

REEs were normalized on chondrite values (Taylor and McLennan, 1985), and their concentration in the studied soils was compared using spider diagrams, together with often used geochemical indicators such as the Eu and Ce anomalies, calculated using equations 3 and 4:

$$Eu/Eu^{*} = Eu_N/Sm_N^{0.45} \times Gd_N^{0.55} \quad \text{(eq. 3)}$$

$$Ce/Ce^{*} = Ce_N/La_N^{0.48} \times Pr_N^{0.52} \quad \text{(eq. 4)}$$

2.5 Statistical analysis

Semiquantitative clay mineralogical and elemental composition data were used to perform a cluster analysis (CA, function hclust in Vegan R package, Oksanen et al., 2020), using complete linkage method and Euclidean distance algorithm. Five different SD compositions were also included in the analysis, using literature data (Moreno et al., 2006 - SD1-4; Di Mauro et al., 2019 – SD5). Considering elemental composition, the CA was performed on three different datasets: total elemental composition, major elements, REEs. This was done to highlight if and which element or group of elements were able to differentiate soils and related them to their possible different parent materials. The best number of clusters was determined each time by checking the significance of the Dufrene-Legendre Indicator Species values, obtained using the indval function in the labdsv package (Roberts, 2019). The compositional data were normalized before performing the statistical elaborations.

3 – Results

3.1 Soil types in the Corna Bianca Plateau

An extremely high diversity of soil types was observed in the studied karst plateau (Fig. 1), verified by the presence of many diagnostic horizons in different soil profiles (Table 1). Podzols (P1 and P2) were well developed on DolSi. They had thick eluvial whitish (albic) E horizons overlapping dark reddish Bhs spodic ones (Fig. 2a, Table 1). The deepest horizon, in contact with the weathered dolostone, was black, discontinuously cemented by spodic materials and particularly rich in organic matter (Bhs(m), Table 1, S1). All morphological and chemical requirements for Podzol definition were met (IUSS Working Group WRB, 2022, Supplementary Materials, together with a more detailed morphological description of the genetic horizons). Rendzic Phaeozems and Leptosols (e.g. P5 and P9, Fig. 2b), common on Dol, and on DolSi on steep slopes, had very dark Ah horizons, lying above weathering and partly fractured rocky substrate.

Cambisols and Luvisols (P3, P6, P7, P8 and P10) were found in accumulation areas, on gentle slopes or on flat surfaces. Rhodic Luvisol and Lixisol horizons (treated here together as Terra Rossa soils, P3, P4 and P8), occupied the bottom of some dolines and sinkholes. In one case (P3-2Btb), the mineralogy and the low CEC (9.8 cmol kg^{-1}, equal to 23.6 cmol kg^{-1} of clay) of the red materials matched the characteristics of a Rhodic Lixisol (Fig. 2c); the red Bt horizons in P4 and P8 are classified as part of Rhodic Luvisols; in the latter horizons, the CEC was respectively 10.81 and 25.05 cmol kg^{-1}, equal to 33 and 31 cmol kg^{-1} of clay respectively. These Terra Rossa horizons were usually buried beneath ca. 70-150 cm of less weathered (younger) materials in which Bw, Bws and Bt properties were differentiated (Table 1, Fig. 2d), characterized by brown colours (10-7.5YR hue), and they can be interpreted as paleosols. The surface soils were, in fact, Phaeozems, Cambisols and brown-coloured Luvisols (P6, P7, P8, P10, Fig. 2d). P10-Bw1 and P10-Bw2 horizons had the typical loess appearance (10YR 5/4 colour, silty texture and coarse blocky aggregation, as in e.g. Negri et al., 2021).

3.2 Textural properties

The physical and chemical properties were very diverse in the different soil types, as expected (Table 1; Supplementary materials). The lowest silt and clay contents were measured in Podzols and Rendzic Leptosols/Phaeozems; the highest clay values were in rubified Bt horizons (>50%), while intermediate values were measured in the brown-coloured Luvisol samples in the doline bottoms. Silt contents were high in some soil horizons observed in doline bottoms and in accumulation zones on slopes (up to more than ca. 40%). Horizons recognized as weakly weathered loess (P10-Bw1 and Bw2) were particularly rich in silt (68.9 and 64.2%), while their clay fraction was 18.9 and 21.0% respectively. In these two horizons, coarse to fine sand was particularly scarce (< 1.6 %). Coarse to fine sand contents below 10% were measured in all Terra Rossa horizons (P3-2Bt, P4-Bt, P8-3Bt1, P8-3Bt2), in the Rendzic Leptosol (P9) as well. This fraction represented a very small amount of soil mass (< 20%) also in brown Bt horizons in P7 and in surface Bw ones in P8. Coarse to fine sand represented more than 50% of the soil mass in Podzols, in the top layer in P3, and in one Rendzic Phaeozem (P5) developed on DolSi.

3.3 Micromorphology

3.3.1 Podzols (P1)

In the AE horizon (Table S2, Fig. S3), mineral particles were angular quartz sand grains, not weathered, and not arranged in peds of any shapes (single grained or coarse monic arrangement). Fine organic pellets were well separated from mineral particles and their quantity quickly decreased with depth. a few 2-3 mm thick dark lamellae enriched in silt and organic matter were locally visible.

The thin section of the E horizon evidenced a single grain microstructure, in which clear quartz grains were loosely arranged and well separated from few small irregular organic pellets (probably enchytraeid droppings) located in the intergranular compound packing voids. Thin fine sandy-silty horizontal layers were locally observed, together with some mm-sized lamellae composed of spongy spodic materials (Fig. 3a, 3b).

Bhs horizons were similarly weakly structured, but much richer in organic pellets partly filling the compound packing voids (Fig. 3c, 3d), and with well developed, continuous amorphous spongy, cracked coatings covering the sand grains, typical of spodic horizons (Van Ranst et al., 2018).

The deep Bhs(m) had coarse subangular blocky aggregates both in the field and under microscopic observation. The aggregates were separated by compound packing voids and cracks and were characterized by very low porosity in agreement with the weak cementation by dark, organic matter-rich spodic materials (Fig. 3e, 3f).

3.3.2 Terra Rossa soils

In P3, the upper A horizon showed a high biological activity with roots, hyphae and abundant organic pellets (Fig. 4a). Well-defined organic pellets were the majority of the non-quartzitic material. The slightly larger dimension of the organic pellets, compared to the podzol AE and E horizons, showed a higher activity by the soil fauna, despite the rather similar chemical properties. Larger arthropod and worm droppings were however not observed. A high porosity characterized this horizon, with compound packing voids and coarser vughs (not shown). A few small pedorelicts were visible in the lower part of the Bws horizon (Fig. 4b), while thin and discontinuous spongy amorphous organo-metal coatings and fine granular organic matter aggregates suggested that podzolization is active at present in this deep part of the upper section of P3. The differences with P1-Bhs were quite large.

Between the Bws and the deeper CR/2Bt horizon, many rounded red pedorelicts (Fig. 4c) and remnants of disrupted clay coatings and clay bridges between quartz grains (Fig. 4d), sometimes forming more or less rounded aggregates, were observed within the irregularly laminated groundmass. The red pedorelicts were parts of the underlying Terra Rossa horizon, and their disruption and rounded shape demonstrates transport along the lower boundary of a solifluction/gelifluction layer. Inside the upper part of the weathered CR horizon, few small reddish coatings and aggregates, sometimes disrupted and discontinuous, were visible as well in the compound packing voids and on the rock fragment surfaces (Fig. 4e).

The red 2Bt horizon showed a chitonic distribution pattern with a massive microstructure, where few angular quartz grains were surrounded by a clayey and silty matrix and few rounded pores (Fig. 4f). Reddish, limpid clay coatings were developed on the void surfaces, sometimes completely filling pores and cracks (Fig. 4f). The overall porosity was much lower than in upper horizons. In polarized light, a few orange clayey laminations and a localized striated microfabric appear within the reddish matrix as well (Fig. 4g). Clay coatings were very abundant in the sectors richest in quartz sand grains (Fig. 4h). Some orthogonal cracks were also observed in the clayey matrix, partly infilled with black Fe-Mn accumulations (Fig. 4i). A few Fe-Mn accumulations were also developed within the matrix as small rounded nodules, dendritic/ameboidal concretions and endocoatings around some pores. Such features were mostly visible only under high magnification (not shown in Fig. 4).

Near the border between the 2Bt and the 2CR horizons, quartz grains became abundant, and the compound packing voids increased in quantity (Fig. 4h).

3.3.3 Rendzic Leptosol/Phaeozem

In P5, the A horizon showed a high biological activity with abundant organic pellets, which had a similar dimension as in P3-Bws, and roots (Fig. S4). These well-defined organic pellets were the majority of the non-sandy material. Larger arthropod or worm droppings were not observed. A high porosity characterized this horizon, with compound packing voids and coarser vughs. The mineral phase was mostly sand-grained dolostone and quartz.

3.3.4 Eutric Cambisols / Luvisol

P6-Bt1 showed quite coarse blocky subangular peds, which were in turn divided into many fine platy aggregates, separated by horizontal wavy cracks (Fig. S5). The orange groundmass had a closed porphyric distribution, with a quite compact fine matrix and quartz sand grains. Very few traces of biological activity were observed in the form of organic pellets and roots. Few of the pores were partly filled with reddish clay coatings, sometimes underlain by silty accumulations. Very few rounded clayey aggregates (pedorelicts) were also immersed in the groundmass.

P10-Bw1 was compact, with a closed porphyric distribution (Fig. S6). The sandy fraction was mostly composed of muscovite flakes, evidencing the mostly aeolian origin of this horizon. The structure was coarse blocky subangular, and few coarse cracks and vughs separated the peds. Almost no clay coatings and pedorelicts could be observed, while a few Fe-Mn concentrations were inside the groundmass.

3.4 Soil mineralogy

Bulk mineralogy of Dol and DolSi was dominated by dolomite (and quartz in DolSi); no other minerals were detected in the XRD spectra. Bulk powder, not-oriented soil samples evidenced a large dominance by quartz in most soils (not shown); dolomite was detected only in Phaeozems (P5-A) and in deep P7-3C horizon. Hematite (peak at 0.269 nm) was detected in some Terra Rossa samples, while goethite was present in all Bt horizons (peak at 0.418 nm).

Many different secondary and primary minerals were observed in the clay fraction of the different soils (Fig. 5).

Quartz and illites were detected in small amounts in all samples. Many minerals were widespread as well, such as kaolinite, observed in considerable quantities in all analyzed samples. Vermiculites and HIVs were widespread as well, but with strongly varying contents in the different clusters. Gibbsite was detected in most samples; it was not observed only in Phaeozems and in some Bs-Bhs horizons. Traces of smectite were recognized in few samples by the decrease of the intensity of the 1.4 nm peak and the appearance of a small, broad one around 1.65 nm after glycol-ethylene solvation (not shown); its absence in the podzolic E horizon is noteworthy.

The cluster analysis evidenced that four main groups of horizons could be detected, based on semi-quantitative clay mineralogy: cluster 1 included many different A, Bw and most Luvisol Bt ones, characterized by the presence of many different clay minerals and quite high vermiculite-HIVs contents; cluster 2 included some Bw and a Terra Rossa Bt horizons, characterized by the absence of illite and particularly high contents of vermiculites-HIVs; cluster 3 included a Terra Rossa Lixisol Bt horizon and the weathering silica-rich dolostone underneath (P3-2Bt and P3-2CR), particularly rich in gibbsite in agreement with its high Al_2O_3 concentration; cluster 4 included strongly acidified podzol horizons and associated ones (P3-Bws), particularly rich (>40%) in kaolinite.

Primary minerals were sometimes observed as well in the clay fraction: feldspars were detected in traces in most samples belonging to clusters 1 and 2, all characterized by rather high silt contents (P6-Bt1, P6-Bt3, P7-BA, P7-Bt, P7-2Bt, P8-2Bw and P10-Bw1), while dolomite was observed only in shallow Rendzic Leptosols / Phaeozems (P5).

3.5 Elemental composition

The chemical composition of the bedrock was almost pure Ca-Mg carbonate (Table 2), with a variable silica content (between 0.3 and 28.0% wt.), in agreement with the mineralogical observations. The Ca/Mg weight ratio was around 1.45 (typical ratio for almost pure dolomite), while other elements were in traces (e.g., Al_2O_3 and Fe_2O_3 were around 0.03-0.12 % and 0.03-0.08 wt.% respectively, with lower values in silica-rich dolostone). Stable elements such as Ti and Zr were also very scarce (Table 2).
The PL samples (P10-Bw1 and Bw2) had a completely different chemical composition compared to the rocky substrate. SiO_2 was between 63 and 66%, Al_2O_3 was ca. 20%, Fe_2O_3 was ca. 8%. Ti and Zr were abundant as well.

The CA performed on the major elements divided the samples into four groups (Fig. 6), characterized by a rather high number of significant *indval* values for the indicator elements (Table 3). In particular, the Rendzic Leptosol (P9) developed on Dol was associated with its own substrate (cluster 1), characterized by high CaO and MgO and low SiO_2 contents. DolSi was associated with P5 (Skeletic Phaeozem developed on it), with Podzol samples and with some deep horizons belonging to P7, in the karst valley bottom (cluster 2); these samples were characterized by high SiO_2 (>75%) and low Al_2O_3 and Fe_2O_3 contents. PL samples were associated with surface samples from P7, P8 and with Terra Rossa sample P3-2Bt; SD samples (from literature data) were included in the same cluster, making it impossible to differentiate the two possible aeolian sources (cluster 3); this cluster was characterized by high SiO_2, Al_2O_3, Fe_2O_3, and high contents of most other elements; the concentration of these elements was one order of magnitude larger than in the previous clusters. The other Terra Rossa sample (P8-3Bt2) was in a separate cluster, only broadly associated with aeolian sources and not with substrate (cluster 4).

Most soils showed different element ratios from the ones measured in the rocky substrate, also in soils clustered with the two dolostone rock types based on major elements (Table 4). High SiO_2/TiO_2 and SiO_2/R_2O_3 characterized DolSi and were much lower in Dol and in PL; for example, SiO_2/Al_2O_3 ratio was ~1500 in DolSi, ~5 in Dol and ~3 in PL. These ratios were highly varied in the soil samples, with rather high values in soils clustered with DolSi (cluster 2) with the exception of P6-Bt1, in which the values were similar to PL. SD reaching Italy has average values between 2.4 and 7.3 (Moreno et al., 2006; Nava et al., 2012; Scheuvens et al., 2013). Fe/Al, TiO_2/Al_2O_3, Na/K and Ti/Zr were similar in the different soil and parent material samples; for example, the Fe/Al ratio in the studied soil horizons was between 0.25 and 0.45 with the highest values in cluster 3 (samples clustered with PL and SD); the ratio in SD collected above the Tyrrhenian Sea had a Fe/Al ratio between 0.39 and 0.8 (Guieu et al., 2002; Moreno et al., 2006; Nava et al., 2012; Ridame et al., 1999). R_2O_3/TiO_2 was highest in DolSi, followed by Rendzic Leptosols and Phaeozems; all other samples could not be separated into recognizable groups.

As the sand fraction in P1, P2, P5 and P6 was composed purely of quartz (and dolomite in P5), all other major elements were mostly concentrated in the silt and clay fraction. Thus, we calculated some element ratios in the fine fraction as well: the SiO_2/Al_2O_3 ratio was between 0.3 and 4.1, and widely changing amidst the different horizons. The values in the finest earth thus approach the ones characterizing loess and PL.

3.6 Rare earth elements analysis

Total REE pool (Fig. 7) was able to associate soils in a similar way as the major elements CA: PL, SD, Terra Rossa, and Luvisol samples had higher contents and were thus associated geochemically, while Podzols and Rendzic Leptosols/Phaeozems were geochemically associated with each others, characterized by lower contents. The two dolostone samples were the poorest in REEs. One Luvisol sample (P6-Bt1), which was geochemically associated with silica-rich dolostones in the major elements CA, was associated with aeolian materials when considering REEs.

The Eu* anomaly (Table 5) differentiated between rock samples and all the others, as it was negative in all soil, PL and SD samples, and neutral or slightly positive in Dol and DolSi. The Ce* anomaly was slightly negative in dolostones, Rendzic Leptosols/Pheozems, Terra Rossa, deep Podzols samples (P1-Bhs(m)) and in deep colluvial sandy materials in the karst valley bottom (P7-3C). It was strongly positive in upper spodic horizons (P1-Bhs) and in one PL sample, while it was close to neutrality in all other samples.

The ratio between light and heavy REE (LREE/HREE) did not significantly change in the different soil and PL samples. It was particularly low in Dol, in the Rendzic Leptosol developed on it (P9) and in Terra Rossa Bt samples, while it was highest in DolSi and in SD. Intermediate values characterized all other soil samples.

3.7 Mass balance calculations

The volumetric strain Ɛ, based on stable Zr (Table 6), showed a strong volume reduction (between -87% and -99%) in the analyzed soil horizons associated with the dolomitic substrate, likely mostly caused by carbonate dissolution. On the other hand, the samples associated with aeolian deposits had neutral or slightly positive strains (P8-2Bw), indicating no significant volume changes compared to PL.

The mass transfer function coefficients τ (eq. 2) showed different trends of losses or gains for most elements in most soils, depending on reference parent materials (Table 6). Compared to the Dol and DolSi, intense weathering and leaching were pointed out by significant depletion of CaO and MgO throughout the profiles (between 82% and 100%). Rendzic Leptosol and Phaeozem showed the smallest losses (82-96%). Na_2O losses were much smaller (between 51 and 96%), while positive values, indicating element enrichment, were calculated for K_2O for most samples. SiO_2 showed important net losses in most samples developed on DolSi, while a strong enrichment was observed in all soils developed on Dol. Fe_2O_3 and Al_2O_3 showed strong accumulation in most samples, with higher values for Al_2O_3. The increases were largest in spodic horizons and in the deep, sandy P7-3C. Al_2O_3 and Fe_2O_3 showed strong accumulations only in deep spodic horizons (P1-Bhs(m)), while, in the other cases, only small variations were observed. Compared to aeolian materials, no significant variations in SiO_2, Al_2O_3 and Fe_2O_3 were calculated most soil horizons associated to PL-SD.

4 - Discussion

4.1. Soil types distribution and pedogenesis

The richness of soil types in the Corna Bianca plateau is large, characterized by the presence of Podzols and polycyclic soils including Terra Rossa horizons, associated with Luvisols, Cambisols and others, describing a complex pedogenic history. High vegetation diversity also marks the different distribution of Rendzic Leptosols and Phaeozems, hosting calcicole plant communities, well differentiated from the acidophilous ones growing on deeper and more acidic soil types. Substrate lithology and topography are the main factors driving pedogenesis in the site, but they are not sufficient to explain the geochemical composition of the soils.

The Podzols developed on DolSi represent a soil endemism (Bockheim, 2005): podzolic soils are extremely unusual in carbonate rocks landscapes, and their formation is known to require a long time after dissolution of all carbonates and leaching of most of the bases from the soil profiles (Lundström et al., 2000). Their formation is also dependent on a sandier texture than normally observed in soils on carbonate parent materials, which are characteristically rich in clays. In the Jura range (France-Switzerland), podzolization is active on carbonate substrates if the soil is thicker than 35 cm (Michalet and Bruckert, 1986), sometimes strong enough to create real Podzols (Baize et al., 2016). Podzols have sometimes been observed where carbonate rocks are covered by glacial drifts (e.g., Smirnova and Gennadiev, 2011; Ferrè et al., 2020), or where carbonate till is enriched in volcanic ash and aeolian inputs (King and Brewster, 1976; Smith et al., 1983; Duffy, 2011; Zech and Neuwinger, 1974; Vrščaj et al., 2020), or on mixed carbonate/sialic till (Schaetzl and Isard, 1996), or on particularly stable surfaces where the carbonate parent rock is rich in silicic elements such as chert, in conditions of extremely long weathering under a perhumid climate (e.g., Balme, 1953; Webb, 1947). In the Corna Bianca plateau, Podzols developed directly on a peculiar quartz-rich dolostone, able to release large quantities of residual sand constituting the soil parent material. However, the Fe and Al contents in the original quartz-rich dolostone is too low to justify the presence of such well-developed Podzols.

The other soil types are more common in Alpine karst terrains: Rendzic Leptosols/Phaeozems on steep slopes, associated to Cambisols and Luvisols on gentle slopes. The presence of Terra Rossa is more sporadic, even if it is frequently observed on many unglaciated karst plateaus near the south alpine margin (Castiglioni et al., 1990; D’Amico et al., 2016), as results of long periods of subtropical weathering. Due to strong periglacial activity during the Quaternary glacial periods, Terra Rossa soils suffered a strong erosion and could be preserved only in karstic depressions such as dolines and sinkholes. In the Corna Bianca plateau, all Terra Rossa horizons were indeed found in doline bottoms and sinkholes.

Silty layers with brown yellowish colours in surface soils (below thick A horizons) were widespread on gentle slopes, particularly in protected, southward aspects; they were interpreted as Pleistocene loess layers, as in other karst plateaus close to the southern Alpine margin (Castiglioni et al., 1990; Sauro et al., 2009). The almost complete absence of coarse to fine sand in the Bw horizons in P10 verifies the almost pure aeolian origin of these layers, and our assumption that they represent a good example of weakly weathered loess.

4.2 Relative ages of the different soils in the study area

The observation of microstructures in thin sections can give information on past processes, characteristic of different climatic conditions (such as cryoturbations), able to suggest minimum ages for different soil horizons. In particular, E, Bhs, and Bws horizons in Podzols and Protospodic Cambisols (P3 surface layers), A horizons in Phaeozems/Rendzic Leptosols and upper Bw horizons in silty Cambisols did not show any of the most common signs of ancient frost activity retained by soils (D'Amico et al., 2019, Longhi et al., 2021), such as platy aggregates, silt caps, reticulate patterns. Deep glossae at the E-Bhs horizons boundary were likely caused by roots, as no micro- or macro-morphological evidences of infilling and frost action could be recognized. Holocene pedogenesis is thus highly likely, both for Podzols and Rendzic Leptosols/Phaeozems horizons.

On the contrary, frost action could be recognized in P6-Bt1, with some silt coatings in the largest pores, a fine platy aggregation, and horizontal cracks visible in thin section, which are common signs of at least deep seasonal frost (Van Vliet-Lanoë, 1998). The larger orthogonal cracks observed in P3-2Bt, separating aggregates with very dense and fine-grained groundmass, could indicate permafrost during the existence of these horizons (French and Shur, 2010; D'Amico et al., 2021). An older age can thus be presumed for Terra Rossa horizons and Eutric Luvisols, than for Podzols, Rendzic Leptosols/Phaeozems and for upper horizons of polycyclic soil sequences, which were likely pedogenized during the Holocene. These considerations agree with the scarcity of fines in Podzols, developed during the Holocene, even though the rate of podzolization on carbonate materials is considered very slow (Carroll and Hathaway 1954).

Loess deposition, in fact, typically happened mostly during or immediately after the LGM and other cold periods during the Lateglacial (Gild et al., 2018; D'Amico et al., 2021; Waroszewski et al., 2021).

The different pedogenic trends and ages were reflected in the clay mineralogy, which requires very diverse pedogenic environments and different origins for the soil forming materials. Bw and Bt horizons were usually dominated by vermiculite and HIV, while strongly acidified podzolic horizons were particularly rich in kaolinite, likely because kaolinite is usually an end product of clay mineral weathering in acidic soils. Gibbsite was particularly abundant in P3-2Bt, in agreement with the high Al content. The Al contents and the particular mineralogy of these red horizons could be related to an even older age of this horizon compared to the other Terra Rossa ones, and it was probably caused by leaching of other elements under a tropical/subtropical ferrallitic weathering environment.

4.3 Geochemistry and dolostone dissolution rates

As expected in temperate humid climates, large element losses are associated to Holocene soil formation on dolostone, caused by carbonate dissolution (Table 6) and base leaching. In soils apparently formed from substrate dissolution, mass balance calculations can help to understand the dissolution rates of the parent materials and can give important information on elements which likely arrived from outside to the soil system. The Podzol is one of these suitable profiles to understand the origin of the soil forming materials and the dissolution rate of the dolomitic substrate in the study area. In fact, DolSi basically releases only quartz sand after dissolution, and the Podzol is very poor in fines. Based on quartz sand content, 160 cm of parent DolSi must have dissolved to form 82 cm of Podzol (thickness of P1, very similar to the average thickness of Podzols in the study area). This calculation obviously does not include possible mass transfers due to slope processes. Considering the likely Holocene age of the studied Podzols, we can assume a DolSi dissolution rate of 160 cm 11,500^{-1} years, equal to ca. 1.4 cm 100^{-1} years. This rate is higher than the postglacial rate of limestone dissolution in the German Alps (0.28 cm 100^{-1} years, Hüttl, 1999, or 0.34-0.39 cm 100^{-1} years, Küfmann, 2008), but not much higher than the 0.9 cm 100^{-1} years in limestone in the Swiss Jura below soil materials (Burger, 1959; Obert, 1969). These higher rates could be caused by the easier dissolution of DolSi due to the presence of the quartz grains which disrupts the compact texture of the rock, and to the development of Podzols themselves, characterized by much more acidic percolation waters than normally found in soils on carbonate rocks. Making the same calculation for Phaeozems (P5, 35 cm of thickness), the very low bulk density due to the biogenic porosity reduces the necessary DolSi dissolution to 17 cm. We can easily assume that this soil is Holocenic, but the precise age cannot be hypothesized because of the slope steepness, so we cannot derive a substrate dissolution rate for this soil type. Due to the higher fine contents in the other soils, the calculation based on quartz sand would be meaningless.

Calculating mass losses and the consequent dissolution rate of the parent Dol and DolSi using immobile Zr, the required amount of rock that should have been dissolved increases manyfold. For example, 1450 cm and 490 cm of DolSi should have been dissolved to create the Podzol and the Phaeozem respectively. Ca. 3500 and 4000 cm of DolSi should have been dissolved to create 29 and 45 cm of Lixisol (P3-2Btb) and P6-Bt1 horizons respectively; 6240 cm should have dissolved to create only 85 cm of P7-BA-Bt. 430 cm of Dol should have dissolved to create a 25 cm thick Rendzic Leptosol (P9). These data are not compatible with the hypothetical ages of these soils, with the exclusion, maybe, of the very ancient Lixisol-Terra Rossa horizon.

In the Podzol on dolostone, we can assume that Al_2O_3 is in a closed system. The cheluviation from the A and E horizons likely stops in the Bhs and Bhs(m) horizons without any downward loss. In fact, the neutral pH in the low Bhs(m) and the saturation with Ca and Mg at the soil/substrate boundary efficiently block the soluble organo-metal compounds. Al_2O_3 can thus be used to calculate mass balances as well: almost 2500 cm of dolostone should have dissolved to release enough aluminum to the Podzol system.

These amounts of dissolution are unlikely in only Holocene times, thus Al_2O_3 can be considered mostly derived from external inputs of aeolian materials. These inputs are at present mostly Saharan dust (e.g. Varga et al., 2016; Di Mauro et al., 2019), since the end of the African humid period ca. 6000 years BP and the beginning of the desertification of the Sahara (de Menocal, 2015). Consequently, 86 to 146 kg/m^2 (for P1 and P2 respectively) of SD would be required to give the measured Al stock to the Podzol soil system, considering average Al_2O_3 contents of ca. 13.4% in the dust arriving in Europe (Moreno et al., 2006; Di Biagio et al., 2019). The weighted average of fines in the Podzol is 10.85%, which corresponds to a total weight of ca. 94 to 127 kg/m^2 of clay plus silt (for P1 and P2 respectively), well matching the SD inputs including some mineral dissolution and erosion losses. The amount also matches quite well the measured dust deposition in the Western Alps (Wagenbach and Geis, 1989), the Mediterranean Sea (Guerzoni et al., 1997) and the Pannonian Basin (Varga et al., 2016). The dust inputs in the Southern European Alps during the Holocene can thus be considered much smaller than in other mountain ranges, such as the Uinta Mountains in North America (Munroe et al., 2020), where almost 60% of the soil materials in the surface horizons is Holocene aeolian silt.

4.4 Geochemical differences and parent materials

The cluster analysis based on geochemical composition clearly attributed different soil horizons to different parent materials, separating dolostone from aeolian-derived soils. High SiO_2, low concentration of all other elements and sandy textures characterized soils developed on DolSi (Podzols, Phaeozems and deep colluvial horizons), without large inputs of external materials (e.g., only 10.85% of external additions in Podzols). On the contrary, finer textured horizons were associated to PL and/or SD. Only the Lixisol Terra Rossa samples were not associated with any of the considered parent materials, thanks to the extremely strong pedogenesis which deeply modified their composition, increasing Al and other metal concentration.

The aeolian materials (SD and PL) could not be statistically separated, as they both derived from well-mixed upper continental crust (Muhs et al., 2009). A main contribution of PL to the formation of Eutric Cambisols (P10) and Luvisols (P6, P7, P8) and one Rendzic Leptosol/Phaeozem (P9) is however highly likely. In fact, very little silt inputs occurred during the Holocene, as demonstrated by the Podzols. This is different from what happens in the Northern Limestone Alps in Germany, where large quantities of silt are still derived from the silica-rich rocks of Central Alps (Küffmann, 2003). According to Stuut et al. (2009), SD inputs in Alpine soils are frequent but are not able to form discrete layers; the inputs can however be observed as soil mixtures between autochthonous and aeolian materials, without clear horizonation effects, in agreement with the proposed Al origin in the Podzol. On the contrary, Terra Rossa and Rendzic Leptosols found in southern Mediterranean areas have horizons in which SD is detectable as one of the main soil-forming materials (Stuut et al., 2009; Muhs et al., 2010; Andreucci et al., 2012). In the northern Mediterranean, Terra Rossa is likely formed from different sources, such as local aeolian and slope materials, with additions of SD (e.g. Razum et al., 2023).

Many element ratios have been calculated in the literature to detect signatures of SD in soils (Scheuvens et al., 2013). However, no specific SD signature has been recognized, able to

distinguish PL or SD origin, both in the bulk soil material and in the fine fraction of DolSi-derived soils. This could be due by differential element mobility in podzolized soils, or in these acidified soils in temperate humid environments, making geochemical ratios unreliable.
Also REES did not help in the separation between samples linked with PL or SD. High REES contents characterized samples with a fine texture, associated with both PL and SD. The ratio between LREE and HRSS was usually below 4.5, while SD has values higher than 7.3.
Similarly, the Eu/Eu* and Ce/Ce* were not able to separate samples developed from PL or from other dust sources. The Eu/Eu* however separated rock samples from all soil and aeolian materials, suggesting generalized aeolian inputs in the soils.
The mineralogy of SD has been sometimes used to detect aeolian inputs in soils as well. Some minerals are good Saharan (dryland) indicators, such as palygorskite, illite, calcite, and smectite (e.g. Guerzoni et al., 1997; Rodriguez-Navarro et al., 2018). Some of these, however, are unstable in acidic soils under humid conditions, and cannot thus be preserved in the soil after deposition; moreover, we could find only small quantities of smectites and illites in the clay fraction of sandy soils. The intense pedogenesis in the humid climate of the Prealps strongly modifies the clay mineralogy as well. Kaolinite is particularly abundant in podzolic horizons, likely residually concentrated as the least soluble clay phyllosilicate mineral.
From a mineralogical point of view, a strong indicator of aeolian inputs was feldspar, which was observed only in samples statistically associated with aeolian materials and in P6-Bt1. This last sample was much richer in silica than the analyzed PL, likely inherited from the substrate, but also it had measurable feldspar amounts in the clay fraction; its origin could thus be hypothesized as a mixture between Si-dolostone insoluble residues and aeolian inputs.

5 – Conclusions

The multidisciplinary approach used to detect the nature and origin of the highly diversified soils on the Corna Bianca karst plateau allowed us to attribute the different soil horizons to different parent materials, in relation to fine fraction contents and mineralogy, geochemistry, micromorphology and age. Pleistocene loess was the main source of materials for some soil types such as Cambisols, Luvisols and some Terra Rossa horizons. Even though no specific geochemical or mineralogical indicators was able to differentiate Pleistocene loess and Saharan Dust, all the used indicators allowed us to differentiate Holocene soils mainly derived from dolostone dissolution with the addition of Saharan Dust, from the more ancient ones mainly developed from loess. In fact, for the other soil types (Rendzic Leptosols, Phaeozems, and Podzols), rock dissolution was an important source of soil materials in the study area, but it was not sufficient to explain their geochemistry nor texture. This is particularly well visible in the Podzol developed on silica-rich dolostone, in which the input of ca. 86 to 146 kg/m^2 of Saharan dust was necessary to enrich the soil materials of the measured metal elements and fines during the Holocene. The calculated amount of Saharan dust arrived and transformed in our Podzols during the Holocene agrees with other measured data available in the scientific literature, and it can thus be considered the normal value for Southern Alpine soils.

The use of more specific geochemical analysis, such as isotopic ratios, and datings of different soil horizons might give us more final information on the origin and differentiation of soils developed in karst landscapes in unglaciated regions.

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Figure captions

Fig. 1: The location of the Corna Bianca plateau, the soil sampling locations and soil types.

Fig. 2: some of the different types of soils observed in the Corna Bianca karst plateau: Podzol (P1), Phaeozem (P5), Lixisol under Protospodic Cambisol (P3) and Eutric Luvisol (P6).

Fig. 3: thin section images taken from the Podzol (P1): a, b) the lamella composed of spodic materials and amorphous organic matter and organic pellets, ; silty accumulations around coarser quartz grains are also visible. c, d): Bhs horizon, with large quantities of organic pellets, and amorphous, spongy coatings on coarse sand grains. e, f): Bhs(m) horizon, with well-developed blocky aggregates with little porosity and large amounts of cracked metal-associated monomorphic organic matter and coatings filling the pores and around sand grains.

Fig. 4: thin section images from P3 (Cambisol over Rhodic Luvisol): a) upper part of the Bws horizon, with many organic pellets and granular aggregates partly filling the vughs and compound packing voids between the sand grains, and few black root fragments; b) lower part of the Bws horizon, showing a few rounded pedorelics and cracked coatings around sand grains evidencing podzolization; c), d), e) rounded aggregates and disrupted reddish clay coatings, and subrounded fragments, at the limit between the CR and the 2Bt horizons; f) massive microstructure with very low porosity; g) clayey laminations and locally striated microfabric visible under plane-polarized light; h) abundant clay coatings filling the voids between the sand grains at the limit between the 2Bt and the deeper 2CR horizon; i) orthogonal cracks, partly filled with Fe-Mn oxides, in the massive matrix in the 2Bt horizon.

Fig. 5: cluster dendrogram based on clay minerals in the analyzed soil samples (complete linkage method, Euclidean distance), and the semi-quantitative clay minerals

Fig. 6: cluster dendrogram based on major elements in the analyzed soil samples and in the parent material references (complete linkage clustering algorithm, Euclidean distance).

Fig. 7: spider diagram of chondrite-normalized REEs in the analyzed samples; SD data were derived from literature (Moreno et al., 2006).