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# **Contrasting environmental memories in relict soils on different parent rocks in the South-western Italian Alps**

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## **Abstract**

Soils on the Alps are usually weakly developed, both because of the extensive Pleistocene glaciations, and because of slope steepness and climate enhancing erosion. However, on some stable, relict surfaces, particularly in the outermost sections of the Alpine range, some highly developed soils are apparently in contrast with Holocene soil forming conditions. In this work we wanted to assess the extent of pedogenesis in some of these soils, located under montane-level vegetation in the Ligurian Alps (SW Piemonte, Italy), and relate it to the effects of climate and parent material.

The considered well developed profiles showed signs of extremely different pedogenetic processes on the different lithotypes. In particular, podzols with extremely thick E horizons (up to more than 2 m thick) and very hard, thick ortstein or placic horizons were formed on quartzite. Reddish "terra rossa" Luvisols were formed on limestone. Red, extremely acidic Alisols were formed on shales.

The chemical properties, the micromorphology and the clay mineralogy demonstrated high intensity pedogenic trends, and were characteristic of processes usually occurring under different climates. They may therefore represent excellent pedo-signatures of different specific past climatic/environmental conditions, as a response of different lithologies to specific soil-forming environments, which range from warm and humid climates typical of red Alisols and Luvisols, to cool and humid/wet climates leading to the formation of Podzols with ortstein/placic horizons.

**Keywords:** Alps; paleoenvironmental indicators; pedogenic processes; relict podzols; terra rossa soils

## **1 Introduction**

35 Soils in mid-latitude mountain areas are usually weakly developed (Legros, 1992) because of  
36 geomorphic processes associated with active orogenesis and steep slopes, such as erosion and  
37 deposition, and Pleistocene glaciations which erased most of the pre-existing soils. In fact,  
38 normally, pedogenesis in these environments lasted for less than ca. 12000-16000 years (e.g. Egli et  
39 al., 2006). Due to these constraints, only pedogenic processes associated with organic matter  
40 dynamics reach a steady state and allow the development of Podzols or soils with Umbric/Mollic  
41 horizons. These latter are known to form in less than 1000 years (Sauer, 2010), while Podzols may  
42 develop in 500-3000 years under subalpine environments on the Alps (Egli et al., 2006; D'Amico et  
43 al., 2014), although, if favorable conditions are maintained, the cheluviation phase may proceed  
44 further and deepen the E horizons at the expenses of illuvial ones (McKeague et al., 1983). Intense  
45 mineral transformations normally occur in longer periods and reflect climatic conditions. In  
46 Mediterranean climates, well developed Bt horizons formed by clay lessivage are observed in early  
47 Holocene or late Pleistocene soils (Sauer, 2010), while they can be observed in younger soils in  
48 colder and wetter conditions (Sauer et al., 2009). Rubification, linked to abundant hematite  
49 crystallization, is another slow process involving mineral weathering, and it is one of the most  
50 widely used indicators of specific environmental conditions: it becomes visible only in soils older  
51 than 100,000 years (Sauer, 2010).

52 Given the long time spans necessary for their formation, strongly weathered soils are very rare in  
53 mid-latitude mountain ranges, where they can be preserved only on scattered stable surfaces located  
54 outside the limits of Pleistocene glaciations (relict surfaces) and represent paleosols (when buried)  
55 or relict soils (Ruellan, 1971). Both paleosols and relict soils keep traces of pedogenic processes  
56 that have operated in the past and have been preserved for a long time, but in the case of relict soils  
57 more recent processes are superimposed and polygenesis is the rule. The interpretation of soil  
58 features as paleoenvironmental proxies should take into account therefore the most persistent  
59 characteristics. Normally, the persistence of a soil property is inversely associated with its facility of  
60 formation. Yaalon (1971) and, more recently, Targulian and Krasilnikov (2007) grouped soil  
61 properties and horizons according to the time required for the attainment of a dynamic steady state  
62 and, hence, their relative persistence: they can be rapidly adjusting and easily altered (developed in  
63 less than  $10^3$  years), such as mollic and salic horizons and mottles, and slowly adjusting or  
64 relatively persistent, as in the case of cambic, umbric, spodic and calcic horizons. Due to the very  
65 long time needed for formation, oxic, albic, placic, argillic, petrocalcic, fragic and natric horizons  
66 are considered very resistant to alteration. However, different pedogenic processes act on soils  
67 during different periods of their existence, thus different properties superimpose in the same soil

horizons, creating a complex "combinations of older and newer records" (Targulian and Goryachkin, 2004), and complicating the possible paleoenvironmental interpretations. In this paper we report the morphological, chemical, mineralogical and micromorphological characteristics of some well developed soils found on relict surfaces in a non-glaciated Alpine region. The aim was to assess the pedogenic processes that have occurred to distinguish inherited pedofeatures and link the soils with present and past environmental conditions, with special emphasis on the effect of the parent material. We focused on soils showing traces of two main weathering trends: two profiles had morphological evidences of rubification, while three profiles were podzolic.

## **2 Regional setting and study area**

Pleistocene glaciers occupied only small and scattered cirques above 1700-2000 m a.s.l. in the Ligurian Alps (Piemonte, NW Italy) (Vanossi, 1990; Carraro and Giardino, 2004). The geomorphology is therefore dominated by long term tectonic uplift, temporary peneplanation or cryoplanation, followed by river incision, and periglaciation during cold Pleistocene periods. All the geomorphic features derived from these processes are particularly well preserved in the Upper Tanaro Valley (Fig. 1), where a series of relict surfaces (uplifted bedrock valley floor remnants) are easily recognizable as flat summits and plateaus perched high above the valley floor, at different altitudes on the north and south slopes because of differential tectonic uplift. On the south slopes, many relict surfaces are located at different altitudes, possibly associated with different periods of formation, while on the north slope all the surfaces are located at more or less the same level, gently dipping from ca. 1600 m to 900 m a.s.l. following the valley downstream. On these gently sloping plateaus and erosion terraces, erosion and deposition processes are very limited. Thus, they are generally characterized by single rock substrates, without any significant colluvial/alluvial cover layers. Morphologic indicators of relict preglacial or Early Quaternary surfaces (Goodfellow, 2007), such as thick saprolite layers, blockfields and tors derived from in situ weathering and frost shattering of the bedrock, are widespread on many of the considered surfaces and on the nearby slopes. A precise chronology of the geomorphic events leading to the formation of the relict surfaces is missing, but in other portions of the Ligurian Alps, some 50 km east from our study area, remnants of analogous relict surfaces perched some hundreds of meters above the valley floors are considered fragments of Pliocene alluvial terraces (Rellini et al., 2014). We described and sampled in detail 5 well developed soil profiles on some of the relict surfaces preserved in the Upper Tanaro Valley, chosen amidst a much larger number of observations because of their good state of preservation and high degree of pedogenic development, in

102 topographic positions where visible disturbances due to erosion and deposition were minimal. The  
103 main environmental properties of the sampling sites are shown in Table 1. A wide range of different  
104 rock types were observed, ranging from sandy-textured quartzite (ALB soil, on "Quarzite di Ponte  
105 di Nava"), to coarse quartzitic conglomerate (PLC soil, on "Porfiroidi di Melogno"), to quartzite-  
106 andesite conglomerate (ORT soil, on "Porfidi di Osiglia"), to Fe-chlorite rich shales (ALI soil, on  
107 "Formazione di Murialdo - Scisti di Viola"), to dolomite (TR soil, on "Dolomie di San Pietro dei  
108 Monti") (Vanossi, 1990). The soil parent material was always the residuum formed from in situ  
109 disintegration of the bedrock (regolith and saprolite). On quartzitic rocks, the unweathered substrate  
110 appeared only as residual tors on the edges of the relict surfaces, otherwise thick layers of saprolite  
111 (up to 20-50 m), which locally included some corestones (blocks of unweathered rock) represented  
112 the parent materials for these soils.

113 Present day land use is montane *Castanea sativa* Mill., *Fagus sylvatica* L., *Ostrya carpinifolia*  
114 Scop., *Pinus sylvestris* L. or *Pinus uncinata* Mill. forest (Table 1). The average annual temperature  
115 ranges between 4° and 8°C, decreasing with altitude and with local variability with slope aspect.  
116 The annual precipitation is around 800-1200 mm, with spring and fall maxima and summer minima  
117 (Biancotti et al., 1998). Normally, water scarcity is not a limiting factor for plant growth (udic  
118 moisture regime), even during the rather dry summer months (average July rainfall is around 40  
119 mm). Summer fogs are common, thanks to the proximity with the Mediterranean Sea, and increase  
120 available moisture in the surface soil layers. Snow cover normally lasts from November to  
121 March/April in the considered altitudinal range, but snow thickness does not reach very high values  
122 because of frequent winter rain episodes associated with warm Mediterranean air masses.

123

### 124 **3 Methods**

125 At the selected sites pits were opened and the soil profile described according to the FAO guidelines  
126 (2006). In this work, we used qualifiers in brackets in horizon designation to indicate minor but  
127 detectable characteristics. The soil samples were taken from the whole thickness of the genetic  
128 horizons, air dried, sieved to 2 mm and analyzed. When not otherwise specified, the analyses  
129 followed the methods reported by Van Reeuwijk (2002). The pH was determined potentiometrically  
130 in water extracts (1:2.5 w/w). The total C concentration was measured by dry combustion with an  
131 elemental analyzer (CE Instruments NA2100, Rodano, Italy). The carbonate content was calculated  
132 by volumetric analysis of the carbon dioxide liberated by a 6 M HCl solution. The organic carbon  
133 (OC) was then calculated as the difference between total C measured by dry combustion and  
134 carbonate-C. The particle size distribution was determined by the pipette method after treating the  
135 samples with H<sub>2</sub>O<sub>2</sub> and dispersing with Na-hexametaphosphate. Exchangeable Ca, Mg, K, Na were

determined after exchange with  $\text{NH}_4$ -acetate at pH 7.0. Acid ammonium oxalate and Na-dithionite-citrate-bicarbonate were used to extract Fe and Al ( $\text{Fe}_o$ ,  $\text{Al}_o$ ,  $\text{Fe}_d$  and  $\text{Al}_d$ ). The total element concentrations ( $\text{Al}_t$ ,  $\text{Si}_t$ ,  $\text{Fe}_t$ , etc) were determined after HF- $\text{HNO}_3$  hot acid digestion (Bernas, 1968). In all extracts, the elements were determined by Atomic Absorption Spectrophotometry (AAS, Perkin Elmer, Analyst 400, Waltham, MA, USA). The presence of poorly crystalline allophane or imogolite-type materials was assessed by pH measured in 1M NaF solution. The mineralogical investigations were carried out using a Philips PW1710 X-ray diffractometer (40kV and 20 mA,  $\text{CoK}\alpha$  radiation, graphite monochromator). The mineralogy of the parent materials was evaluated ( $3\text{--}80^\circ 2\theta$ ) on backfilled, randomly oriented powder mounts. The Mg saturated clay fraction ( $< 2\ \mu\text{m}$ ) was separated by sedimentation, flocculated with  $\text{MgCl}_2$ , washed until free of  $\text{Cl}^-$ , and freeze-dried. Scans were made from  $3$  to  $35^\circ 2\theta$  at a speed of  $1^\circ 2\theta\ \text{min}^{-1}$ , on air dried (AD), ethylene glycol solvated (EG), and heated ( $550^\circ\text{C}$ ) oriented mounts. The presence of hydroxyl-interlayered vermiculite (HIV) and/or hydroxyl-interlayered smectites (HIS) was ascertained, and their thermo-stability assessed, by heating the samples to 110, 330 and  $550^\circ\text{C}$ . Crystalline Fe and Al oxi-hydroxides were detected on backfilled, randomly oriented mounts of the separated clay fraction ( $5\text{--}40^\circ 2\theta$ ), at a speed of  $0.5^\circ 2\theta\ \text{min}^{-1}$ . Oriented and undisturbed bulk soil samples or aggregates were collected from the profiles and impregnated with resin to prepare  $60\times 45\ \text{mm}$  thin sections. The thin sections were observed using a polarizing microscope (Leitz Wetzlar HM-POL) and described following Stoops (2003). Hue, chroma and value of the Munsell notation were used to calculate the redness rating following the procedure described by Torrent et al. (1980). The set of analyses performed was selected depending on the type of soil and horizon to be studied.

158

## 159 **4 Results**

### 160 **4.1 ALB: Morphology, chemistry and clay mineralogy**

161 ALB developed on sand-grained quartzite; the XRD and total elemental analysis of the parent  
162 material confirmed that the sandy-textured, weakly metamorphosed quartzite was mainly composed  
163 of quartz, with only traces of micas and feldspars. On this substrate, on flat topography, soils had  
164 extremely thick E horizons (more than 2.1 m, Table 2). Only the top 35 cm (AE horizons) likely  
165 developed in a periglacial cover bed, evidenced by a few weakly weathered cobbles, separated from  
166 the 2EA and 2E horizons below by a sharp discontinuity which included some thin soil wedge cast-  
167 like structures (Fig. 2A). Below the periglacial cover bed, the thick E horizons were composed of  
168 strongly weathered, white-greyish quartzitic coarse sand locally impregnated by percolated organic  
169 matter and abundant fungal hyphae associated with the pine deep root system. Two Bs horizons,

170 with different morphologies, were collected nearby. The first one (Bs-old in Tables 2, 3 and 4) was  
171 observed ca. 30 m south-east of the main profile, below a fallen tree on a slightly steeper, recently  
172 eroded surface. Below a thinner E horizon, very similar to the deep E in the main profile, the upper  
173 limit of the Bs was wavy and irregular, and its pale yellowish-brown material was interrupted by  
174 many whitish/greyish spots. This Bs horizon was much paler than those developed on the steep  
175 surfaces around (Bs-young in Tables 2, 3 and 4).

176 The 2E horizon had the smallest textural clay content (Table 3) and was the most depleted in total  
177 and oxalate extractable metals (Table 4). In the Bs-old horizon the concentration of extractable  $\text{Fe}_o$   
178 and  $\text{Al}_o$  was much lower than in the Bs-young (SI, i.e. spodic index:  $\text{Al}_o + 0.5\text{Fe}_o$ , 0.23% and 0.84%,  
179 respectively, Table 4), as well as the  $\text{pH}_{\text{NaF}}$  (9 and 12.5, respectively, Table 3), indicating a smaller  
180 amount of short range-ordered materials, such as imogolite, proto-imogolite and allophane.

181 In the E horizon, the shift of the 1.4 nm peak and of the broad one around 1.2 nm to, respectively,  
182 1.63 and 1.3-1.4 nm after EG solvation evidenced that clay was dominated by smectites and  
183 smectite-illite mixed layered minerals. Illite and quartz, inherited from the parent material, were  
184 detected as well. A good collapse upon heating was observed and indicated the absence of Al  
185 polymers in the interlayer (Fig. 3A).

186 Smectitic minerals were detected in the clay fraction of the Bs-old as well, associated with  
187 interstratified minerals, such as illite and non-swelling components. Even after heating at 550°C,  
188 the peak at 1.0 nm was asymmetrical, indicating the presence of HIV (Fig. 3A).

189

#### 190 **4.2 ORT: soil morphology, chemistry, clay minerals and micromorphology**

191 The weakly metamorphic quartzitic conglomerates with andesitic inclusions, parent material of  
192 ORT soil, included small quantities of mafic minerals, such as pyroxenes and amphiboles, in  
193 addition to quartz (still the most important mineral by far), micas and feldspars. It was slightly Fe  
194 and Al-rich than the parent material of the ALB soil (section 4.1). The thick saprolite layer was  
195 depleted in mafic minerals compared to the unweathered rock, but without detectable amounts of  
196 any pedogenic materials.

197 Although the eluvial horizon of ORT was thinner than that observed in ALB, it still showed a  
198 remarkable development of cumulatively ca. 140 cm (Fig. 2B). The albic horizons were followed  
199 by a thick and strongly cemented sequence of ortstein horizons (Table 2). The upper loose,  
200 bioturbated E horizon was probably developed in a periglacial cover bed, as shown by sharp  
201 variation in structure and consistence, by the higher stone content and the much weaker weathering  
202 degree of the stone fraction. Below, the 2Ex and 2E(h) had a hard consistence, almost cemented in  
203 the field, and showed many darker patches distributed on net-like structures, apparently enriched in



204 illuvial organic matter. Though these horizons cannot be considered true fragipans, the net-like  
205 appearance and the quick slacking of hard dry aggregates in water evidenced fragile properties.  
206 Below, a thin 2Btm(s) horizon was observed, characterized by reddish clay coatings on the upper  
207 faces of cemented peds. The 2Bsm horizon was a typical ortstein, strongly cemented and with  
208 abundant macroporosity, as often observed in ortstein horizons on the Alps (e.g., Catoni et al.,  
209 2014). Also the thick deeper 2Btsm horizon was characterized by strong cementation, but it showed  
210 thick reddish illuvial clay coatings on the upper faces of peds. Both 2Btsm and 2Btm(s) horizons  
211 showed an increase in clay content compared to the nearby E and Bsm ones (Table 3). The bottom  
212 yellowish brown 2Bsh<sub>m</sub> was darker than the horizons above, likely because of decay of present-day  
213 roots, which were concentrated in the fissures between cemented, coarse aggregates. Between the  
214 2Bsh<sub>m</sub> and the hard, unweathered rock, a pale and weakly cemented C<sub>m</sub> and a strongly weathered  
215 saprolitic Cr horizons were visible along a nearby roadcut.

216 The micromorphology of E and Bsm/Btm horizons confirmed many of the macromorphological  
217 features observed in the field (Table 5). The groundmass of the two thick E horizons was  
218 characterized by a close porphyric coarse/fine (c/f) related distribution pattern, with few coarse  
219 vughs or cracks (Fig. 4A, 4B). Some cracks were partially filled with rounded silty quartz grains  
220 and thin monomorphic organic matter infillings; these cracks were cut both through the fine matrix  
221 and the shattered coarse fragments. Silt infillings and oriented fine sand/silt caps were common.  
222 The groundmass was locally thinly laminated. A few reddish clay coatings and pedorelicts were  
223 locally observed in the 2Ex, while the white groundmass was locally slightly darker because of  
224 organic matter or redoximorphic Fe-Mn impregnations.

225 The 2Bsm horizon had a high porosity (Table 5, Fig. 4C), which separated strongly developed  
226 subangular blocky peds characterized by a closed porphyric c/f related distribution (Fig. 4C). Many  
227 reddish or yellowish brown clayey pedorelicts were observed in the groundmass. Locally, disrupted  
228 reddish clay coatings were preserved on the void walls, surmounted by thinly laminated silt and fine  
229 sand accumulations. In turn, these accumulations were covered by thick, composite, cracked  
230 yellowish-brown coatings, characterized by at least 3 paler or darker layers. Both the groundmass  
231 and the silt accumulation were impregnated by yellowish-brown amorphous materials. These  
232 amorphous coatings represented almost 13% of the total solid volume, in agreement with the high  
233 Fe<sub>t</sub> and Al<sub>t</sub> measured in this horizon (Table 4).

234 The micromorphology of the 2Btsm below was distinctly different (Table 5, Fig. 4D). In particular,  
235 a banded distribution of differently sized particles was observed, usually associated with varying c/f  
236 related distribution patterns (Fig. 4D). Closely packed layers with porphyric related distribution,  
237 where small or medium angular quartz grains were included in a fine matrix impregnated by black

238 and dark reddish-brown materials, were in continuity with layers composed of thick, thinly  
 239 laminated silt accumulations covered by thick crescentic clay coatings and infillings. These layers  
 240 rich in illuvial clay were in continuity with loose layers with chitonic related distribution and  
 241 abundant compound packing voids, where coarse angular quartz fragments were surrounded by  
 242 cracked yellowish-brown coatings probably consisting of Fe-Al oxi-hydroxides and monomorphic  
 243 organic matter.  
 244 Despite the clear podzolic morphology, low amounts of  $Fe_o$  and  $Al_o$  were measured (Table 4), and  
 245 the SI never reached the 0.5%, required by most taxonomic systems in the spodic horizon  
 246 definition. Particularly low values of poorly crystalline Fe-Al (hydr)oxides were measured in the  
 247 top 2Btm(s) and a low  $Fe_o/Fe_d$  ratio was measured in the other illuvial horizons as well; only the  
 248 deep 2Bshm had a high proportion of poorly crystalline Fe oxides. The  $pH_{NaF}$  had low values in the  
 249 2E(x) and in the 2Btm(s) horizons, and reached the highest values (11.0 and 11.8 respectively) in  
 250 the 2Bsm and in the 2Bshm. Abundant short range-ordered imogolite-type minerals thus  
 251 characterized these horizons. The many-fold increase of  $Fe_t$  and  $Al_t$  from the E to the ortstein  
 252 horizons indicated a strong redistribution of these metals, but an irregular trend in the different  
 253 2Bsm and 2Btsm (Table 4). In the illuvial horizons, more than 40-50% of total Fe was in the form  
 254 of pedogenic oxides, with the exception of the 2Bsm, which showed a low  $Fe_d/Fe_t$ .  
 255 In spite of the unusual distribution of metal forms along the profile, clay mineralogy was consistent  
 256 with that typically characterizing Podzols. E horizons contained smectites, illite-smectite, and traces  
 257 of chlorite-vermiculite interlayered minerals (Fig. 3B). The clay mineralogy of the illuvial 2Bsm  
 258 and 2Btsm horizons was similar to each other. Small traces of swelling minerals were evidenced by  
 259 the appearance of a small peak at 1.64 nm after EG solvation only in the top 2Btm(s) horizon, while  
 260 the most abundant minerals were illite, mixed layer minerals with an illitic component and HIV.  
 261 Some chlorite seemed also to be present, since a small peak at 0.7 nm remained after heating at  
 262 550°C. Kaolinite (double peak near 0.72 nm completely collapsing at 550°C) was detected as well.  
 263 Quite large amounts of gibbsite (peaks at 0.48 nm) were observed in the 2Bsm and in the 2Btsm  
 264 horizons. Only quartz and primary chlorites and micas were detected in the saprolitic Cm and Cr  
 265 horizons; here, the mafic minerals included in the unweathered rock were not detected.

#### 267 **4.3 PLC: Morphology, micromorphology, chemistry and clay minerals**

268 PLC was sampled on hard and coarse metamorphic quartzitic conglomerates, which included the  
 269 same primary minerals of quartzite (see section 4.1), but with a larger muscovite content. On gentle  
 270 slopes near the surface edges, placic horizons were common and well developed between the E  
 271 horizons and the underlying cemented ortstein ones. These soils had thinner (ca. 70 cm) E horizons;

the deep E horizon (2E(x)) had a very similar macro-morphology compared to the ones observed in the ORT (section 4.2.2), with hard consistence and weak fragic properties (Table 2, Fig. 2C). Despite the hard consistence, the 2E(x) horizons in thin section had a rather high void content (Table 5, Fig. 4E). The c/f related distribution of the aggregates was open porphyric, with a dense silt and fine sand matrix surrounding angular to subrounded sand grains, and larger gravel-sized clasts. The matrix was thinly laminated and convoluted and it was locally impregnated with monomorphic organic matter. Well developed silt caps and compression caps were visible close to the coarse fragments (Fig. 4E). A few pores had reddish-brown clayey infillings, while a few reddish pedorelicts were included in the matrix. The placic horizon had a double-spaced to open porphyric c/f related distribution (Fig. 4F): coarse and fine quartz grains, subangular in shape, with few weakly weathered feldspars and strongly weathered phyllosilicates were included in a dark reddish matrix with black bands (as normal in placic horizons, Wilson and Righi, 2010). The black bands were convoluted. A very low porosity was detected. Below, the placic horizon graded into the 2Bsm2, characterized by a higher porosity (compound packing voids) and a geric c/f related distribution. The matrix was impregnated by yellowish-brown materials, which covered the pore walls as compound cracked coatings, characteristic of spodic horizons. Above the placic horizon, dense and layered fine sand accumulations were developed. Despite the hard cementation of the placic and ortstein horizons, only small quantities of  $Fe_o$  and  $Al_o$  were detected (Table 4), likely because of the quartzitic coarse sand matrix diluting the illuvial spodic materials. However, the high  $Fe_o/Fe_d$  ratio indicated that Fe illuviation is still active.  $Al_o$  was not significantly translocated to these cemented horizons, while the  $Fe_o$  increased 15 times from the Fe-depleted E to the cemented 2Bsm1 and 2Bsm2. Lepidocrocite was detected by XRD (evidenced by the sharp 0.63 nm peak) in the cemented Bsm horizons, and it was most abundant in the placic Bsm1 (Fig. 3B). As normal in Podzols, smectite and illite-smectite interlayered minerals were abundant in the clay fraction of E horizons, while illite, HIVs and chlorites were dominant in the underlying placic and ortstein horizons.

#### 4.4 TR: Soil morphology, chemistry and clay mineralogy

The dolostone, parent material of TR, was composed of pure dolomite but included some thin marly veins with micas, chlorites, feldspars and quartz. Upslope from this profile, Fe-chlorite rich shales outcropped. On this dolostone, soils were typical Mediterranean "terra rossa", with hue of 2.5YR in all B horizons (Table 2). On the quarry scarp where the samples were collected, the thickness of these red soils varied from 50 cm to more than 5 m, filling cracks and hidden sinkholes.

305 A very high clay content (up to 73% in the Bt1), abundant and thick clay coatings on the ped  
306 surfaces and near-neutral pH values characterized these soils (Table 3). The ratio between CEC and  
307 clay may be as low as 0.27 in the Bt1 horizon (Table 3) where the highest decrease in the  $\text{Si}_t/\text{Al}_t$   
308 molar ratio was also visible: it passed from 2.0 in the Cr layer to 1.8 (Table 4). In all horizons,  
309 pedogenic Fe oxides were abundant and the  $\text{Fe}_o/\text{Fe}_d$  ratio indicated a high crystallinity of Fe forms.  
310 The calculated redness rating of 15 lied within the range found in Spanish pre-Riss (MIS 11 and  
311 older) Luvisols where it corresponded to hematite contents of about 2% (Torrent et al., 1980). As  
312 the molar weight of hematite is 160, around  $14 \text{ g kg}^{-1}$  of  $\text{Fe}_d$  should originate from 2% of hematite.  
313 The  $\text{Fe}_d$  amounts of 43-45  $\text{g kg}^{-1}$  (Table 4) suggested therefore that pedogenic Fe forms in Bt  
314 horizons consisted of a 1:2 mixture of hematite and goethite (molar weight=89). As hematite is  
315 highly pigmenting, particularly in Mediterranean soils (Torrent et al., 1983) even small amounts  
316 may give the soil the red and bright colour (2.5YR 4/8 in the Bt horizons).  
317 The clay fraction was a mixture of regularly interstratified swelling minerals, as visible from the  
318 partial shift of the 1.4 nm peak to 1.55 nm upon EG solvation and the concomitant shift of the 2.83  
319 nm peak, some chlorite, vermiculite, illite and kaolinite (Fig. 5). Although not present any more in  
320 the clay fraction, dolomite was still visible in the powdered bulk samples, thus favouring a high Ca  
321 and Mg concentration in the soil solution and the consequent high base saturation.

322

#### 323 **4.5 ALI: Soil morphology, chemistry and mineralogy**

324 ALI developed on shales, which were composed by Fe-rich chlorites, muscovite, biotite, quartz, and  
325 smaller quantities of feldspars, amphiboles and margarite.

326 Very red colours (2.5YR 4/6 or 2.5YR 5/8 in the Bt horizons) characterized also highly weathered,  
327 extremely acidic and desaturated Alisols (Table 2, Fig. 2E). These soils had well-expressed argic  
328 horizons, with more than 50% of clay and common clay coatings and Mn coatings, covering the  
329 faces of well-expressed angular peds (Tables 2 and 3).

330 Also in this case, large amounts of  $\text{Fe}_t$  (50-60  $\text{g kg}^{-1}$ , Table 4) were found in the Bt horizons. The  
331 redness rating (11.25) was slightly lower than that of the TR soil (section 4.4), suggesting a  
332 hematite content of about 15  $\text{g kg}^{-1}$  (Torrent et al., 1980). On average, the  $\text{Fe}_d$  content in the Bt  
333 horizons was 36  $\text{g kg}^{-1}$ , thus the ratio between hematite and goethite should be around 1:2.6. The  
334 ratio CEC/clay was always above 50 and also in this case, a slight depletion of Si with respect to Al  
335 was visible from the changes in  $\text{Si}_t/\text{Al}_t$  molar ratio (from 2.24 in the parent rock to 2.16 in the 2Bt2).  
336 XRD analysis of powder samples from the most weathered and least disturbed 2Bt2 horizon  
337 confirmed a strong mineral weathering, evidenced by the differences with the parent material. The  
338 ratios between the 1.4 nm peak of chlorite and the 4.26 of quartz changed from 2.1 in the parent

339 material to 0.7 in the 2Bt2 horizon, indicating a strong depletion of chlorite compared to quartz.  
340 Micas were depleted as well, with ratios passing from 3.0 to 0.7. Furthermore, lithogenic chlorite  
341 was probably completely degraded as no peaks at 1.4 or 0.7 nm were found after heating to 550°C.  
342 The collapse of the 1.4 nm phase started at 330°C and at 550° only a broad diffraction peak at 1.2  
343 nm was visible (Fig. 5). This behaviour suggests the presence of a mixed layer component made by  
344 HIV with a high degree of Al-polymerization together with a more resistant 1.4 nm phase  
345 (Tolpeshta et al., 2010). Kaolinite and traces of smectite were present as well.

346

## 347 **5 Discussion**

### 348 **5.1 Pedogenic processes in strongly developed podzolic soils**

349 On quartzitic materials, podzolization has apparently been active for extremely long periods, as  
350 shown by the extreme development of E horizons (in the ALB and ORT soil) or the strong  
351 cementation of thick ortstein layers (ORT soils). Soils of probable Holocene age, formed on nearby  
352 steeper slopes on the same parent materials, are Podzols with 20-40 cm thick E horizons and thin  
353 weakly cemented layers. Extremely thick E horizons have sometimes been observed in tropical  
354 Podzols (e.g., Dubroeuq and Volkoff, 1998), created during long periods of pedogenesis associated  
355 with warm and wet climate. At mid and high latitudes, E horizons are usually thinner also in ancient  
356 soils developed on permeable sandy materials on stable marine terraces: for example, the extremely  
357 impoverished and ancient Podzols (more than 500,000 years old) developed below the pygmy forest  
358 in California on Pleistocene sandy beach deposits have ca. 30-40 cm thick E horizons (Jenny et al.,  
359 1969).

360 Despite the strong features left by long lasting podzolization, normally associated with cool and  
361 humid climates and acidifying coniferous forests and/or ericaceous shrubs, many different  
362 environmental memories are imprinted in these podzolic soils, pointing to an ancient polygenetic  
363 origin as well (Tursina, 2009). Cryoturbation features (Cremaschi and Van Vliet-Lanoë, 1990; Van  
364 Vliet-Lanoë, 2010), created during cold phases, were well preserved. In fact, we observed small  
365 wedge cast-like figures at the contact between the cover bed and the in-situ E horizons in ALB, hard  
366 consistence, silt accumulations, dense packing and other properties characterizing fragic horizons in  
367 ORT, hard consistence, convoluted platy microstructure and abundant silt caps in PLC. All these  
368 features suggest that more than one glacial period has elapsed since the beginning of soil formation.  
369 We can assume that these cold phases correspond with Pleistocene glacial periods, as during the  
370 coldest Holocene periods (i.e., the Little Ice Age, Joerin et al., 2006) the temperatures were only ca.  
371 1°C lower than present day ones (Lühti, 2014); temperatures at least 4-7°C lower than present day  
372 ones would be necessary for the development of large and thick solifluction and gelifluction

deposits (Harris, 1994) and these conditions were likely verified only during the coldest Pleistocene climatic phases. Moreover, these landforms could not form under dense beech or pine forests, which have covered the area throughout the Holocene (Ortu et al., 2008).

The 2Bsm and 2Bt<sub>sm</sub> horizons in the ORT soil bring many other indicators of strong polygenesis, each associated with different glacial and interglacial periods. In particular, in the 2Bsm, the reddish clayey rounded pedorelicts included in the groundmass and the disrupted clay coatings around a few voids are remnants of an ancient well developed Bt horizon, likely similar to the 2Bt<sub>sm</sub> below. The thick layered silt accumulations observed above the disrupted argillans were probably deposited during periods of intense frost disturbances, which may have also destroyed the previously existing clay coatings (Collins and O'Dubhain, 1980; Kemp, 1998). The most recent pedogenic features seem to be the accumulation of thick amorphous yellowish-brown, cracked coatings, which are characteristic of spodic horizons and are caused by the desiccation of the hydrated illuvial organic matter associated with amorphous Al and Fe (Buurman and Jongmans, 2005). In the Bt<sub>sm</sub> horizon, layers of silt are deposited between thick reddish clay coatings, demonstrating different phases of cryoturbation followed by warm and seasonally wet periods, during which the vegetation was possibly converted from coniferous forest to other, less acidifying vegetation types. Also in this horizon, the last phase seems dominated by the deposition of thin coatings of spodic materials in the pore-rich, chitonic portions of the horizon. The superimposition of different Bsm and Bt<sub>m</sub> horizons, their very different c/f related distribution and the chemical composition might suggest the existence of unnoticed lithological discontinuities associated with ancient periglacial cover beds, which could improve the interpretation of the chronology of the different pedogenetic phases.

Memories of particularly humid environmental conditions are preserved in the PLC soil while they were not detected in the ALB and PLC soils, because of topographic position and parent material granulometry. Placic horizons are often found in hydromorphic soils, usually in humid oceanic or montane tropical climates (e.g., Lapen and Wang, 1999; Jien et al., 2010), and they are uncommon in Holocene soils on the Alps, where they have only been described in the much more humid north-western French Alps (Thouvenin and Faivre, 1998). Placic horizons form upon the crystallization of Fe/Mn oxi-hydroxides from dissolved divalent ions, triggered by changes in redox potential (Bockheim, 2011), thus periodical waterlogging is essential. Lepidocrocite was detected in the placic horizon, and in the underlying ortstein, confirming the shift in redox conditions. This mineral is common in redoximorphic soils in many environmental conditions, but its stability is strongly enhanced by the presence of complexing organic molecules (Krishnamurti and Huang, 1993) and by dissolved Al (Schwertmann and Taylor; 1989, Chiang et al., 1999), and is thus well preserved in periodically waterlogged podzolic soils, and in placic horizons (Campbell and Schwertmann, 1984).

407 On the other hand, the cementation of the ortstein horizon below the placic and the typically  
408 cracked, yellowish-brown monomorphic coatings on the aggregate surfaces indicate that a strong  
409 illuviation of organic Fe-Al complexes has been active, at least in some periods along the history of  
410 this soil. Moreover, clay mineralogy, both in the E and in the ortstein horizons, has the normal  
411 depth trend for podzolic soils, nonetheless the weak  $Al_o$  redistribution with depth.

412 The PLC soil was therefore characterised by both podzolization and hydromorphism, and in these  
413 cases, the horizons above the cemented layer tend to partially loose the spodic characteristics, which  
414 are instead well maintained below the placic horizon (Bonifacio et al., 2006).

415 Waterlogging and related redox processes are unlikely active in present day climate, unless maybe  
416 during periods of intense snow-melt in spring, but might have been common during wet Quaternary  
417 phases, or when permafrost inhibited internal drainage in this soil, or when large quantities of water  
418 were available during permafrost melting. These horizons, thus, bring memories of past, more  
419 humid conditions which seem to have occurred after a first phase of intense podzolization and are  
420 not imprinted in the other studied soils. PLC is thus another example of a highly polygenetic soil,  
421 where podzolization associated with ortstein cementation, followed by waterlogging, placic horizon  
422 formation and lepidocrocite crystallization acted during different periods, yet to be discovered.

423 Cryoturbation features such as laminated and convoluted microstructure and silt and compression  
424 caps around coarse fragments in the 2E(x) horizon, suggest that also in this case more than one  
425 Pleistocene glacial period has elapsed since the beginning of pedogenesis.

426 Other indicators of old age for the ALB, ORT and PLC soils are the high crystallinity of the Fe  
427 oxides in the podzolic horizons (evidenced by the low  $Fe_o/Fe_d$  ratio) and the abundant gibbsite in  
428 the ORT B horizons. Abundant gibbsite in soil horizons and saprolite layers has often been  
429 associated with pedogenetic phases occurred during warm Early Pleistocene interglacials or during  
430 the Tertiary (e.g., Mellor and Wilson, 1989). However, this assumption has sometimes been  
431 challenged by other studies (e.g., Goodfellow et al., 2014), which state that gibbsite can form from  
432 the early dissolution of Al-bearing feldspars in saprolitic layers also in cold and slightly acidic soil  
433 environments, thus reducing the pedogenetic and paleoenvironmental significance of this mineral.

434 However, the saprolite at the ORT base did not include gibbsite, thus its abundance in the cemented  
435 ortstein horizons could point to a crystallization from amorphous materials, following the  
436 mineralization of the Al-complexed organic matter (Righi et al., 1999).

437 Despite the ancient origin, the podzolization process is still active in the considered soils. The E  
438 horizons of all these ancient Podzols clearly bring evidence of percolation of soluble organic matter  
439 and show the typical clay mineral associations of present-day podzolic E horizons, with abundant  
440 smectites and smectite-interlayered minerals (Ross, 1980), derived from the transformation of micas

441 and chlorites to vermiculite (Wilson, 1999). Many Bs or Bts horizons are likely being depleted in Fe  
442 and Al oxi-hydroxides and in imogolite-type materials because of the expansion of the E horizon at  
443 depth. The Bs-old in the ALB soil shows a particularly advanced degradation, as indicated by the  
444 suite of minerals in the clay fraction, that contains HIV, non-swelling mixed layers and smectite.  
445 Smectitic minerals are seldom detected in the Bs horizons of Podzols (e.g., Righi et al., 1982;  
446 Cornelis et al., 2014). It seems therefore that present-day conditions favour the removal of Al-  
447 polymers from the interlayer in the Bs, which occur upon downwards migration of podzolic sequa  
448 (Falsone et al., 2012). The light greyish or yellowish patches, and the wavy irregular upper limit of  
449 the pale yellowish brown Bs-old horizon were likely related to zones with higher or lower porosity,  
450 which favoured or inhibited water percolation and, thus, locally promoted chelation and depletion  
451 of the accumulated spodic materials by soluble organic matter (as often observed in tropical  
452 Podzols, Buurman et al., 1999). The 2Btm(s) in the ORT soil, which was impoverished in oxalate-  
453 extractable elements and had some smectite in the clay fraction, evidences the same degradation  
454 process, likely associated with a deepening of the E horizon.  
455 Podzolic soils are characteristic on quartzitic parent materials in the study area, and variations in  
456 specific properties depend mostly on parent material mineralogy and texture. In fact, the strong clay  
457 illuviation detected in the ORT soil was possible because of the presence of small quantities of  
458 weatherable mafic minerals which permitted the formation of a large amount of phyllosilicates. On  
459 purer quartzite and quartzitic conglomerate, this clay formation and illuviation was not possible,  
460 even under presumably similar climatic regimes.  
461 The different topographic position could explain other variations in soil features: for example, the  
462 coarser texture characterizing the PLC soil compared to the ALB and ORT can be associated with  
463 the closeness to the edge of the relict cryoplanation surface that could have helped the selective  
464 removal of fines, particularly during highly erosive cold periods. The strong waterlogging indicators  
465 characterizing the PLC soil are widespread on similar surface morphologies on the same substrate  
466 lithology in the non-glaciated Upper Tanaro Valley.

467

## 468 **5.2 Pedogenic processes in the rubified soils**

469 Terra Rossa soils are typical of the Mediterranean areas, but may occur also in axeric climatic  
470 regimes (Boero and Schwertmann, 1989) if a highly permeable substrate, such as coarse limestone  
471 glacial and alluvial deposits, enhance summer desiccation. Present-day climatic conditions in the  
472 study area are quite far from the Mediterranean, as no warm and dry seasons occur (Biancotti et al.,  
473 1998) or have occurred during the whole Holocene; in fact, despite the lack of precise rainfall  
474 reconstructions, summer precipitations were abundant also during the warmest period (i.e., the



475 climatic optimum, ca. 8000-4000 years B.P.) as shown by the lack of Mediterranean or xerophilous  
476 taxa in palynological records collected in nearby valleys (Ortu et al., 2008). Like many rubified  
477 paleosols in non-Mediterranean areas, the TR soil has probably developed during previous  
478 interglacials or even during the early Quaternary or Late Tertiary, when the climate was  
479 characterized by warmer temperatures and a stronger rainfall seasonality (Busacca and Cremaschi,  
480 1998). The distribution of Fe forms, in both the TR and the ALI soil, confirm the long time elapsed  
481 since the beginning of pedogenesis and climatic changes during soil formation. A mixture of  
482 hematite and goethite is typical of many Terra Rossa soils (e.g. Boero and Schwertmann, 1989;  
483 Durn et al., 1999; Jordanova et al., 2013) and has been explained by the shift in climatic conditions  
484 that, when hot and dry, favour the transformation of ferrihydrite into hematite, and when moister  
485 promote ferrihydrite dissolution and goethite precipitation (Schwertmann and Taylor, 1989). In both  
486 soils goethite dominated over hematite but the calcareous soil was slightly more hematite-rich. The  
487 larger hematite content in TR may be related to the presence of a more compact and fractured  
488 parent material that favours drainage of excess water even during the moistest periods.  
489 The genesis of Terra Rossa soils is still a matter of debate as the insoluble residue of the calcareous  
490 parent material has been shown to be insufficient in many cases to permit soil formation. Based on  
491 mineralogy, rare earth elements, particle morphology and other indicators (Durn, 2003), colluvial  
492 processes and aeolian dusts, mainly from Sahara, are thought to extensively contribute (Yaalon,  
493 1997), as well as loess sediments from Middle Pleistocene (Durn et al., 1999). The mineralogy of  
494 Saharan dust in the Western and Northern Mediterranean region is dominated by quartz, illite,  
495 palygorskite, with minor amounts of smectites, feldspars and dolomite (Avila et al., 1997). With the  
496 exception of palygorskite, unstable in non-aridic soils, all other minerals were found in the TR soil,  
497 but being ubiquitous, may have many origins and most of the detected minerals in the bulk soil  
498 were also present in the marly veins included in the substrate, and in nearby shale outcrops.  
499 Moreover, despite the increase in  $\text{TiO}_2$  contents from the Cr to the Bt horizons (i.e. from 0.1 to  
500 0.8%, data not shown), the ratio between  $\text{Al}_t$  and  $\text{Fe}_t$  remained almost constant in all soil horizons,  
501 suggesting an autochthonous origin. By assuming that Ti is not leached nor added to the soil during  
502 pedogenesis and therefore its concentration in a soil horizon fully originated from the dissolution of  
503 the parent material and depletion of other more mobile elements, we calculated the losses of all  
504 element oxides following the approach illustrated by Krauskopf and Bird (1985). According to  
505 these calculations, the weight loss when passing from the saprolite to the Bt horizons was around  
506 80-82%, thus the dissolution of 1 kg of saprolite may have originated 180-200 g soil. Although  
507 higher than the average insoluble residue reported for the parent material of Terra Rossa soils in  
508 Mediterranean environment (Yaalon, 1997), these data are compatible with the presence of the

509 marly veins. Assuming an average dissolution rate of  $40 \mu\text{m y}^{-1}$  (i.e. the maximum of the range  
510 reported by Yaalon, 1997) and a content of insoluble residue of 20%, no much less than 700,000  
511 years would have been necessary to form the 5 m soil thickness locally observed on the quarry  
512 scarp. Considering that limestone dissolution was probably much slower during cold and dry glacial  
513 periods (as hypothesized by Priori et al., 2008), the time frame could become even longer.  
514 Both TR and ALI soils keep traces of previous warm, seasonally dry environments, but it is the  
515 difference in parent materials that mainly differentiate present-day properties. The dissolution of  
516 carbonatic rocks in TR maintained a high Ca and Mg concentration and a high pH that favoured the  
517 stability of smectite (Wilson, 1999), while in the ALI soil, on Fe-rich chloritic shales, only traces of  
518 swelling minerals were found. Despite the presence of smectite, the clay CEC was rather low in  
519 both soils, although slightly higher in ALI than in the TR, in agreement with the trend in Si losses  
520 during soil formation. The solubility of Si is almost independent from pH below pH 8.5 (Drees et  
521 al., 1989), a pH value that is not reached in the presence of calcite, but may be overcome when the  
522 more soluble dolomite is present (Bloom, 2000). Dolomite may have therefore induced a higher Si  
523 depletion, favouring the stability of kaolinite in the TR soil, while the acidic environment of the  
524 chloritic shales caused lower Si losses and favoured Al mobilization and precipitation in the  
525 phyllosilicate interlayer. As kaolinite was abundant also in ALI Bt horizons, the higher CEC/clay  
526 ratio is likely also related to a decrease in the stability of the Al polymers in the HIV at the acid pH  
527 of the present day Bt horizons.  
528 Thus, these two hematite-rich soils likely formed under subtropical conditions in some ancient  
529 times. The strong mineralogical weathering and the geochemical data are memories of periods  
530 characterized by hot subtropical or Mediterranean climates, which have very different weathering  
531 and pedogenic regimes compared to present day conditions. In fact, Rellini et al. (2014) state that  
532 kaolinite and hematite formation probably occurred during ancient pedogenetic phases, during the  
533 late Pliocene or the early Pleistocene in the Ligurian Alps.

534

### 535 **5.3 Environmental memories and soil processes**

536 Large areas of the upper Tanaro Valley were never glaciated, and many relict surfaces are preserved  
537 on its slopes. Many geomorphic indicators (tors, blockfields, thick saprolite layers, etc.),  
538 particularly well preserved on hard quartzitic substrates, are often considered to be originated before  
539 the Quaternary, or at least in the early Quaternary (Migoñ and Lidmar Bergström, 2001;  
540 Boelhowers, 2004; Goodfellow, 2007) and confirm that the considered relict surfaces are actually  
541 ancient. Moreover, the high clay content (up to more than 20% clay) characterizing saprolite and  
542 soil layers on hard quartzitic rocks, extremely poor in phyllosilicates and in other weatherable

543 minerals, points to a particularly ancient origin of these materials (Boelhowers, 2004). Most of the  
544 morphologic features are not preserved on more easily weatherable substrates, still the analogous  
545 surface shape and position indicate a similar origin and history and, thus, age, for the soils  
546 developed on weatherable shales and dolomite. As the considered relict surfaces lie on an ideal  
547 plane gently sloping north-eastward, following the river Tanaro downstream, the age of formation is  
548 likely the same for all, even if this hypothesis will remain only speculative until some datings will  
549 be available.

550 On these surfaces, strikingly different soils were developed, well associated with specific parent  
551 materials, at close distance from each other. Each considered soil represents an extreme expression  
552 of some features, each apparently developed under different phytoclimatic regimes.

553 However, these soils have lived through similar environmental conditions likely throughout the  
554 Quaternary (or large parts of it), through the same intense pedogenetic phases during warm  
555 interglacials, interrupted by much longer-lasting cryogenic disturbances during glacial periods,  
556 dominated by a different suite of processes which tended to counteract the development of horizons  
557 occurring during warm periods (Munroe, 2007). These processes, in fact, resulted in a strong  
558 polygenesis of many of the considered relict soils.

559 However, despite the polygenesis and the similar environmental conditions to which all the soils  
560 were subjected, the greatest imprintings were left by different pedogenetic process on each different  
561 parent material. These specific pedogenetic processes were likely active in well characterized  
562 pedogenetic environments, probably only existing during limited periods throughout their history  
563 (Fig. 6). Both mineralogical composition and textural properties of the different parent lithologies  
564 deeply influenced the genesis of these soils, and the preservation of specific pedogenetic features as  
565 well.

566 In particular, soils developed on weatherable dolomites and Fe-rich chloritic shales tend to be  
567 particularly rich in clay and Fe oxi-hydroxides, thus limiting the impact of cold periods through  
568 cryoturbation. It is known, in fact, that either high clay contents or sandy textures reduce the frost  
569 susceptibility of soils, by limiting the possibility of water to migrate along the freezing front and the  
570 formation of ice lenses (Van Vliet-Lanoë, 1998). On less weatherable, sandy textured quartzite, the  
571 fast drainage and the paucity of weatherable minerals and primary phyllosilicates created the best  
572 conditions for podzolization, which apparently has been active for extremely long periods.

573 Macroscopic evidences of cryoturbation are limited to the development of localized small soil  
574 wedge-casts, likely because of the sandy texture. On quartzitic substrates including also small  
575 quantities of weatherable silicates (pyroxenes, feldspars, amphiboles, biotite), clay mineral  
576 formation was favoured during warm interglacials, and memories of alternating warm periods

577 characterized by clay lessivage and colder ones characterized by intense podzolization are preserved  
578 in the Bt and Bsm horizons respectively, and in their micromorphology. The higher silt and clay  
579 content in the ORT and PLC compared with the ALB soils favoured a higher frost susceptibility, as  
580 shown by the cryoturbated, dense horizons, which were likely located between the permafrost table  
581 and the active layer. Soils formed on coarse and resistant to weathering quartzitic conglomerates  
582 were subjected to intense podzolization, which led to the formation of ortstein horizons, and to  
583 hydromorphism during particularly humid periods, evidenced by the presence of placic horizons  
584 and the abundant lepidocrocite.

585

## 586 **6 Conclusion**

587 Soils preserved on relict surfaces in the south-western Italian Alps show signs of extremely  
588 different pedogenic trends, each dominating on different lithologies, thanks to different  
589 mineralogical and textural properties that induced to different weathering regimes. These soils, even  
590 if dominated by single main pedogenic processes, such as podzolization, clay illuviation or  
591 rubification, are characterized by strong polygenesis, with different pedogenic processes probably  
592 characterizing different periods because of different climatic conditions. Even if memories of cold  
593 glacial periods (i.e., cryoturbation) and of warm interglacial (i.e., clay illuviation and rubification)  
594 coexist, the associations of pedogenetic phases with precise Quaternary periods is complicated, as it  
595 is not possible at the moment to hypothesize a zero-point for the initiation of pedogenesis on the  
596 considered relict surfaces, which would significantly contribute to the history of pedogenesis and of  
597 paleo-environments during the Quaternary on the Alps, which is largely unknown. However, this  
598 study represents one of the first characterization of polygenetic Quaternary paleosols on the Alpine  
599 range.

600

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603

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## Figure Captions

Fig. 1: The study area in the Western Italian Alps (black circle). A few relict surfaces are evidenced  
 with a white line; the geographical coordinates of the sampling sites are reported in table 1.

Fig. 2: The studied soil profiles. From left to right: ALB (A), ORT (B), PLC (C), TR (D), ALI (E).

Fig. 3: X-ray spectra of air-dried (AD), ethylene glycol solvated (EG) and heated oriented mounts  
 of the E and Bs-old horizons of the ALB soil (A), of 2Bsm of the ORT and of the 2Bsm1-2Bsm2 of  
 PLC soils (B).

774 Fig. 4: X-ray spectra of orientated clay mounts from the TR and ALI 2Bt2 horizons after ethylene  
775 glycol solvation (EG) and heating to 330° and 550°.

776 Fig. 5: Micromorphological features of selected horizons in ORT (4 top images, from left to right  
777 2E(x), 2Eh(x), 2Bsm, 2Bt2 horizons) and PLC (bottom 2 images, 2E(x) and 2Bsm1+2Bsm2  
778 horizons): a) leached albic materials; b) localized Fe and organic matter impregnation of silty  
779 matrix; c) silt infillings in cracks cutting through both the groundmass and the coarse fragments; d)  
780 remnants of localized clay coatings in pores; e) amorphous Fe and Al coatings with or without  
781 monomorphic organic matter characteristic of spodic materials; f) clayey pedorelicts, remnants of  
782 ancient disrupted clay coatings; g) laminated silt and fine sand coatings on pore walls; h) well  
783 developed limpid crescentic clay coatings and infillings; i) laminated sand and silt accumulations; j)  
784 laminar cracks; k) Fe cementation of the placic horizon.

785 Fig. 6: graphical summary of the main paleo-environmental memories imprinted in the considered  
786 relicts soils.

Table 1: Site location, main environmental parameters and soil classification.

Profile code	Location	Coordinates	Substrate / parent material	Geological formation	Slope angle	Elevation (m a.s.l.)	Forest vegetation	Classification (FAO, 2014)
ALB	Toria - Pian del Pino	44°08'51.29"; 7°47'37.81"	Quartzite	Quarziti di Ponte di Nava	1	1595	<i>Pinus uncinata</i> Mill.	Albic Dystric Arenosol (Protospodic)
ORT	Pornassino - Pian degli Uccelli	44°08'18.17"; 7°48'32.40"	Quartzite - Andesite conglomerate	Porfidi di Osiglia	2	1395	<i>Pinus sylvestris</i> L.	Ortsteinic Albic Skeletic Podzol (Loamic, Hyperspodic)
PLC	Colma di Casotto	44°13'09.01"; 7°56'56.67"	Quartzitic conglomerate	Porfiroidi del Melogno	5	1445	<i>Fagus sylvatica</i> L.	Albic Ortsteinic Skeletic Podzol (Loamic Placic)
TR	Bagnasco	44°14'42.82"; 8°00'54.98"	Dolomite	Dolomie di San Pietro dei Monti	5	950	<i>Ostrya carpinifolia</i> Scop.	Rhodic Luvisol (Clayic, Cutanic)
ALI	Priola	44°17'00.72"; 8°02'31.06"	Chlorite-rich shale	Formazione di Murialdo - Scisti di Viola	10	680	<i>Castanea sativa</i> Mill. - <i>Pinus sylvestris</i> L.	Rhodic Alisol (Clayic, Hyperallic)

Table 2: main morphological properties of selected soil horizons. The set of described properties depend on the type of soil and horizon and, where not specified, the classification follows the guidelines reported by FAO 2006.

Profile	Horizon	Lower boundary <sup>1</sup>	Colours (mottle colors, %) <sup>2</sup>	Structure	Consistence	Rock Fragments	Siltcaps	Frost wedges	Clay cutans	Mn-Fe cutans
		cm	Munsell, humid	Shape <sup>3</sup> , dimension-degree	Class <sup>4</sup>	%, weathering degree <sup>5</sup>	% stones covered, thickness (mm)	Width*depth (cm)	Class of abundance <sup>6</sup>	Class of abundance <sup>6</sup>
ALB	Oi+Oe+Oa	11		M		0				
	AE1	21/23	10YR 4/2	SG	L	20,LA				
	AE2	35	10YR 5/2	SB, ME-WE	L	20,LA		10*50		
	2EA	50	10YR 6/2	SB, ME-WE	L	40,AA		10*50		
	2E	100	10YR 7/1	SB, ME-WE	L	80,AA				
	2EB(s)	210+	7.5YR 6/3	SB, CO-MO	FR	70,AA				
	Bs-old	n.d.	7.5YR7/8 10YR 5/4	SB, CO-ST	CR	80,LA				
	Bs-young	n.d.	7.5YR 5/6	SB, ME-WE	CR	80,LA				
ORT	Oi+Oa	10		M	L					
	E	45/60	10YR 5/3	SG	FR	50,LA	5,0.3			
	2E(x)	80/95	10YR 5/3 10YR 6/3 10YR 7/4	SB, ME-ST	CP	20,AA	10,0.3			
	2Eh(x)	115/140	10YR 7/4 10YR 5/3	PL, VC-ST	CP	20,AA	10,0.3			
	2Eh	120/140*	10YR 4/2	SG	FR	20,AA				
	2Btm(s)	140*	5YR 5/6	PL, VC-ST	C	5,AA			F	
	2Bsm	180/200	7.5YR 5/6	PL, VC-WE	CC	30,AA				
	2Btsm	220/230	5YR 5/8	SB, CO-WE	CC	30,AA			C	
	2Bshsm	270	7.5YR 4/6	SB, CO-WE	CC	50,LA				

			7.5YR 3/3							
	R/Cm/Cr	(Cm) 320	7.5YR 7/3	Massive	C	50,AA				
		(Cr) 350	GLE Y1-8/5GY (7.5YR 6/8, 10%)	PL-R	CP	AA				
PLC	Oi+Oa	4		M						
	A	14/4	2.5Y 3/1	SB, ME-MO, GR, FI-MO	FR	50,LA				
	AE	26	2.5Y 3/2	SB, ME-MO, GR, FI-MO	L	50,LA				
	2EA	44/42	2.5Y 6/2	SB, ME-MO, GR, FI-MO	FR	50,AA	100,3			
	2E(x)	62/67	10YR 10/2 (GLE Y1 7/3, 10%)		CP	50,AA	100,10			
	2Bsm1 (placic)	62.5/67.5	7.5YR 2/2 7.5YR 4/6		CC					
	2Bsm2	69/77	7.5YR 5/6		C	80,LA				
	2Bsm3	103+	10YR 6/8		C	80,LA				
TR	A	2/10	5YR 3/3	GR, CO-ST	L	20,LA				
	BA	53	5YR 4/6	AB, FI-ST	FR	0			F	
	Bt1	120	2.5YR 4/8	AB, VC-MO AB, FI-ST	FR	0			D	C
	Bt2	151/160	2.5YR 4/8	AB, CO-ST SN, ME-ST	FR	2,MA			A	F
	BC	170	2.5YR 4/8 10YR 5/2	PL, CO-WE	CP	20,MA			F	
	Cr	180+				99,MA				
ALI	A/Oe	1/5		GR, FI-ST	L	0				
	A	7	7.5YR 4/4	GR, VF-MO	L	10,AA				
	AB	32/40	5YR 5/8	GR, FI-MO, SB, ME-MO	FR	10,AA				

	2Bt1	50/55	2.5YR 4/6	AB, FI-ST	FR	20,AA			F	F
	2Bt2	125+	2.5YR 4/6	AB, VC-ST	M	3,AA			D	C
	2BC		2.5YR 5/8	PL-R	M	90,MA			A	

<sup>1</sup> discontinuous horizons are indicated with \*;

<sup>2</sup> all the colours detected in the horizon; the colours in brackets represent mottles caused by waterlogging;

<sup>3</sup> Shape: M: matted; SG: single grain; SB: subangular blocky; PL: platy; GR: biogenic granular aggregates; AB: blocky polyhedral; PL-R: platy, weathered rock structure. Dimension: VF: very fine; FI: fine; ME: medium; CO: coarse; VC: very coarse. Degree: VE: weak; MO: moderate; ST: strong.

<sup>4</sup> Consistence: L: loose; FR: friable; CR: crumby; CP: compacted; C: weakly cemented; CC: strongly cemented;

<sup>5</sup> Rock fragments weathering degree: LA: fresh; AA: moderately weathered; MA: strongly weathered, soft.

<sup>6</sup> Abundance class: F: few; C: common; A: abundant; D: dominant

Table 3: main chemical properties of the mineral soil horizons

Name	Horizon	pH H <sub>2</sub> O	pH NaF	CaCO <sub>3</sub>	C org	CEC <sup>1</sup>	BS <sup>1</sup>	Sand	Silt	Clay
				g kg <sup>-1</sup>	g kg <sup>-1</sup>	cmol <sub>c</sub> kg <sup>-1</sup>	%	%	%	%
ALB	AE1	3.4	7.5		34.1			76.3	13.5	10.2
	AE2	3.9	7.5		5.5					
	2EA	4.3	7.5		1.5			79.7	12.8	7.5
	2E	4.8	7.5		0.0			80.1	14.0	5.9
	2EB(s)	4.3	7.5		2.1			77.3	14.9	7.9
	Bs-old	5.1	9.0					48.5	32.9	18.6
	Bs-young	5.1	12.5		21.2			63.7	16.1	20.2
ORT	2E(x)	4.8	7.8		1.0			79.3	11.9	8.9
	2Eh(x)	4.4	8.0		4.3			74.6	13.7	11.7
	2Eh	4.5	7.5		2.4					
	2Btm(s)	5.0	8.8		1.3			78.6	5.1	16.3
	2Bsm	5.2	11.0		3.3			74.7	12.9	12.4
	2Btsm	5.2	10.0		2.3			65.4	11.6	23.0
	2Bshm	5.0	11.8		3.8			66.2	14.4	19.4
PLC	A	3.8	7.5		39.1			64.0	18.4	17.6
	AE	3.9	7.5		24.1			66.0	16.0	18.0
	2EA	3.9	7.5		6.3			64.3	23.4	12.3
	2E(x)	4.3	7.5		2.9			67.0	23.9	9.1
	2Bsm1+2Bsm2	4.6	8.5		2.2			69.5	22.3	8.2
	2Bsm3	4.7	8.2		0.9			57.4	33.9	8.7
TR	A	7.0		3.1	30.4	31.5	86.5	10.3	24.6	65.1
	BA	7.1		2.5	9.5	25.8	84.3	16.7	22.4	60.8
	Bt1	7.3		1.6	4.0	19.7	94.4	8.4	18.2	73.5
	Bt2	7.4		3.6		24.4	100.0	16.4	15.3	68.3
	Cr	8.1		104.9		7.6	100.0	31.6	32.2	36.1
ALI	AB	4.4	8.3		10.1	31.0	2.8	27.2	29.2	43.6
	2Bt1	4.7	8.5		4.4	30.7	4.3	11.5	35.6	52.9
	2Bt2	4.9	8.5		1.4	30.4	7.2	10.9	32.4	56.7
	2CB	4.7	8.3		2.2	15.6	6.4	43.3	25.8	31.0

<sup>1</sup>CEC: Cation Exchange Capacity, BS: base saturation

Table 4: Fe, Al and Si total contents and fractionation

Profile	Horizon	Fe <sub>o</sub>	Al <sub>o</sub>	ISP	Fe <sub>d</sub>	Fe <sub>o</sub> /Fe <sub>d</sub>	Fe <sub>t</sub>	Al <sub>t</sub>	Si <sub>t</sub>	Fe <sub>d</sub> /Fe <sub>t</sub>
		g kg <sup>-1</sup>	g kg <sup>-1</sup>	%	g kg <sup>-1</sup>		g kg <sup>-1</sup>	g kg <sup>-1</sup>	g kg <sup>-1</sup>	
ALB	AE1	0.27	0.27	0.04	1.04	0.26	2.4	11.9	412.5	0.43
	AE2	0.09	0.11	0.02	0.44	0.21	2.2	11.8	435.1	0.20
	2EA	0.04	0.09	0.01	0.36	0.11	1.8	10.3	447.1	0.20
	2E	0.03	0.07	0.01	0.18	0.15	3.3	7.5	450.6	0.05
	2EB(s)	0.08	0.21	0.03	0.12	0.68	3.0	21.8	436.7	0.04
	Bs-old	1.67	1.46	0.23	3.61	0.46				
	Bs-young	5.52	5.63	0.84	8.09	0.68	15.5	41.7	403.9	0.52
	Parent rock						6.3	27.4	409.9	
ORT	2E(x)	0.53	0.42	0.07	1.04	0.51	4.3	15.0	439.4	0.24
	2Eh(x)	1.17	0.76	0.13	3.36	0.35	7.1	21.3	426.8	0.47
	2Eh	1.04	0.68	0.12	2.28	0.46	5.2	17.0	433.9	0.44
	2Btm(s)	0.86	1.29	0.17	6.05	0.14	22.9	77.8	344.7	0.26
	2Bsm	1.45	2.97	0.37	6.78	0.21	93.9	126.2	250.9	0.07
	2Btsm	1.04	2.90	0.34	8.67	0.12	15.7	34.2	396.4	0.55
	2Bshm	2.02	2.40	0.34	5.50	0.37	12.4	33.4	405.4	0.44
	CBm	0.14	0.18	0.03	0.46	0.30	3.3	23.2	438.1	0.14
	Cr	0.23	0.28	0.04	1.15	0.20	22.4	105.6	316.6	0.05
	Parent rock						13.5	22.7	415.6	
PLC	A	1.64	2.12	0.29	4.16	0.39	19.1	37.8	348.1	0.22
	AE	0.95	1.31	0.18	2.40	0.40	16.0	34.7	375.5	0.15
	2EA	0.43	0.68	0.09	1.06	0.40	13.5	28.4	398.5	0.08
	2E(x)	0.20	0.50	0.06	0.65	0.31	13.3	27.6	400.7	0.05
	2Bsm1+2Bsm2	3.17	0.76	0.23	4.57	0.69	20.7	36.9	385.9	0.22
	2Bsm3	2.98	0.77	0.23	4.26	0.70	18.2	37.4	388.9	0.23
TR	A	1.50	2.24	0.30	37.18	0.04	75.9	100.8	195.1	0.49
	BA	1.34	1.59	0.23	42.30	0.03	91.3	103.9	207.8	0.46
	Bt1	1.31	1.58	0.22	43.33	0.03	83.0	110.3	201.0	0.52
	Bt2	1.42	1.35	0.21	44.56	0.03	77.7	89.9	180.9	0.57
	Cr	0.17	0.66	0.07	10.68	0.02	18.6	21.8	45.6	0.57
ALI	AB	1.44	1.44	0.22	34.73	0.04	61.2	115.6	260.7	0.57
	2Bt1	2.03	1.42	0.24	37.64	0.05	60.9	94.6	282.2	0.62
	2Bt2	1.92	1.21	0.22	34.58	0.06	53.0	120.2	269.8	0.65
	2CB	1.90	0.90	0.19		0.05	28.2	122.8	277.5	
	Parent rock						30.1	126.8	295.0	



Table 5: Micromorphological features of selected soil horizons.

Profile	Horizon	Coarse fragments	Primary voids	Secondary voids	Cf-related distribution	b-fabric	Clay coatings	Amorphous OM-metal coatings	Organic matter coatings	Silt accumulation features	Pedorelicts
		%	(%, type)	(%, type)			%	%	%	(%, location)	(%, type)
ORT	2E(x)	70	2, vughs	1, cracks	Close porphyric	Striated	0.2	0.2	1	1	0.1
	2Eh(x)	60	2, vughs	2, cracks	Close porphyric		0.1	0.3	1	2	0.1
	2Bsm	40	30, compound packing voids	5, cracks	Close porphyric		0.2	8	0.1	2	1
	2Btsm	40	7, vughs, compound packing voids	3, cracks	Close porphyric / Chitonic	Striated	6.5	1	0.4	2	0.2
PLC	2E(x)	40	15, planes	5, cracks	Close porphyric	Striated	0.5	0.1	0.2	2	0.2
	2Bsm1	40	5, cracks		Double-spaced - open porphyric	Undifferentiated	0.1		0.2	1.5	0.1
	2Bsm2	40	30, compound packing voids		Gefuric			2	0.2		0.2

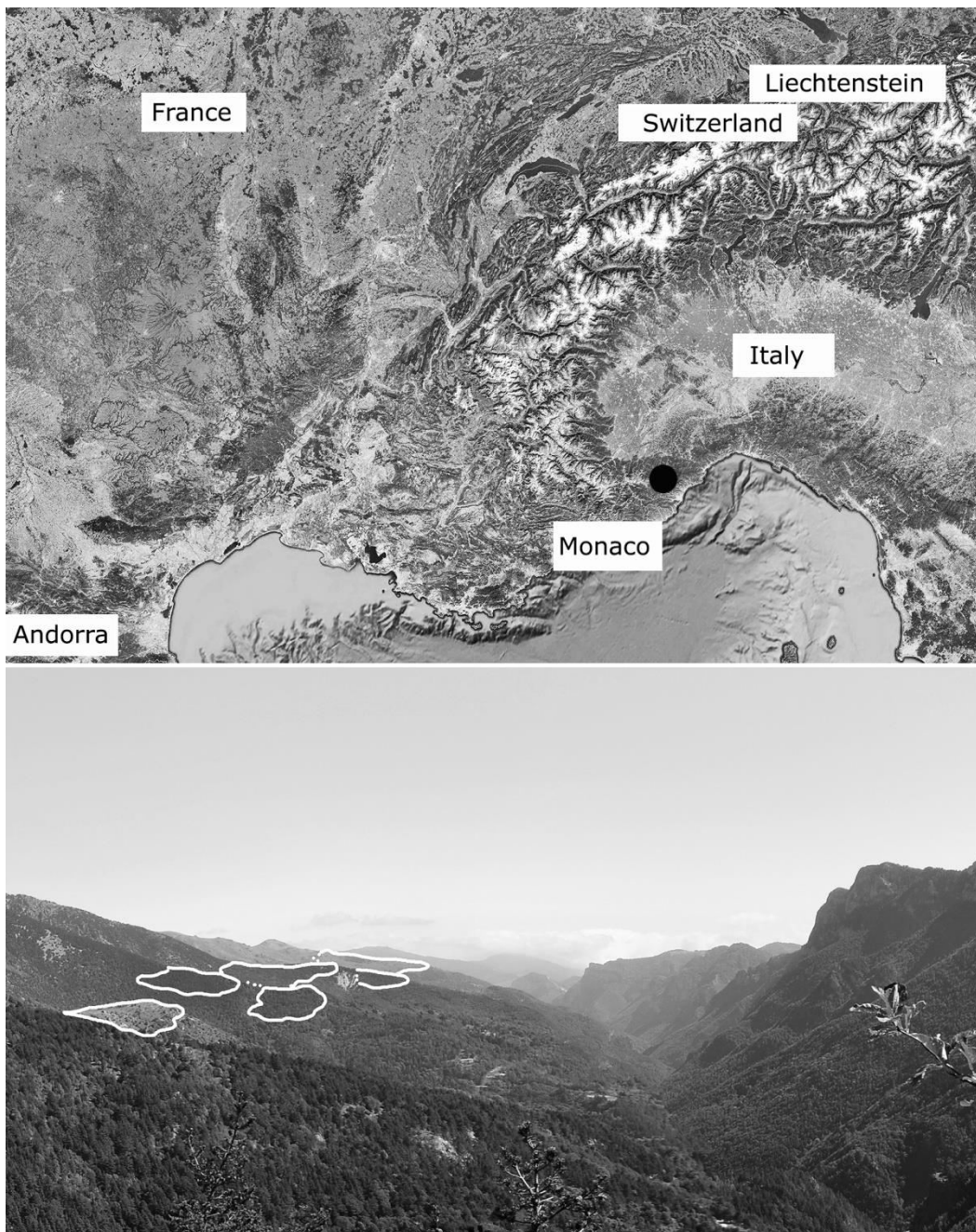


Fig. 1: The study area in the Western Italian Alps (black circle). A few relict surfaces are evidenced with a white line; the geographical coordinates of the sampling sites are reported in table 1.



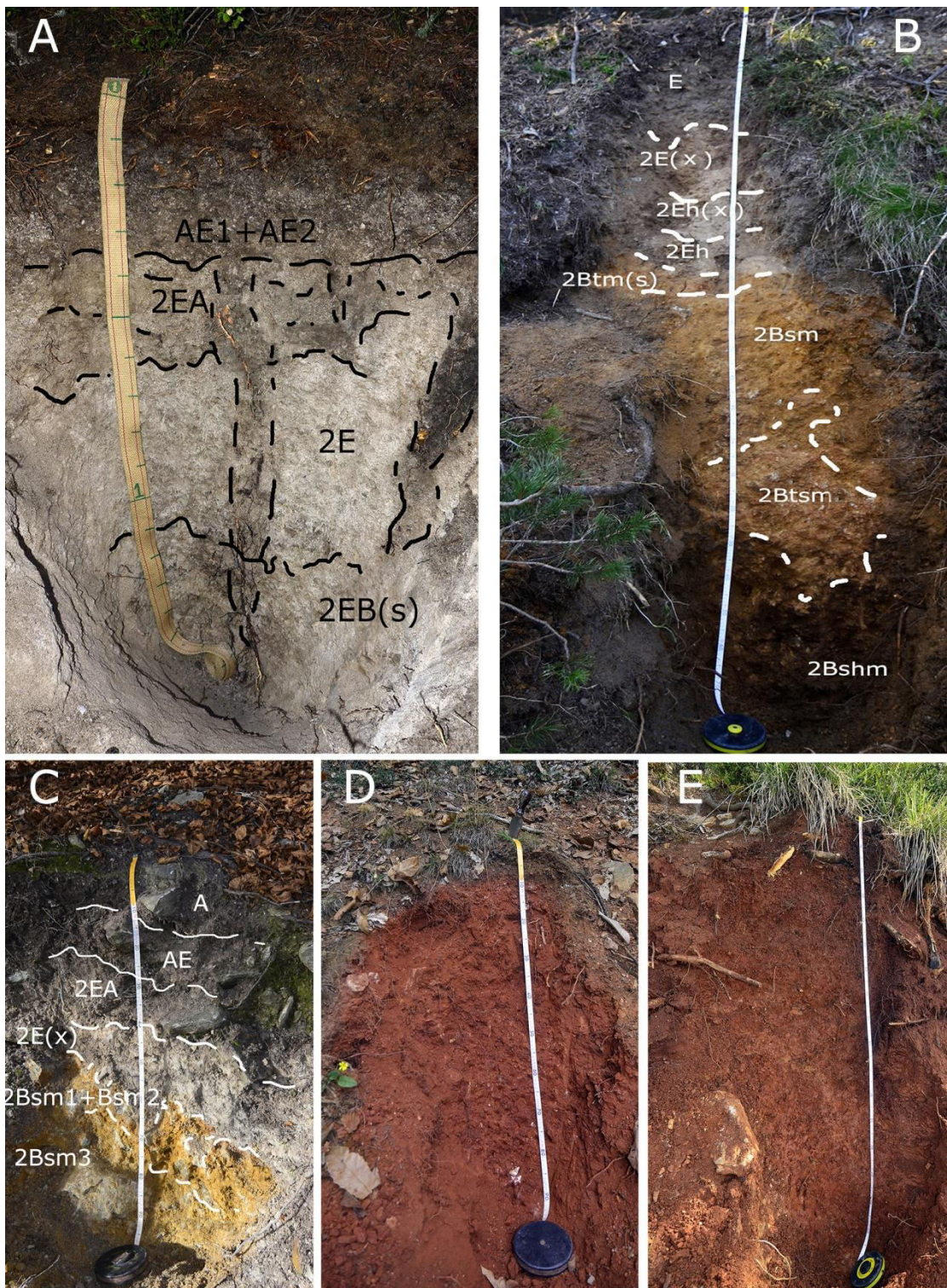


Fig. 2: The studied soil profiles. From left to right: ALB (A), ORT (B), PLC (C), TR (D), ALI (E).

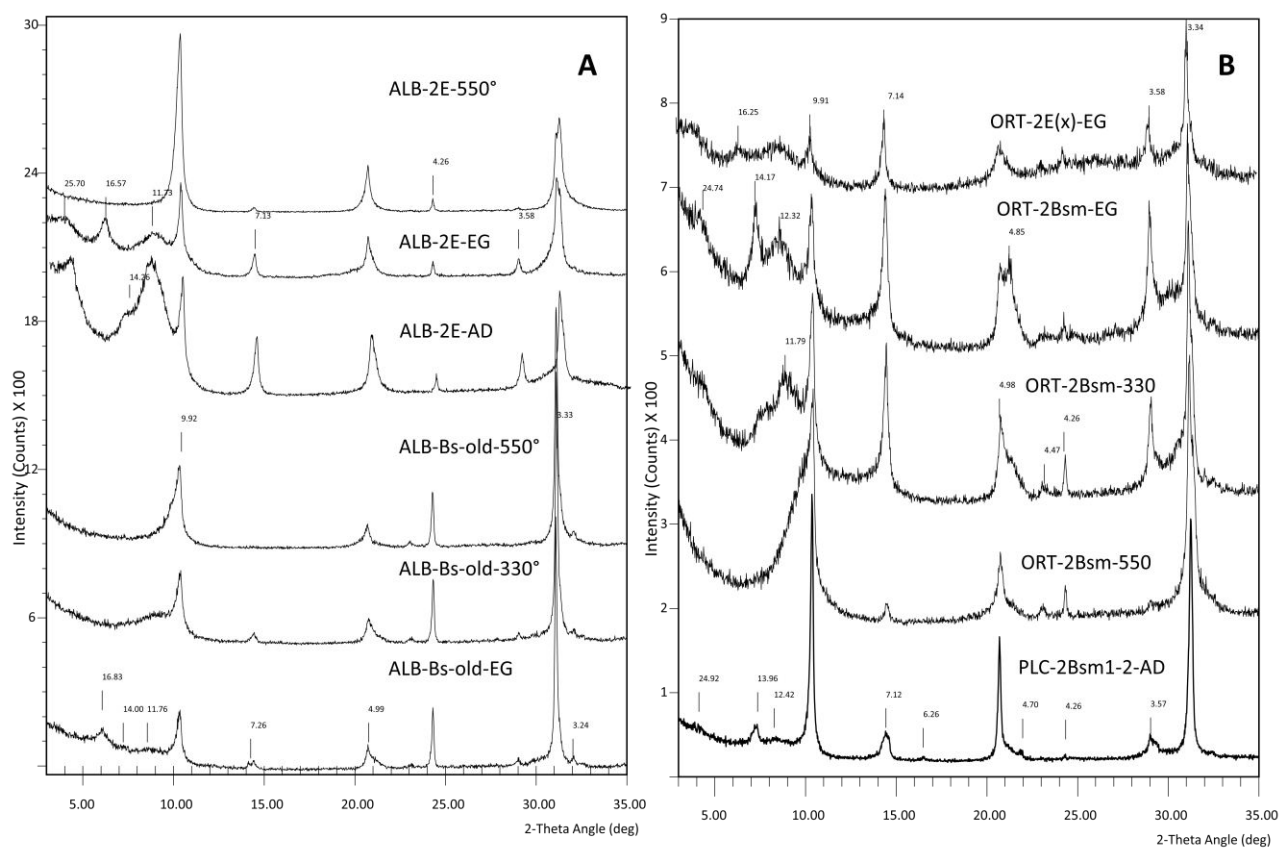


Fig. 3: X-ray spectra of air-dried (AD), ethylene glycol solvated (EG) and heated oriented mounts of the E and Bs-old horizons of the ALB soil (A), of 2Bsm of the ORT and of the 2Bsm1-2Bsm2 of PLC soils (B).



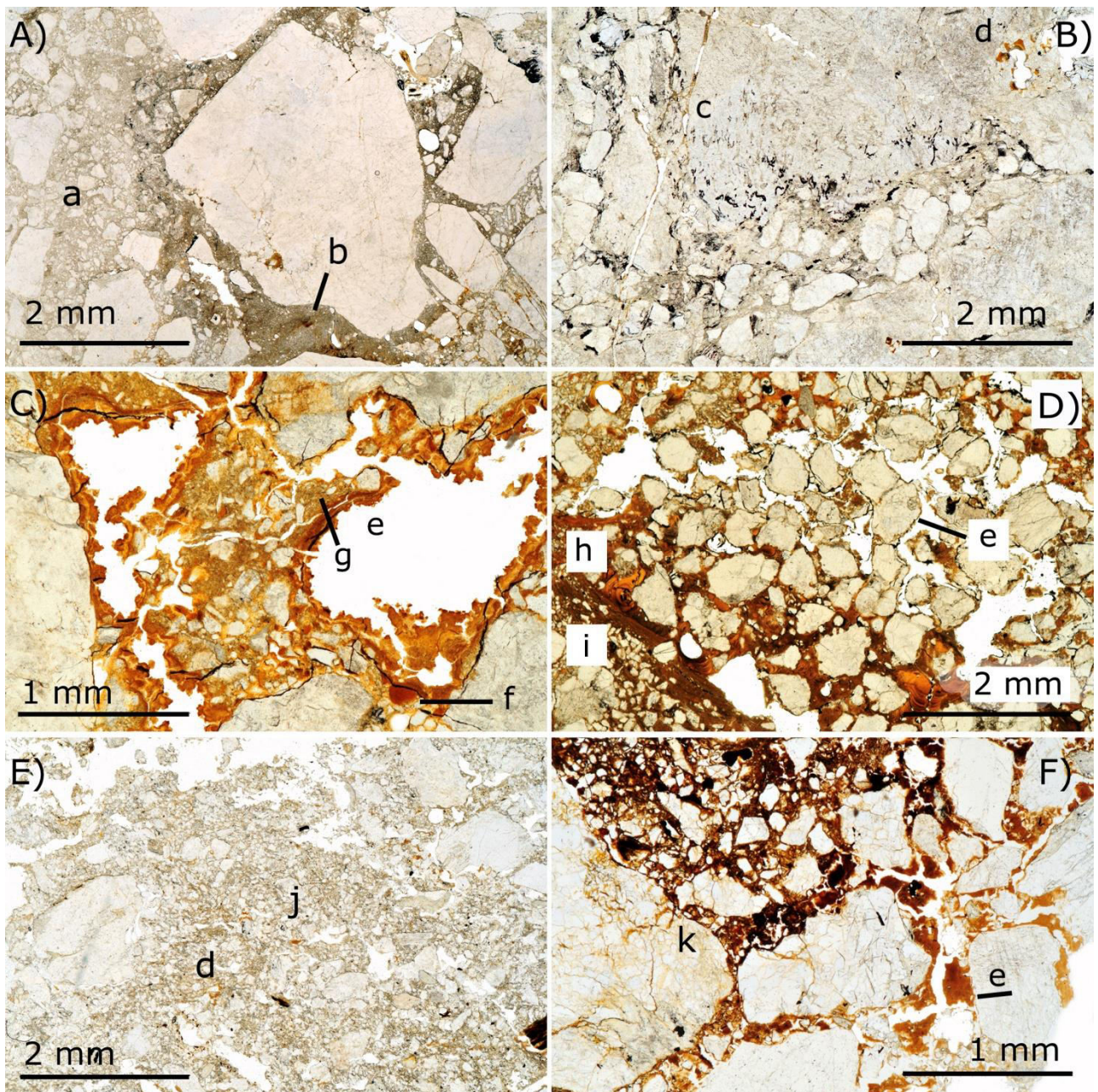


Fig. 4: Micromorphological features of selected horizons in ORT (fig. 4A, 4B, 4C, 4D, corresponding to 2E(x), 2Eh(x), 2Bsm, 2Btsm horizons respectively) and PLC (fig. 4E, 4F, corresponding to 2E(x) and 2Bsm1+2Bsm2 horizons). Some micromorphological features are visible: a) leached albic materials; b) localized Fe and organic matter impregnation of silty matrix; c) silt infillings in cracks cutting through both the groundmass and the coarse fragments; d) remnants of localized clay coatings in pores; e) amorphous Fe and Al coatings with or without monomorphic organic matter characteristic of spodic materials; f) clayey pedorelicts, remnants of ancient disrupted clay coatings; g) laminated silt and fine sand coatings on pore walls; h) well developed limpid crescentic clay coatings and infillings; i) laminated sand and silt accumulations; j) laminar cracks; k) Fe cementation of the placic horizon.

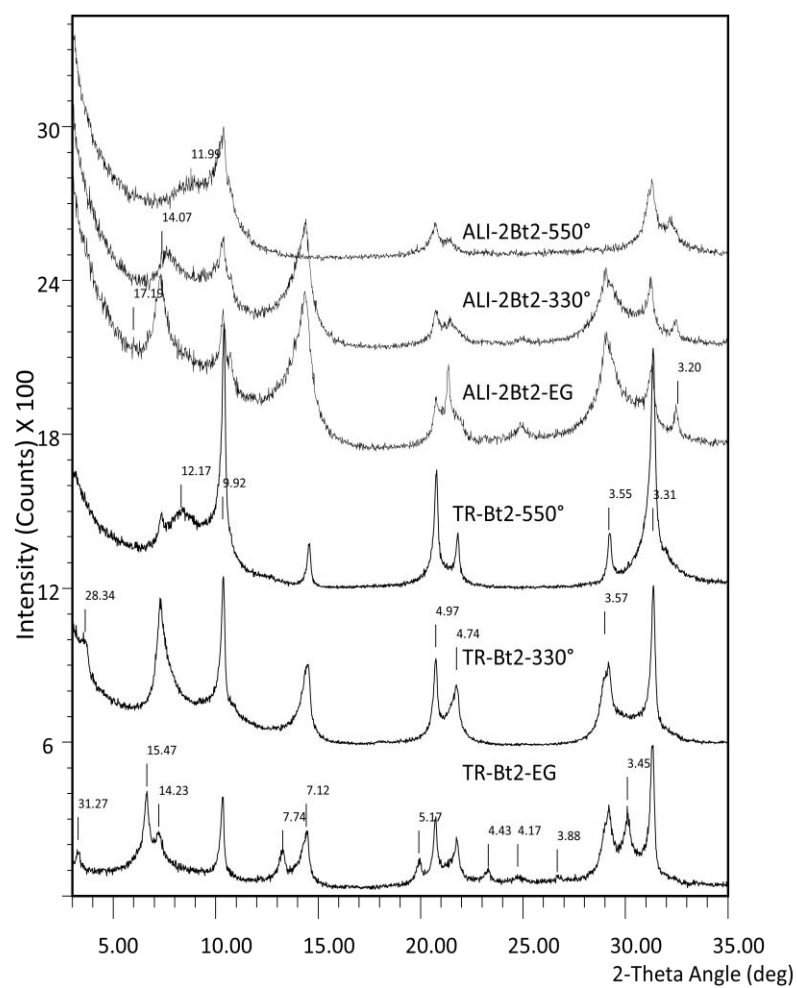


Fig. 5: X-ray spectra of orientated clay mounts from the TR and ALI 2Bt2 horizons after ethylene glycol solvation (EG) and heating to 330° and 550°.

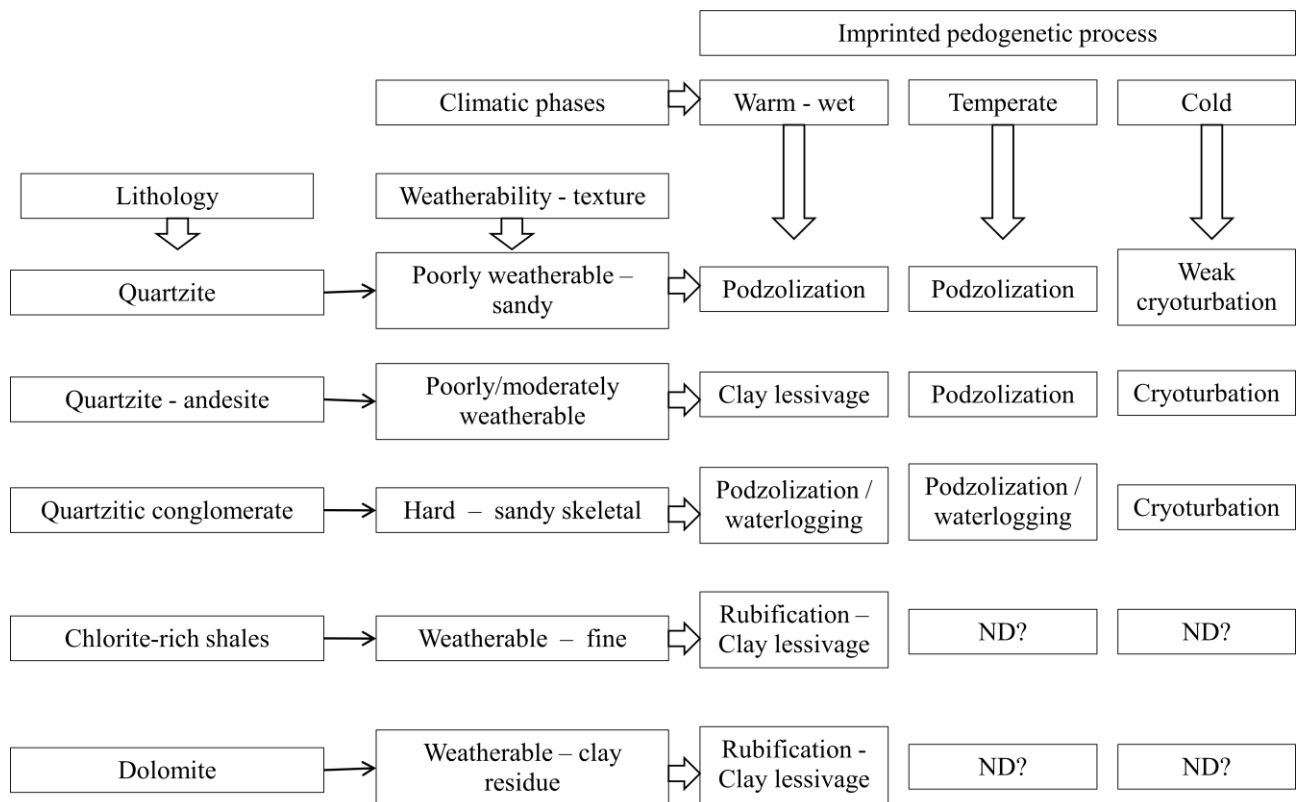


Fig. 6: graphical summary of the main paleo-environmental memories imprinted in the considered relicts soils.