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Bulk and clay mineral composition indicate origin of terra rossa soils in Western Herzegovina

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ABSTRACT

The B horizons of terra rossa soils developed on three different carbonate lithologies having variable insoluble residue contents were studied in Western Herzegovina. Comparison of their composition and properties illustrates to what extent the mineral, (especially clay mineral assemblage) and particle size distribution of those horizons and the insoluble residue of the underlying carbonate rocks can be used as indicators of the polygenetic nature of terra rossa in this region. Terra rossa B horizons have characteristic red colours, neutral to slightly acid pH, high base saturation with calcium as the predominant cation and high CIA (Chemical Index of Alteration). The CIA values obtained are generally in accordance with mineral composition and particle size distribution of the analysed B horizons. The predominant clay mineral phases in B horizons and related insoluble residues match. Kaolinite is the predominant clay mineral phase in the B horizons overlying carbonate rocks containing low amounts of insoluble residue, while smectite predominates in calcarenites areas with a high insoluble residue content. However, the presence of plagioclase, gibbsite, chlorite-vermiculite mixed layer mineral and vermiculite in B horizons overlying carbonate rocks containing low amounts of insoluble residue support a polygenetic origin for the terra rossa. In contrast, terra rossa formed on calcarenites containing high amounts of insoluble residue might have formed almost exclusively from the parent carbonate rock although some influence of external materials (e.g. gibbsite) cannot be excluded. This investigation shows that in Western Herzegovina, an area with no important aeolian input, the content and mineral composition of carbonate rock insoluble residue plays a major role in terra rossa composition. We can tentatively conclude that the lower the insoluble residue content of the parent materials, the greater is the expectation of a more polygenetic origin for the terra rossa.

Keywords: terra rossa, B horizons, parent materials, (clay) mineralogy, Western Herzegovina

1. INTRODUCTION

Terra rossa is a reddish clayey to silty/clayey soil developed over limestones and dolomites and is especially widespread in the Mediterranean region. A diagnostic feature of terra rossa is a bright red colour originating from rubification, a pedogenic process in which preferential formation of haematite over goethite takes place. Due to the underlying highly permeable carbonate rocks, terra rossa is well aggregated and drained, has a slightly alkaline to neutral pH and a base complex almost completely saturated by calcium and/or magnesium. Terra rossa is formed as a result of (1) decalcification, (2) rubification and (3) bisiallitisation and/or monosiallitisation (DURN et al., 1999). Terra rossa is classified as Alfisol (Haploxeralf or Rhodoxeralf), Ultisol, Inceptisol (Xerochrept) and Mollisol (Argixeroll or Haploxeroll) in Soil Taxonomy (SOIL SURVEY STAFF, 1975). According to the FAO system (FAO, 1974) terra rossa is recognised as Luvisol (Chromic Luvisol), Phaeozem (Haplic Phaeozem or Luvic Phaeozem) and Cambisol. In other classification systems using the Mediterranean climate as the major soil differentiating criterion, the term terra rossa is used to describe the soil subclass ‘‘Modal Fersiallitic Red soil’’ when situated on limestones (DUCHAUFOUR,1982). Several national soil classifications (e.g. Croatia, Italy, Israel) retain the term ‘‘terra rossa’’ for limestone-derived red soils. The Croatian classification puts terra rossa in the class of Cambic soils (ŠKORIĆ, 1985). Although different authors have considered terra rossa to be a soil, vetusol, relict soil (non-buried-palaeosol), palaeosol or pedosedimentary complex, most scientists consider terra rossa a polygenetic relict soil, formed during the Tertiary and/or hot and humid periods of the Quaternary (e.g. ALTAY, 1997; BRONGER & BRUHN-LOBIN, 1997; DURN et al., 1999).

The nature and relationship of terra rossa to the underlying carbonates is a long-standing problem which has resulted in different opinions with respect to the parent material and origin of terra rossa. The most widely accepted theory is that terra rossa has developed from the insoluble residue of carbonate rocks (TUĆAN, 1912; KIŠPATIĆ, 1912; KUBIËNA, 1953; MARIĆ, 1964; ĆIRIĆ & ALEKSANDROVIĆ, 1959; PLASTER & SHERWOOD, 1971; ŠKORIĆ, 1979, 1987; BRONGER et al., 1983; MORESI & MONGELLI, 1988). Other authors have emphasised that the addition of various external materials (e.g. afigeolian dust, volcanic debris, clastic sedimentary particles, bauxite particles) might have masked the influence of limestone and dolomite residues as the primary parent material of terra rossa (BALAGH & RUNGE, 1970; YAALON & GANOR, 1973; ŠINKOVEC, 1974; OLSON et al., 1980; MACLEOD, 1980; JACKSON et al., 1982; DANIN et al., 1983; RAPP, 1984; JAHN et al., 1991; NIHLEN & OLSSON, 1995; ALTAY, 1997; DURN et al., 1999, DURN, 2003; DURN et al., 2007; MUHS et. al., 2012). DURN et al. (2007) concluded that in some isolated karst terrains, terra rossa may have formed exclusively from the insoluble residue of limestone and dolomite, but it most commonly comprises a variety of external materials that were carried to the carbonate terrain by various transport mechanisms. Although it is difficult to estimate accurately the proportions of external materials embedded in the terra rossa soils, DURN et al. (2007) estimated that in such a non-isolated karst terrain (such as Istria) their contribution might have been up to 50%. MUHS et al. (2012) investigated the origin of terra rossa soils overlying very pure carbonate substrates of Quaternary age in Bermuda. Based on the detailed geochemical analyses of trace elements that are immobile in the soil-forming environment, they discovered that terra rossa soils have been influenced by a combination of LRT dust from Africa and local volcanic bedrock. They also concluded that soils on islands in a very broad latitudinal belt of the western Atlantic margin have been influenced by African LRT dust inputs over much of the past 500 ka.

BOERO & SCHWERTMANN (1989) suggested that terra rossa is formed in a specific pedo-environment which is characterised by an association of Mediterranean climate, high internal drainage due to the karstic nature of a hard limestone and neutral pH conditions. They also concluded that it is of little relevance for the process of rubification whether the primary Fe sources are autochthonous or allochthonous as long as the general pedoenvironment remains essentially suitable for the formation of terra rossa. Based on new field and petrographic evidence, MERINO & BANERJEE (2008) proposed a new theory of terra rossa formation, by replacement of limestone by authigenic clay at a narrow reaction front and explained why terra rossa and karst are associated. BANERJEE & MERINO (2011) successfully model the new terra rossa–forming process quantitatively and compared model-calculated rates of formation of terra rossa to rates obtained palaeomagnetically.

The term reddish soils refers to all soils of different shades of red colour developed on carbonate sediments. Reddish soils include various types of soils in different phases of soil development: from youngest reddish or brownish calcomelanosols, through terra rossa and calcocambisols to luvisols, which are genetically considered the oldest and most developed soils on carbonate sediments. The basic criterion for distinguishing reddish soils from other soils is the red colour of the diagnostic horizon. Chemical and physical properties of soils in Western Herzegovina, especially reddish soils were subject to investigation by several researchers (BUKOVAC, 1950; RESULOVIĆ et al., 1963; KURTOVIĆ, 1971; 1979). BABIĆ (1989) concluded that the main clay minerals in terra rossa developed on flysch in descending order are smectite, kaolinite and micaceous minerals respectively. TVICA (2008) found high base saturation in terra rossa soils from Herzegovina with calcium being the predominant cation. Terra rossa is the most frequent soil type in Western Herzegovina (Bosnia and Herzegovina). Among 111.944 ha of reddish soils, terra rossa covers 44.554 ha (39,80%) (Fig. 1). According to KURTOVIĆ (1973; 1979), terra rossa has developed on different types of carbonate rocks (e.g. rudist limestone, brecciated limestone, calcarenite). Therefore, terra rossa soils in Western Herzegovina represent promising material to investigate the influence of the underlying carbonates on the mineral composition and grain-size distribution of terra rossa.

The physical, chemical and mineralogical features of the B horizons of terra rossa soils developed on three different carbonate lithologies have been investigated here. The aim of this research was to compare the mineral composition of bulk samples and clay fraction of terra rossa B horizons with the insoluble residues of the underlying carbonate lithologies. This should also show the influence of the insoluble residue content and its grain size on the B horizons of terra rossa for different carbonate lithologies. Finally, this work should show to what extent the mineral, (especially clay mineral assemblage) and particle size distribution of the B horizons and insoluble residue of the underlying carbonate rocks can be used as indicators of the polygenetic nature of terra rossa in Western Herzegovina.

2. MATERIALS AND METHODS

2.1. Study area

The research area is located in the Western Herzegovina region of Bosnia and Herzegovina. This region completely lies within the Dinarides mountains, which are mostly composed of Mesozoic platform carbonates deposited on the Adriatic Carbonate Platform (AdCP) (for details see: DRAGIČEVIĆ

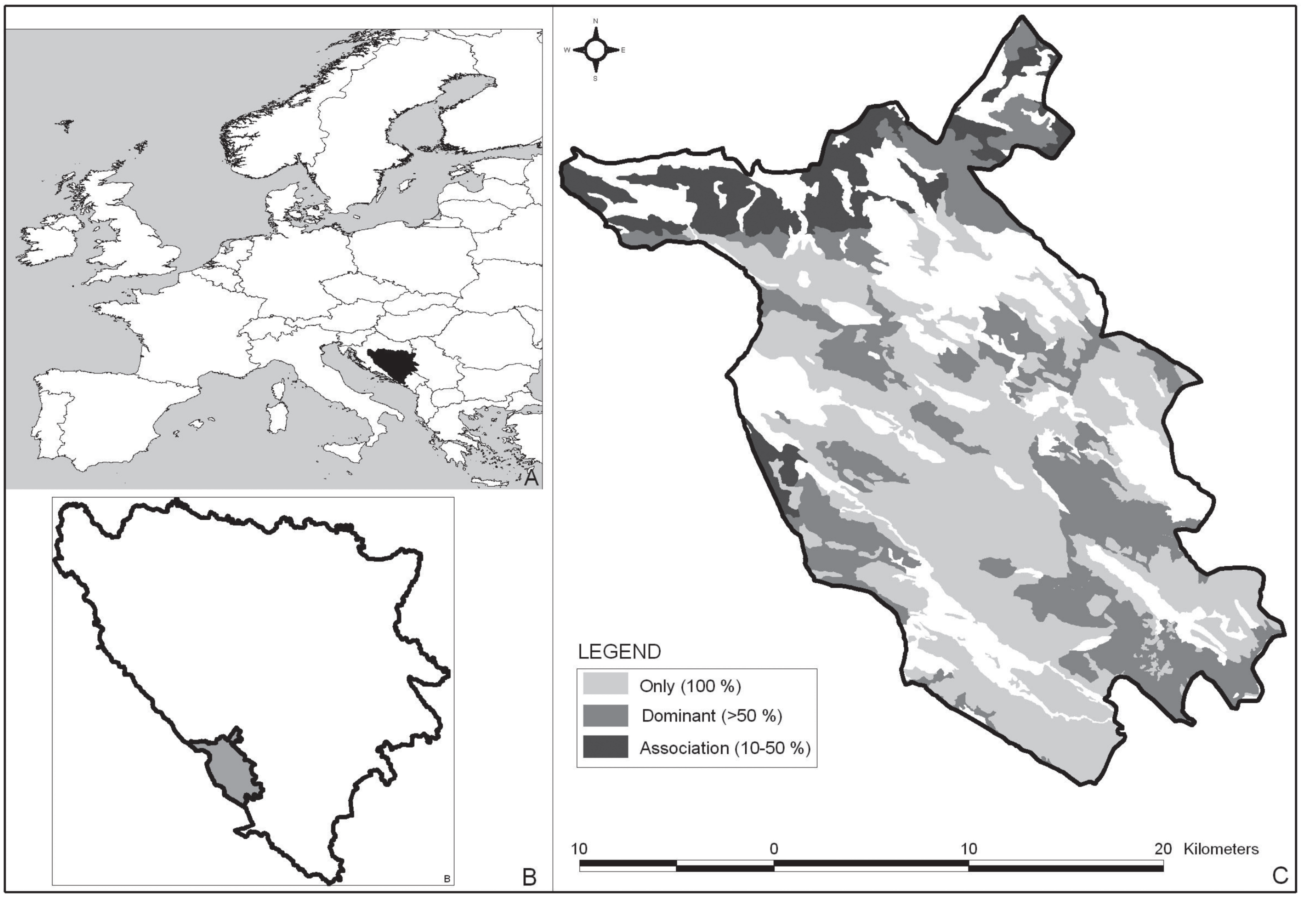

Figure 1: A - location of Bosnia and Herzegovina in Europe, B – Western Herzegovina in Bosnia and Herzegovina, C – distribution of reddish soils in Western Herzegovina.

& VELIĆ, 2002; TIŠLJAR et al., 2002; VLAHOVIĆ et al., 2005). The area between Čitluk and Široki Brijeg is formed from Cretaceous carbonate rocks (various types of limestones and dolomites), Tertiary carbonates and clastics and Quaternary deposits (MOJIČEVIĆ & LAUŠEVIĆ, 1971; RAIĆ et al., 1975). According to summarized data from MOJIČEVIĆ & LAUŠEVIĆ (1973) and RAIĆ & PAPEŠ (1977), the following lithostratigraphic units can be observed in the field: Lower Cretaceous (Berriasian to Aptian) carbonates; Albian to Cenomanian dolomites and limestones; Cenomanian to Turonian chondrodont and rudist limestones; Turonian to Coniacian rudist limestones; Palaeocene (Liburnian) limestones; Palaeocene to Lower Eocene foraminiferal limestones; Middle Eocene clastics; Neogene (Miocene) clastics and carbonates; and Quaternary deposits (Figure 2). Several tectonic phases resulted in folded and overthrust relationships of the Cretaceous and Tertiary units in the field, together forming the Stolac-Čitluk tectonic unit (RAIĆ & PAPEŠ, 1977). Significant amounts of bauxite deposits accumulated during the continental phases (at the boundaries between the Cretaceous and Tertiary and in the Middle Eocene) in the synforms of the developed palaeorelief. In the Neogene, clastic and lacustrine carbonate sedimentation predominated. Quaternary deposits accumulated significantly in the lowlands (in karstic dolinas and poljes and in the river valleys) as fluvioglacial, limnoglacial, alluvial, deluvial, proluvial and colluvial material. Most of the karstic lowlands in the research area are filled with reddish soils, especially terra rossa, overlying different lithostratigraphical units.

2.2. Investigated locations

Three terra rossa profiles at three different locations (profile 2 at Kočerin, profile 5 at Čitluk and profile 9 at Uzarići) were opened in Western Herzegovina (Figs. 2 and 3). At each location GPS coordinates were recorded using Mobile Mapper 6, Magellan professional, as follows: X=6,456,271m, Y=4,805,093m (Kočerin); X=6,474,991m, Y=4,786,373m (Čitluk); X=6,469,858m, Y=4,801,696m (Uzarići). At Kočerin medium deep terra rossa is developed on brecciated micritic limestone (Fig. 3A). At Čitluk Luvic terra rossa overlies calcarenite (Fig. 3B). Shallow terra rossa in Uzarići formed on top of bioclastic floatstone (Fig. 3C). At Kočerin and Uzarići the (B)rz horizon of terra rossa was sampled while at Čitluk samples were taken from the Bt horizon. (B)rz horizons according to ŠKORIĆ et al. (1985) can be correlated with Bw horizons according to FAO (2006). In our investigation this horizon is considered to be in direct contact with the carbonate rock. The lowermost Bt horizon at Čitluk site is also developed on carbonate rock. However, since this profile is that of a Luvic terra rossa, (B)rz (ie.: a residual B horizon) horizon was not present and the Bt horizon was sampled accordingly.

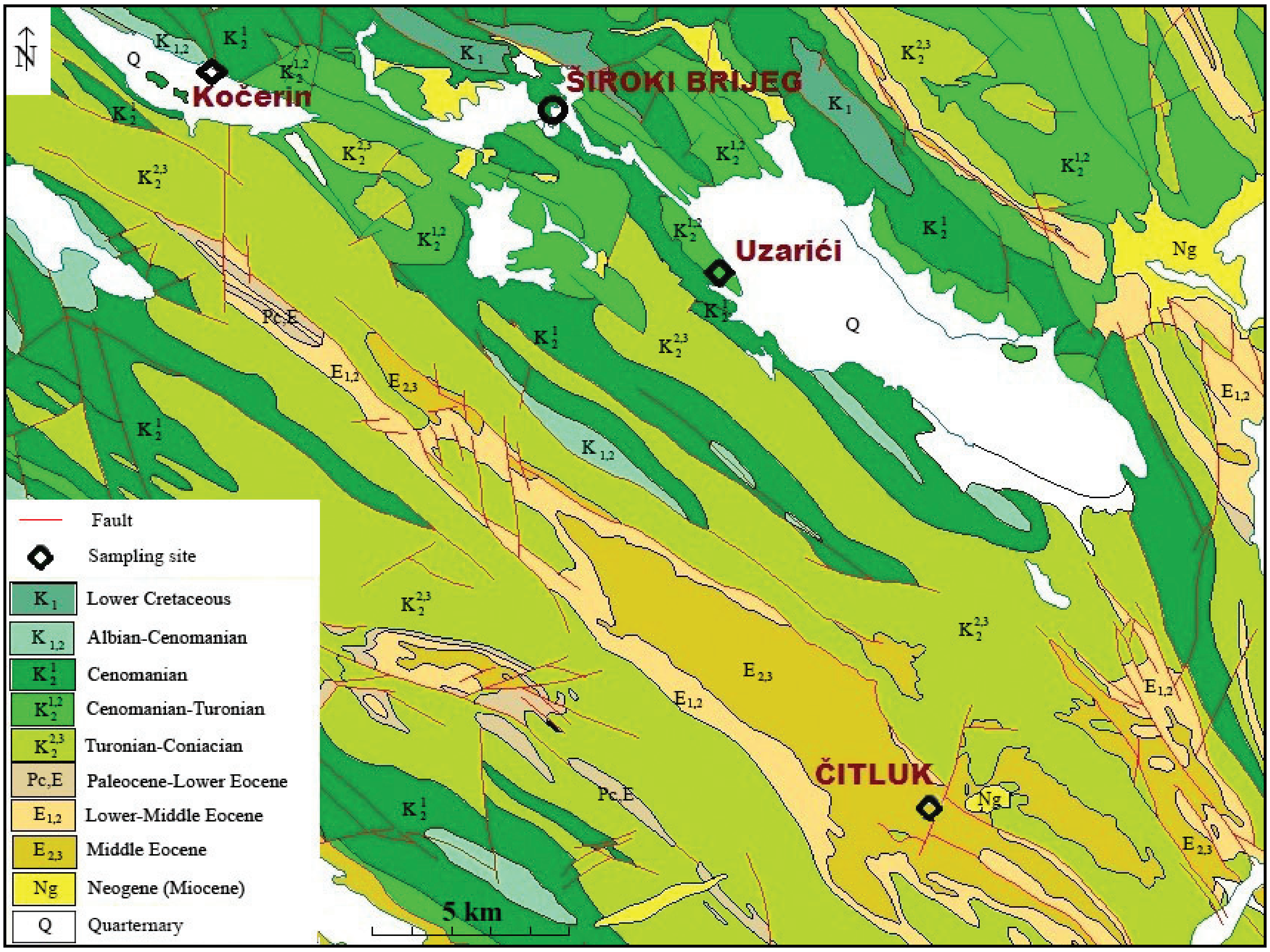

Figure 2: Geological map of the research area with the location of the investigated soil profiles. Lithostratigraphic units summarized and partly modified from MOJIČEVIĆ & LAUŠEVIĆ (1971) and RAIĆ et al. (1975).

2.3. Field and laboratory methods

Soil pits were dug to the contact with carbonate rock, while soil characterization and sampling were done in accordance with ŠKORIĆ (1982; 1986). Samples of carbonate rocks were collected immediately from below the soil profiles. Disturbed soil samples were collected from all genetic soil horizons and air-dried afterwards. A portion of each disturbed soil sample was gently crushed and sieved through a 2 mm sieve for physical, chemical and mineralogical analyses. Soil particle size distribution was determined by the pipette method with sieving and sedimentation after dispersion with sodium pyrophosphate, and interpreted according to FAO (2006). The <2 μm fraction of soil samples was separated by sedimentation in a cylinder and quantitatively obtained after the appropriate settling time. Soil pH in H_2O and in 1 M KCl was measured in 1:2.5 suspension, while the cation exchange capacity (CEC) and base saturation (BS) level were determined using barium chloride according to HRN ISO 11260 (2004). The chemical composition of soil samples was determined by the commercial ACME Analytical Laboratory, Canada. Major oxides were determined by X-ray fluorescence (XRF) spectrometer following $LiBO_2$ fusion.

Thin sections of carbonate rocks were analysed using a Leica DM/LSP petrographic microscope with plane-polarized (ppl) and crossed-polarized light (xpl).

Samples of carbonate rocks were carefully crushed and sieved to pass through a 2 and 4 mm sieve. Fragments in the 2–4 mm range were carefully cleaned in water and only those without impurities were picked. To remove carbonates, the picked fragments of carbonate rocks (2–4 mm) were treated with a 1 M NaOAc solution buffered at pH 5 with HOAc (JACKSON, 1979; TASSIER et al., 1979.) The particle size analysis of the insoluble residues was determined after dispersion in water and ultrasonic treatment. Fractions >63 μm were obtained by wet sieving. The <2 μm fraction was separated by sedimentation in cylinder and quantitatively obtained after the appropriate settling time. The remaining cylinder content was calculated as representing the 2–63 μm fraction.

The mineral composition of <2 mm and <2 μm fractions of soils and the insoluble residue of carbonate rocks (bulk insoluble residue and <2 μm fraction of insoluble residue) was determined by X-ray powder diffraction (XRD) using a Philips diffractometer (graphite monochromator, CuKμ radiation, proportional counter). XRD patterns of clay fractions

Figure 3: Photos of the investigated soil profiles: A - profile 2 (Kočerin), B - profile 5 (Čitluk), C - profile 9 (Uzarići)

were made after the following treatments: (a) air-drying, (b) glycerol solvation, (c) glycol solvation, (d) heating to 550°C for 2 h and (e) dissolution in HCl (18%) for 24 h. The DMSO-treatment was used to differentiate kaolinites which form intercalation compounds with DMSO from kaolinites which do not intercalate with DMSO (RANGE et al.,1969). By means of semi-quantitative XRD analysis, the amounts of quartz, plagioclase, K-feldspar, haematite, goethite, anatase and gibbsite were determined in the <2 mm and <2 μm fractions of soil samples, bulk insoluble residues and <2 μm fraction of insoluble residues. An external standard was applied, by measuring the relative intensities of characteristic diffraction lines. The identification of clay minerals was generally based on the methods outlined by BROWN (1961), BRINDLEY & BROWN (1980) and MOORE & REYNOLDS (1989). The term "illitic material" was used as defined by ŚRODOŃ (1984) and ŚRODOŃ & EBERL (1984). The term "MC" was used for mixed-layer clay minerals in which the type of interstratification and constituent clay minerals were not readily identifiable. Semi-quantitative estimates of clay minerals in the <2 μm fraction were based on the relative intensities of characteristic X-ray peaks following the method of JOHNS et al. (1954). Estimated quantities of minerals were presented with Xs, but no quantitative value was assigned to each X.

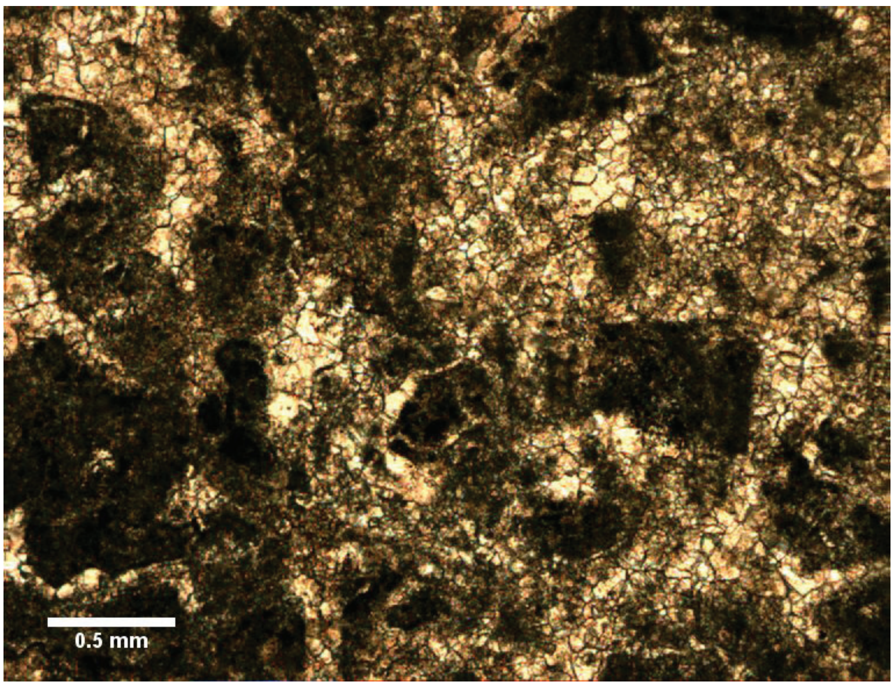

Figure 4: Photomicrograph of bedrock lithology at the Kočerin sampling site. Diagenetic carbonate crust developed in micritic limestone, showing brecciation and recrystalisation features. (ppl)

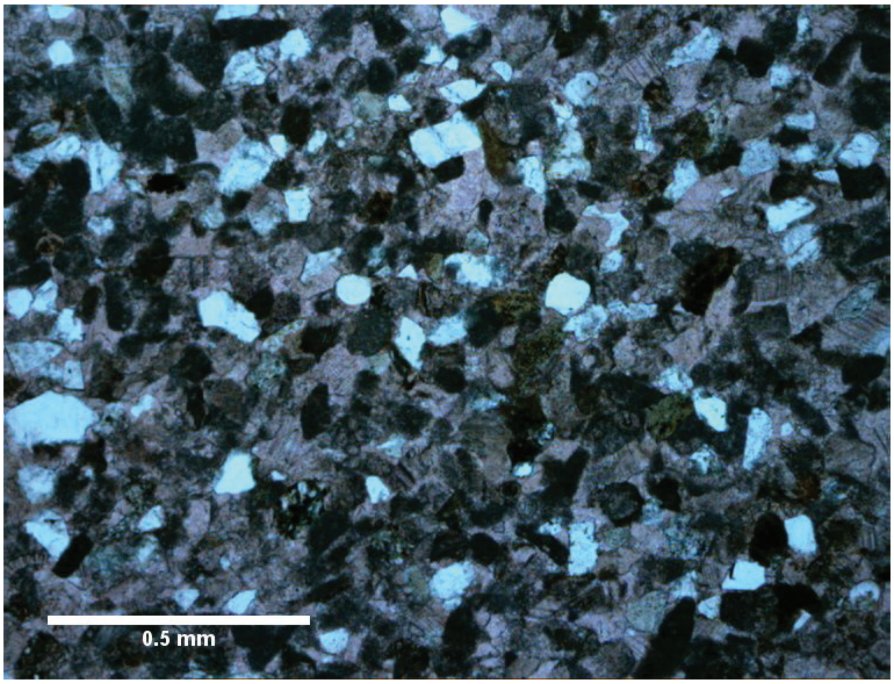

Figure 5: Photomicrograph of bedrock lithology at the Čitluk sampling site. Calcarenite, predominantly consisting of well-sorted bioclasts and intraclasts, accompanied with minor siliciclastic material (white grains). (ppl)

3. RESULTS

3.1. Carbonate rocks

Results obtained from the micropetrographic analysis of the underlying lithologies at Kočerin, Čitluk and Uzarići showed good correlation with previously determined lithostratigraphy presented on the geological map of the investigated area (Fig. 2). The observed profiles with terra rossa were developed on different lithostratigraphic units as follows: (i) Albian to Cenomanian dolomites and limestones (Kočerin); (ii) Middle Eocene clastics (Čitluk) and (iii) Cenomanian to Turonian chondrodont and rudist limestones (Uzarići). At Kočerin, brecciated micritic limestone, showing recrystallisation and development of meteoric diagenetic features

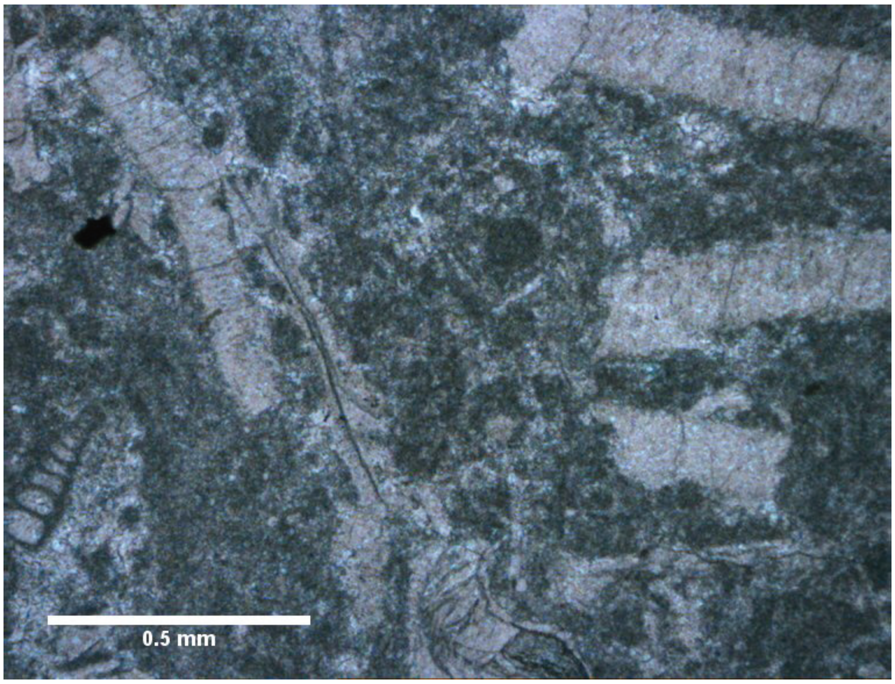

Figure 6: Photomicrograph of bedrock lithology at the Uzarići sampling site. Bioclastic floatstone, containing large bioclasts of chondrodonts and rudists and some benthic forams, deposited together with micritic matrix. (ppl)

was recognized. It is interpreted as a diagenetic carbonate crust, developed in the Albian to Cenomanian dolomite and limestone lithostratigraphic unit (Fig. 4). At Čitluk, a calcarenite was identified containing predominantly well-sorted, intra-basinal carbonate material (bioclasts and intraclasts), accompanied together with a minor proportion of siliciclastic material (mainly quartz grains), cemented by calcitic cement (Fig. 5). According to the observed petrographic characteristics and bioclast assemblage, it belongs to the Middle Eocene clastics lithostratigraphic unit. Rudist and chondrodont limestone, identified as the bioclastic floatstone (DUNHAM, 1962) is observed at Uzarići. It contains large (up to several centimetres) bioclasts of chondrodonts and rudists, accompanied by some benthic forams, together embedded in a micritic matrix (Fig. 6). This bioclastic limestone belongs to the Cenomanian to Turonian chondrodont and rudist limestones lithostratigraphic unit.

3.2. Soil chemical properties

Analysed B horizons of terra rossa have neutral to slightly acid pH and high base saturation with calcium as the predominant cation, followed by magnesium (Table 1). The highest pH (H_2O) was observed in the (B)rz horizon developed on the bioclastic floatstone (Uzarići) while the Bt horizon in the Luvic terra rossa overlying calcarenite has the lowest pH (H_2O). As for pH, the BS and humus content were lowest in the Bt horizon at Čitluk and highest in the (B)rz horizon at Uzarići. As expected, the lowest CEC value was observed in the Bt horizon at Čitluk where the lowest pH (H_2O) and humus content was detected. Namely, the Luvic terra rossa at this location is considered the most developed soil among the three analysed locations, and, in addition contains the lowest amount of the clay fraction (Table 2). It is also in accordance with WRIGHT & FOSS (1972), who concluded that CEC in the lower horizons of soil profiles depended on the clay content and the mineral composition of clay fraction.

3.3. Particle size analysis

The B horizons of terra rossa profiles at Kočerin, Čitluk and Uzarići have characteristic red colours and are composed of clay, clay loam and clay respectively (Table 2). The insoluble residue content of the underlying carbonate rocks is very variable (Table 3). It is extremely low in Uzarići (0.09 wt.%), low in Kočerin (0.61 wt.%) and high in Čitluk (18.55 wt.%). All B horizons are enriched in the clay fraction and depleted in the silt fraction compared to the insoluble residue (Tables 2 and 3). The content of the sand fraction in the B horizon from Kočerin and Uzarići is higher compared to the sand content in the insoluble residue of the underlying carbonate rocks (Tables 2 and 3). In contrast, the Bt horizon developed on calcarenite (Čitluk), which has the highest insoluble residue content dominated by the sand fraction is depleted in the sand fraction compared to the insoluble residue.

Table 1: Basic chemical properties of B horizon of the investigated soil profiles.

Profile	Depth (cm)	Horizon	pH 1M KCl	pH H_2O	Humus (g/kg)	Ca	K	Mg	Na	CEC	Base saturation (%)
						cmol kg^{-1}					
2	12–28	(B)rz	4.32	5.70	15.85	16.87	0.09	1.07	0.05	18.71	96.63
5	32–84	Bt	4.04	5.38	1.90	11.03	0.38	1.73	0.01	15.14	86.85
9	14–38	(B)rz	6.12	7.50	22.10	35.42	0.25	0.76	0.35	36.87	99.76

Table 2: Mechanical composition of B horizon of the investigated soil profiles.

Profile	Depth (cm)	Soil color dry (Munsell Soil Color Chart, 2000)	Sand 2.0–0.063 mm (%)	Silt 0.063–0.002 mm (%)	Clay <0.002 mm (%)	Texture
2	12–28	2,5YR 4/6	6.50	17.30	76.20	Clay
5	32–84	2,5YR 4/6	43.50	24.50	32.00	Clay loam
9	14–38	10R 4/4	7.50	25.10	67.40	Clay

Table 3: Particle size analysis of the insoluble residues of limestone (wt.%).

Profile	I.r. content (%)	Sand 2.0–0.063 mm (%)	Silt 0.063–0.002 mm (%)	Clay <0.002 mm (%)	Texture
2	0.61	4.14	44.33	51.53	silty clay
5	18.55	50.87	26.28	22.85	sandy loam
9	0.09	2.14	33.62	64.24	clay

Ir = Content of the insoluble residue (wt.%).

Table 4: Selected geochemical properties of B horizon of the investigated soil profiles.

Profile	Depth (cm)	CIA Al*100/(Al+Ca+K+Na)	Ti/Al
2	12–28	93.32	0.040
5	32–84	84.73	0.060
9	14–38	86.81	0.051

CIA=Chemical Index of Alteration calculated as Al * 100 / (Al+Ca+K+ Na).

3.4. Geochemical indicators of weathering

In order to characterize the investigated B horizons geochemically, we used the Chemical Index of Alteration (CIA) proposed by NESBITT & YOUNG (1982) and considered the measure of feldspar minerals weathering and their hydration to form clay minerals (SHELDON & TABOR, 2009) and Ti/Al molecular ratio, which can also be used as provenance indicator (e.g. SHELDON, 2006; STILES & STENSVOLD, 2008). CIA values range from 84.73 in Čitluk to 93.32 in Kočerin and can be considered as very high (Table 4). The Ti/Al ratios in bulk samples range from 0.040 in Kočerin to 0.060 in Čitluk (Table 4).

3.5. Bulk and clay mineralogy

Mineralogical analyses were performed on the <2 mm and <2 μm fractions of the B horizons (Tables 5 and 6; Figs. 7 and 9) and the insoluble residue of carbonate rocks (bulk insoluble residue and <2 μm fraction of insoluble residue) (Tables 7 and 8: Figs. 8 and 10). Though the mineralogical composition of non-clay minerals in all three B horizons was relatively uniform (Table 5), significant differences in clay mineral composition among the investigated B horizons were observed (Table 6). Each B horizon contained quartz, K-feldspar, haematite, goethite, gibbsite, kaolinite, MC and

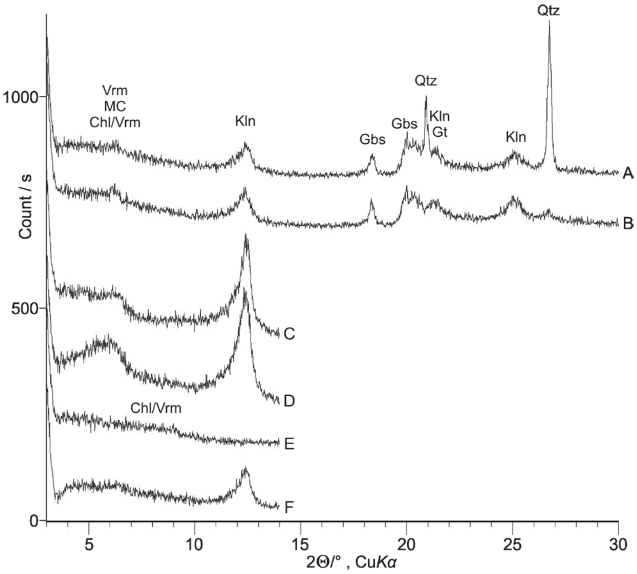

Figure 7: X-ray diffractograms of bulk sample (A) and clay fractions (B to F) of the analyzed (B)rz horizon from Kočerin, A-untreated, B-untreated, C-glycerol solvated, D-ethylene glycol solvated, E-heated for 2 hours at 550°C. F-treated 24 hours with HCl (18%). Qtz: Quartz. Pl: Plagioclase. Kfs: Potassium feldspar. Gbs: Gibbsite. Gt: Goethite. M: Micaceous mineral. Kln: Kaolinite. Vrm: Vermiculite. S: Smectite. Ill: Illitic material. MC: Mixed-layer clay mineral. Chl/Vrm: Mixed-layer chlorite/vermiculite.

XRD-amorphous inorganic compounds. Both kaolinite which does not form intercalation compounds with DMSO and kaolinite which intercalates with DMSO were detected. The presence and distribution of plagioclase, anatase, smectite, vermiculite, micaceous clay minerals (illitic material and mica) and chlorite–vermiculite mixed layer mineral (C/V) varied among the different B horizons. The Bt horizon from Čitluk contains the highest amount of quartz (in both

Table 5: Semi-quantitative mineral composition of the <2 mm fraction of B horizons of the investigated soil profiles. Phyllos.+am.= phyllosilicates + amorphous inorganic compound, + = mineral is present in the sample. ? = mineral is probably present in the sample but due to the low content and/or overlapping of diffraction peaks cannot be confirmed with certainty.

Profile	Depth (cm)	Quartz (%)	Plagioclase (%)	K-feldspar (%)	Hem.+Goeth. (%)	Anatase	Gibbsite (%)	Phyllos.+am. (%)
2	12–28	18	?	<1	7	+	10	60
5	32–84	60	<1	<1	4	?	+	30
9	14–38	23	?	<1	7	?	+	65

Table 6: Semi-quantitative mineral composition of the <2 μm fraction of B horizons of the investigated soil profiles. + = mineral is present in the sample. ? = mineral is probably present in the sample but due to the low content and/or overlapping of diffraction peaks cannot be confirmed with certainty. C/V=Mixed-layer chlorite-vermiculite.

Profile	Depth (cm)	Quartz (%)	Plagioclase (%)	K-feldspar (%)	Hem.-Goeth. (%)	Gibbsite (%)	Anatase	Kaolinite	Smectite	Vermiculite	Illitic material	Mixed-layer clay mineral	Am. matter
2	12–28	?	?	–	9	14	+	XXX	–	XX	?	XX (C/V)	X
5	32–84	9	?	–	8	–	?	X	XXX	–	?	X	X
9	14–38	3	–	–	8	–	?	XXX	?	–	X	XX (C/V)	X

X - relative abundance of clay minerals within horizons based on X-ray diffraction (no quantitative value is assigned to X)

Table 7: Semi-quantitative mineral composition of the insoluble residues of limestone. Phyllos.+am.= phyllosilicates + amorphous inorganic compound, + = mineral is present in the sample. ? = mineral is probably present in the sample but due to the low content and/or overlapping of diffraction peaks cannot be confirmed with certainty.

Profile	Depth (cm)	Quartz	Plagioclase	K-feldspar	Goethite	Hematite	Anatase	Gibbsite	Phyllos.+am.
2	30–50	32	–	–	10	?	?	5	50
5	90–110	48	12	8	+	–	–	–	30
9	40–60	20	–	–	+	–	–	–	75

Table 8: Semi-quantitative mineral composition of the <2 µm fraction of the insoluble residues of limestone. + = mineral is present in the sample. ? = mineral is probably present in the sample but due to the low content and/or overlapping of diffraction peaks cannot be confirmed with certainty. * = the amount of insoluble residue was very low (see Table 3) and clay fraction was not separately analysed. ** = Insoluble residue contains only kaolinite as a clay mineral phase. C/V = Mixed-layer chlorite-vermiculite. I/S = Mixed-layer illite/smectite.

Profile	Depth (cm)	Quartz (%)	Goethite (%)	Gibbsite (%)	Anatase	Kaolinite	Smectite	Vermiculite	Illitic material	Mixed-layer clay mineral	Am. matter
2	30–50	?	12	+	?	XXX	XX	–	X	X (I/S)	XX
5	90–110	7	+	–	–	X	XXX	–	XX	X (I/S)	XX
9*	40–60					XXX**					

X - relative abundance of clay minerals within horizons based on X-ray diffraction (no quantitative value is assigned to X)

fractions) and only in this sample was the presence of plagioclase confirmed with certainty. Although gibbsite was recognized in all B horizons, its content is highest in the (B) rz horizon from Kočerin (in both fractions).

Kaolinite is the predominant clay mineral phase in the clay fraction of the (B)rz horizons from Kočerin and Uzarići while smectite is the predominant clay mineral phase in the clay fraction of the Bt horizon from Čitluk (Table 6; Figs. 7 and 9). Kaolinite is followed by vermiculite and C/V as the main mineral phases in Kočerin and by C/V and illitic material in Uzarići. It is important to emphasize that illitic material was confirmed with certainty only in the (B)rz horizon from Uzarići. Kaolinite and MC follow smectite in Čitluk in terms of quantity.

Significant differences in both the non-clay and clay mineral composition of the analysed insoluble residues (IR) were observed (Tables 7 and 8). Each IR contained quartz, goethite, kaolinite and an XRD-amorphous inorganic compound. Both kaolinite which does not form intercalation compounds with DMSO and kaolinite which intercalates with DMSO were detected. The presence and distribution of plagioclase, K-feldspar, haematite, anatase, gibbsite, smectite, micaceous clay minerals (illitic material and mica), MC, C/V and illite/smectite mixed-layer mineral (I/S) varied among the different IR. IR from Čitluk contains the highest amount of quartz (in both fractions), and plagioclase and K-feldspar were detected in this sample alone. IR from Kočerin contains the highest amount of goethite and is the only sample with gibbsite (in both fractions).

Kaolinite is the predominant clay mineral phase in the clay fraction of IR from Kočerin and Uzarići while smectite is the predominant clay mineral phase in the clay fraction of IR from Čitluk (Table 8; Figs. 8 and 10). Kaolinite is followed by smectite, illitic material and I/S in Kočerin and is the only clay mineral phase in Uzarići. Smectite is followed by illitic material, kaolinite and I/S in Čitluk.

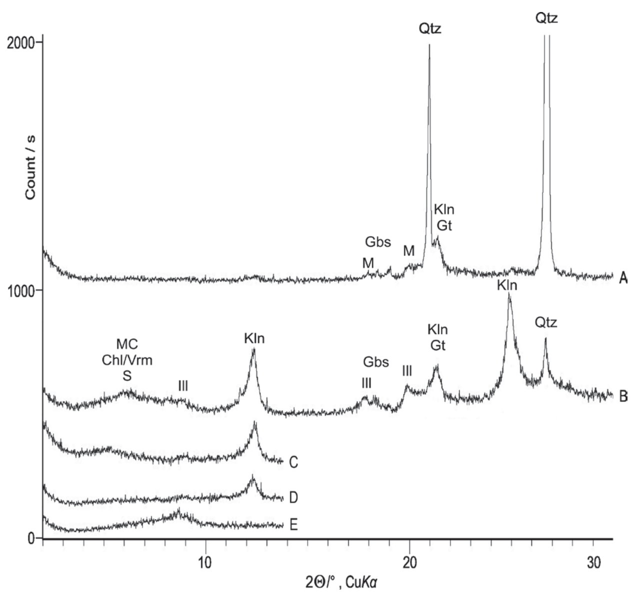

Figure 8: X-ray diffractograms of bulk sample (A) and clay fraction (B to E) of insoluble residue of limestone from Kočerin, A-untreated, B-untreated, C-ethylene glycol solvated, D-glycerol solvated, E-heated for 2 hours at 550°C. For abbreviations see Fig. 7.

4. DISCUSSION AND CONCLUSION

The terra rossa soils analysed from Western Herzegovina occur over carbonate rocks of different ages and lithologies (Figs. 2, 4, 5 and 6) having very variable IR contents (Table 3) ranging from extremely low (0.09 wt.% in Uzarići) to

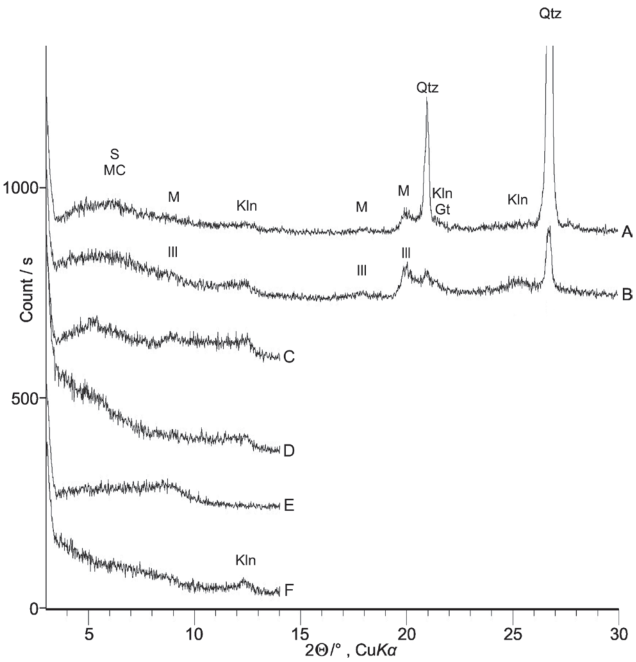

Figure 9: X-ray diffractograms of bulk sample (A) and clay fraction (B to F) of analyzed Btg horizon from profile Čitluk, A-untreated, B-untreated, C-glycerol solvated, D-ethylene glycol solvated, E-heated for 2 hours at 550°C. F-treated 24 hours with HCl (18%). For abbreviations see Fig. 7.

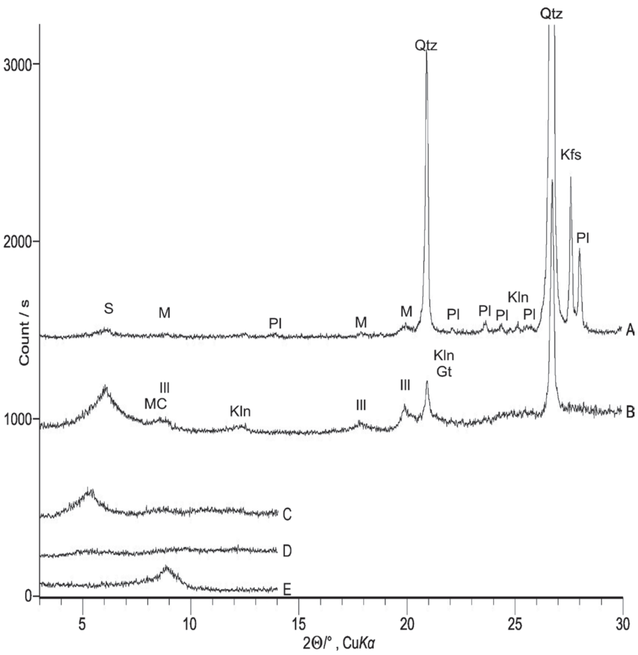

Figure 10: X-ray diffractograms of bulk sample (A) and clay fraction (B to E) of insoluble residue of limestone from Čitluk, A-untreated, B-untreated, C-ethylene glycol solvated, D-glycerol solvated, E-heated for 2 hours at 550°C. For abbreviations see Fig. 7.

high (18.55 wt.% in Čitluk) values. Terra rossa B horizons have characteristic red colours (Table 1), neutral to slightly acid pH and high base saturation, with calcium as the predominant cation, followed by magnesium (Table 1). It is in accordance with TVICA (2008) who observed high base saturation in terra rossa soils from Herzegovina with calcium as the predominant cation.

Very high CIA values in the B horizons of the analysed soils clearly indicate intensive weathering (Table 4). According to SHELDON & TABOR (2009), parent materials that have already been cycled as sediments or which are clay-rich, may start out with CIA values of 60 to 70%. They state that as weathering progresses from, for example, microcline to illite and kaolinite, CIA values would increase from 50 to 75 (pure illite) and 100 (pure kaolinite), respectively. The CIA values obtained in this study are generally in accordance with the mineral composition and particle size distribution of the analysed B horizons. Traces of K-feldspar and plagioclase, the predominance of kaolinite as well as the clay fraction content are in favour of high CIA in the (B)rz horizons from Kočerin and Uzarići (Tables 2, 4, 5 and 6). The slightly lower CIA value observed in the Bt horizon from Čitluk is due to the significantly lower clay fraction (higher amount of silt and especially sand fraction) and to smectite as the predominant clay mineral phase. However, it has to be stressed that CIA values are partly masked by the presence of gibbsite (i.e. aluminium hydroxide) that was detected in all the analysed B horizons. The effect of particle size distribution is also evident in the Ti/Al ratios because the highest ratio was observed in the Bt horizon from Čitluk with the highest amount of sand fraction and, likewise, the highest Ti content, while the lowest ratio was found in the (B)rz horizon from Kočerin with the highest clay content. Unfortunately, due to this effect of particle size, the Ti/Al ratio could not be used as a provenance indicator.

The content of the insoluble residue may indicate that in the case of Kočerin and Uzarići locations, an excessive thickness of carbonate rocks must have been dissolved to form the (B)rz horizons of terra rossa, and that also the extent of the preservation of that residue must have been very high. In contrast, it is quite plausible that the Bt horizon at Čitluk might have formed from the insoluble residue of the calcarenite. Although the insoluble residue of carbonate content of carbonate rocks below the (B)rz horizons in Kočerin and Uzarići is not compatible with the development of terra rossa entirely by the dissolution of carbonate rocks, its grain size distribution provides a different picture. Namely, if terra rossa has developed only from the insoluble residue of limestone or dolomite, its clay content, due to weathering should be higher than that observed (Tables 2 and 3). In order to resolve such questions, the clay fraction may be of great importance because its composition could be a result of different processes which may have taken place during soil formation. Namely, soils may contain "detrital"clays inherited from the parent material (in this case soil clays represent the IR of carbonate rock) and they may contain clays formed by sequential weathering of unstable parent minerals of the IR (including clay mineral phases). There are also neoformed (pedogenic) clay minerals and clays added to the soil due to allochthonous inputs (e.g. aeolian dust, volcanic debris and clastic sedimentary particles; DURN et al., 2007). This is even more complex when soils are formed on carbonate rocks that are extremely low in non-carbonate mineral phases.

With regard to the previous statement, the situation is clearest at Čitluk because there the calcarenite contains a high amount of IR, 18.55 wt.% respectively (Table 3). Luvic terra rossa at this location is thickest (Table 1) and is considered to be the most developed soil of the three analysed locations. The clay mineral composition in the Bt horizon and IR match quite well (Tables 6 and 8). The presence of smectite as the predominant clay mineral phase in both the IR and Bt horizons clearly indicates that this mineral phase was inherited from the parent material. Kaolinite is present in both the IR and Bt horizons and can also be, at least partly, considered as inherited. Namely, the Bt horizon contain both types of kaolinite while kaolinite which forms intercalation compounds with DMSO is the predominant type of this mineral phase in the IR. This may indicate that the kaolinite which does not intercalate with DMSO is predominantly pedogenic kaolinite, i.e., an authigenic mineral in terra rossa, while kaolinite which intercalates with DMSO is inherited from the kaolinite containing parent material which means it is of a lithogenic origin (DURN et al., 1999). Illitic material and I/S detected in IR were not found with certainity in the Bt horizon probably due to their very low content. However, the presence of MC in the Bt horizon may indicate these phases were the source material for more weathered clay minerals. A much higher content of kaolinite would be expected in the Luvic terra rossa but smectite seems to be the (meta)stable mineral phase in this pedoenvironment because the pH was not low enough to inhibit smectite stability, (e.g. DOUGLAS, 1982; KARATHANASIS & HAJEK, 1984) and Ca and Mg are the predominant cations in the soil solution (Table 1). Due to their chemical composition, the dissolution of smectite minerals is driven by different mechanisms. In particular, hydrolysis of octahedral Mg is interpreted as the primary driving force behind the dissolution of saponite in dilute acid, while reduction should play a major role in the decomposition of nontronite (RYAN et al., 2008). A higher content of quartz and much lower contents of unstable mineral phases including plagioclase and K-feldspar in the Bt horizon compared to IR (Tables 5 and 7) also favour calcarenite as the parent material for the Luvic terra rossa at Čitluk. Therefore we can conclude that both the mineral composition and the particle size distribution of the Bt horizon and IR suggest calcarenite as terra rossa parent material. Minor external material contributions by various transport mechanisms cannot be excluded as documented by gibbsite which we consider to be the only external material in terra rossa at this location.

As previously stated, in the case of Kočerin and Uzarići, the IR content of carbonate rocks below terra rossa may indicate that an excessive thickness of carbonate rocks was dissolved to form the (B)rz horizons, and that the degree of the preservation of that residue must have been very high. Kaolinite is the predominant clay mineral phase in both the IR and the (B)rz horizon at those locations. We tentatively propose the same origin of kaolinite as in the case of Čitluk. However, two clay mineral phases (C/V and vermiculite) were detected in the (B)rz horizons from these locations that were not found in the IR of brecciated micritic limestone (Kočerin) and bioclastic floatstone (Uzarići) (Tables 6 and 8).

We tentatively propose three possible explanations for the C/V and vermiculite origin in the analysed (B)rz horizons with the first or/and third one being the most probable. Firstly, C/V and vermiculite are considered as soil clay minerals because those mineral phases were not detected in the IR of the corresponding carbonate rocks. The presence of C/V may indicate that both mineral phases formed as a result of chlorite destabilization, with C/V as an intermediate step during the vermiculitization process of chlorite sensu WILSON (2004). This explanation is valid only when chlorite was present as an allochthonous mineral phase because this mineral was not detected in the IR of corresponding carbonate rocks. The presence of vermiculite in (B)rz horizon from Kočerin and lack of this clay mineral in (B)rz horizon from Uzarići can probably be attributed to the lower pH of Kočerin (Table 1).

Secondly, it is possible that vermiculite formed by weathering of the illite, mineral phase detected in the IR of carbonate rocks from Kočerin and Čitluk. For example, OTTNER et al. (2013) state that illite can be the source material for more weathered clay minerals in the Oberlab loess-palaeosol sequence in Upper Austria. However, the lack of illite in the IR from Uzarići, as well as the lack of vermiculite in the Bt horizon from Čitluk do not support this explanation. This second explanation also does not provide an answer for the origin of C/V.

Thirdly, it is possible that both mineral phases were not formed in soil from allochthonous chlorite but are derived as mineral phases already present in “external” material. The presence of plagioclase as a trace mineral phase in Kočerin (plagioclase was not detected in IR of brecciated micritic limestone) and the presence of gibbsite in both (B)rz horizons locations support both the first and/or the third explanation.

We can conclude that both the mineral composition of the (B)rz horizon and IR as well as the very low IR content of carbonate rocks below terra rossa strongly suggest a substantial contribution of external material during the genesis of terra rossa in Kočerin and Uzarići compared to Čitluk. The positions of the three investigated locations on the geological map (Fig. 2) clearly indicate that the sampling sites in Kočerin and Uzarići are situated in the vicinity of Quaternary deposits which could have been the possible source of external materials while Čitluk is situated in a more isolated position where the influence of external materials is less important. Although the IR of brecciated micritic limestone from Kočerin contains gibbsite, (probably from cracks in limestones and, therefore, of secondary origin), we relate the presence of this mineral phase in all B horizons to reworked particles of Palaeogene bauxites which are sporadically present in the area of investigation (RAIĆ & PAPEŠ, 1977).

Based on their studies of terra rossa soils in Istria DURN et al. (2007) concluded that in some isolated karst terrains, terra rossa may have formed exclusively from the IR of limestone and dolomite, but it is most commonly composed of a variety of external materials, including aeolian dust, volcanic debris and clastic sedimentary particles that were carried to the carbonate terrain by various transport mechanisms. They found that the most likely additional flux influencing terra rossa formation in Istria is aeolian dust, followed by flysch sediments and their contribution might have been up to 50%. Based on investigation of the B horizons of terra rossa on three locations in Western Herzegovina we can conclude the following:

(1) terra rossa situated on isolated carbonate rocks containing high amount of IR may have formed almost exclusively from the parent carbonate rock (Čitluk) although some influence of external materials cannot be excluded (e.g. gibbsite).

(2) terra rossa formed on non-isolated carbonate rocks containing low amounts of IR (Kočerin and Uzarići) clearly shows the influence of external materials on its genesis (e.g. chlorite, plagioclase, gibbsite) and can be regarded as polygenetic soil (DURN et al., 1999; 2007). It is important to stress that compared to Istria where loess deposition has been a recurrent process since the early Middle Pleistocene and influenced terra rossa formation (DURN et al., 1999; 2007) no data on loess deposition in Western Herzegovina is reported in the literature.

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