Distribution of iron and manganese in terra rossa from Istria and its genetic implications

Durn, Goran; Slovenec, Dragutin; Čović, Marta

Distribution of Iron and Manganese in Terra Rossa from Istria and its Genetic Implications

Goran **DURN**, Dragutin **SLOVENEC** and Marta **ČOVIĆ**

Abstract

Haematite and goethite are the predominant pedogenic mineral phases in terra rossa from Istria. Limited variation of selected Fe oxide characteristics in analysed samples indicates the specific pedogenic environment in which terra rossa is formed. The mean value of the Fe_d/Fe_t ratio, taken as an index of weathering is 0.7 and reflects quite a high degree of weathering of Fe-containing primary silicates. Relatively uniform Fe_d/clay ratios clearly indicate a predominance of co-illuviation of clay and Fe oxides. Low values of Fe_o point to the low content of poorly crystalline Fe oxides in analysed terra rossa. Fe_o/Fe_d ratios in the analysed profiles vary. In the upper part of the Pomer, Poreč and Novigrad profiles Fe_o/Fe_d ratios are higher than in the lower part of those profiles which may be explained as a result of different pedogenic environments and/or additions of external materials in the upper part of those profiles. The lack of positive correlation between Mn_d and clay and Mn_d and Fe_d is a consequence of remobilization of manganese due to hydromorphic processes which post-dated co-illuviation of clay and Fe oxides.

During the Late Tertiary and Quaternary the pedogenic environment on hard carbonate rocks of the Jurassic-Cretaceous-Palaeogene carbonate plain of southern and western Istria generally remained suitable for rubification. However, (Neo)tectonic activity and the input of external material, as well as various climatic fluctuations might have significantly effected terra rossa through the processes of erosion, colluviation, yellowing and secondary hydromorphy.

1. INTRODUCTION

Pedogenic iron oxides and manganese oxides and hydroxides frequently occur in soils of different climatic regions. Due to their high pigmenting capacity they may influence the colour of soils or particular soil horizons. Manganese oxides and hydroxides have a stronger pigmenting effect upon soils than iron oxides and tend to overwhelm their colour when both constituents are present (SCHWERTMANN & FANNING, 1976). Iron oxides may occur evenly dispersed throughout the soil, concentrated in particular horizons or in certain morphological features such as mottles and nodules

University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Pierottijeva 6, HR-10000 Zagreb, Croatia.
e-mail: gdurn@rudar.rgn.hr

(SCHWERTMANN & TAYLOR, 1989). Manganese oxides and hydroxides mainly occur as coatings on other soil particles, as concretions and mottles, in cracks and veins or are mixed with iron oxides and other soil constituents in nodules (FANNING & FANNING, 1989; McKENZIE, 1989). The most common pedogenetic iron oxides in soils are goethite and haematite. Lepidocrocite, maghemite and ferrihydrite are less common and occur in more specific pedogenic environments. Although manganese oxides and hydroxides in soils are often reported to be amorphous (e.g. SIDHU et al., 1977) this is probably caused by difficulties in detecting small concentrations of poorly crystalline phases as with amorphous iron oxides (SCHWERTMANN & TAYLOR, 1989). According to McKENZIE (1989), the most common crystalline manganese oxides in soils are birnessite, vernadite, lithiophorite and hollandite.

Both the type of Fe-oxide in soil and its degree of crystallinity may be regarded as indicators of the pedogenic environment because it seems to reflect the conditions under which they form (SCHWERTMANN & TAYLOR, 1989). Consequently, they are sensitive to changing soil environment. This means that, for example, Fe-oxides can be remobilized by reduction and again reoxidized in another favourable environment. The behaviour of manganese in soils also depends on changing soil environment. However, oxidized forms of manganese may be reduced to the mobile Mn^{2+} at a higher Eh than that at which Fe^{3+} may be reduced to the more mobile Fe^{2+} (FANNING & FANNING, 1989). Namely, LOVLEY (1995) stated that at pH 7 and 25 °C reduction of Mn^{4+} begins below a redox of 526 mV, while reduction of Fe^{3+} starts at Eh <-47 mV. According to LOVLEY & PHILLIPS (1988) between the zone of Mn reduction and that of Fe reduction, there is little overlap because soil bacteria show an enzymatic preference for Mn^{4+}, and Fe^{3+} reduction will not begin until Mn^{4+} is depleted.

Identification of Fe oxides and especially Mn oxides and hydroxides in soil by X-ray diffraction (XRD) may be complicated due to their small amounts, overlapping of diagnostic lines with those of associated minerals and the poor crystallinity of some phases. For identification and even quantification of secondary Fe oxides in soils, several differential dissolution treatments can
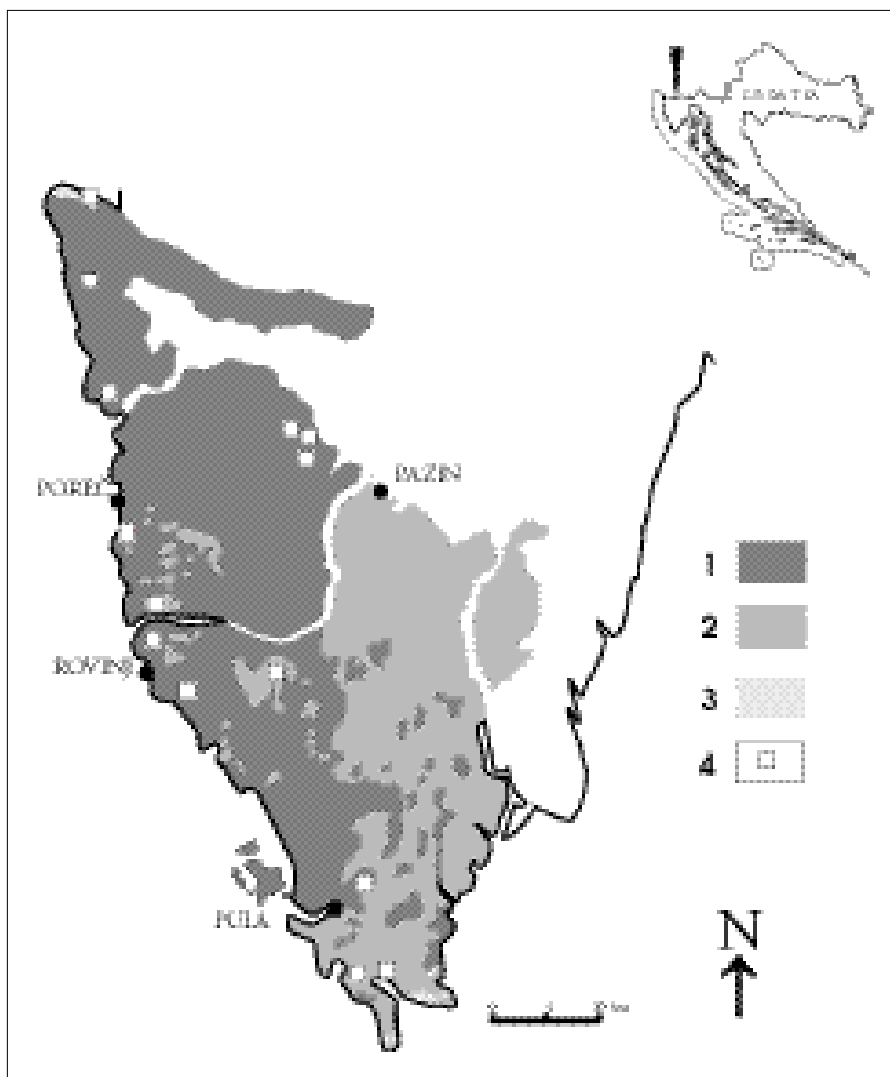
Fig. 1 Distribution of terra rossa in Istria (modified after ŠKORIĆ, 1987). Legend: 1) terra rossa, calcocambiosol, eutric cambiosol, rigosol from terra rossa (area of terra rossa >70%); 2) terra rossa, calcocambiosol, eutric cambiosol (area of terra rossa is 50-70%); 3) eutric cambisol on loess, luvisol on loess, rigosol from luvic and eutric cambiosol (40:30:30); (4) location of terra rossa samples.

be used. The most useful among them are an acid ammonium oxalate treatment and dithionite-citrate bicarbonate treatment. The former treatment extracts only poorly crystalline Fe oxides, predominately ferrihydrite (SCHWERTMANN, 1964; SCHWERTMANN et al., 1982; SCHWERTMANN & TAYLOR, 1989), while the dithionite-citrate bicarbonate treatment (proposed by MEHRA & JACKSON, 1960) extracts practically all secondary Fe oxides (SCHWERTMANN & TAYLOR, 1989). Acid ammonium oxalate extractable iron and manganese are usually labelled Fe_o and Mn_o while dithionite-citrate bicarbonate extractable iron and manganese are labelled Fe_d and Mn_d. Those parameters, when compared to total contents of given elements can be very helpful in understanding some aspects of the genesis of soils which contain iron oxides and manganese oxides and hydroxides such as Red Mediterranean soils which are situated on hard limestones and dolomites and are called terra rossa. For example, the occurrence and transformations of iron and manganese in a colluvial terra rossa toposequece of Northern Italy are excellently presented by BOERO & SCHWERTMANN (1987).

The Croatian soil classification puts terra rossa in the class of Cambic soils (ŠKORIĆ, 1986). F.A.O. legends (FAO, 1974) and Soil Taxonomy (SOIL SURVEY STAFF, 1975) classify most of terra rossa as Luvisols or Alfisols. However, the problem of classification of Red Mediterranean soils is still open and controversial. Namely, ROQUERO (1993) insisted on a more accurate classification of Red Mediterranean soils while FEDOROFF (1997), recognised and proposed six different types of argillic horizons in these soils, based on abundance and morphology of textural features in the B horizons. RACZ (1999) proposed a new approach for the classification of terra rossa soils in Croatia.

The aim of this paper is to present data on the distribution of iron and manganese in terra rossa from Istria and to evaluate any genetic implications. Terra rossa is the most extensive soil type in Istria. Its diagnostic feature is a red colour (5YR to 10R Munsell hues) and is the result of rubification, i.e. formation of haematite. Terra rossa covers hard limestone and dolomite in the form of a discontinuous layer ranging in thickness from a few centimetres to several metres and is considered a polygenetic palaeosol or pedo-sedimentary colluvial

complex (DURN, 1996; DURN et al., 1999). DURN et al. (1999) presented evidence for the polygenetic nature of terra rossa in Istria, based on a detailed mineralogical and geochemical investigation. They concluded that both loess, older than that of the Upper Pleistocene age, and flysch might have contributed to the genesis of terra rossa. DURN et al. (1999) also found that the arithmetic means of two populations (Fe_d in 45 terra rossa samples from various locations around the world and Fe_d in 40 samples from Istria) represent two independent estimates of the same population (Fe_d in terra rossa) and concluded that this supports BOERO & SCHWERTMANN's (1989) conclusion, that the rather limited extent of the variation of selected Fe-oxide characteristics may indicate a specific pedogenic environment in which terra rossa is formed.

In this paper terra rossa refers to reddish soils (5YR to 10R dry Munsell colours) overlying hard and permeable limestone and dolomite.

2. STUDY AREA

The Istrian peninsula belongs to the NW part of the Adriatic Carbonate Platform and is composed of Upper Jurassic and Cretaceous shallow water carbonate-rocks, Palaeogene carbonate and clastic rocks, and Neogene and Quaternary sediments. The Jurassic-Cretaceous-Palaeogene carbonate plain of southern and western Istria, Cretaceous-Palaeogene carbonate-clastic zone characterised by overthrusting structures in eastern and north-eastern Istria, and the Palaeogene flysch basin of central Istria are three main regions in Istria from the geological point of view (VELIĆ et al., 1995). Istria is an example of a non-isolated karst terrain which was effected by karst processes, (Neo)tectonic activity and input of external material since the Late Tertiary (DURN et al., 1999). The most important external material was loess, the deposition of which, according to CREMASCHI (1990), has affected Istria and the Dalmatian Archipelago since the early Middle Pleistocene.

Terra rossa is dominantly situated on the Jurassic-Cretaceous-Palaeogene carbonate plain of southern and western Istria (Fig. 1) in the form of a discontinuous surface layer up to 2.5 metres thick or the infill of cracks and sinkholes. Pedo-sedimentary colluvial complexes which are found in karst depressions and are up to 14 metres thick also contain terra rossa like material (DURN 1996; DURN et al., 1999).

3. MATERIALS AND METHODS

Terra rossa samples from B horizons on limestone and dolomite of Jurassic and Cretaceous age were sampled. Forty samples were taken at 14 localities. Particle size analysis was determined on the <2 mm fraction after dispersion in water and treatment with ultrasound. Selected fractions were obtained using wet sieving and quantitative separation by sedimentation in cylinders after the appropriate settling time. Total iron (Fe_t) and manganese (Mn_t) were measured in <2 mm fraction of terra rossa samples with an XRF spectrometer (Philips PW 1404) using pressed powder pellets. Iron and manganese extractable with Na dithionite-citrate bicarbonate (Fe_d, Mn_d) were obtained after the method of MEHRA & JACKSON (1960) modified after U. SCHWERTMANN (pers. comm.), and measured with AAS (Pye-Unicam SP9). Iron and manganese extractable with ammonium oxalate (Fe_o, Mn_o) were acquired according to SCHWERTMANN (1964) and measured with AAS (Pye-Unicam SP9).

The iron oxide mineralogy of the clay fraction (<2 µm) of terra rossa was determined by X-ray powder diffraction (XRD) using a Philips diffractometer (graphite monochromator, CuK radiation, proportional counter). XRD patterns of non-oriented samples were taken after the following treatments: (a) air-drying and (b) dissolution in HCl (1:1).

4. RESULTS

4.1. Mineralogy

XRD analysis showed that the clay fraction of all terra rossa samples from Istria contains both haematite and goethite (Fig. 2). Broadening of diagnostic haematite and goethite XRD peaks indicates a low degree of crystallinity and their pedogenic origin. Munsell hue of dry terra rossa samples ranges between 5YR and 10R (Table 1) which indicates that red haematite masks the yellow colour of goethite. Ferrihydrite (which also gives a red colour to soil) and Mn-oxides or hydroxides were not detected by XRD, probably due to their small amounts and poor crystallinity.
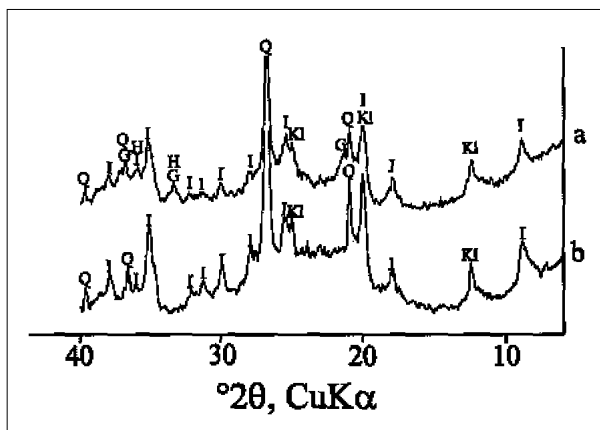

Fig. 2 Characteristic parts of XRD patterns of terra rossa sample 1 (<2 µm fraction). Legend: a) air dried; b) treated with HCl (1:1, 24 h); Kl - kaolinite; I - illitic material; Q - quartz; H - haematite; G - goethite.

Sam.	Depth (cm)	Color	Clay*	Silt*	Sand*	Fe_t*	Fe_d*	Fe_o	Fe_t/Fe_d*	Fe_o/Fe_d	$Fe_d/$clay	Mn_t	Mn_d	Mn_o	Mn_d/Mn_t	Mn_o/Mn_d
Profile Sjenokoša																
1.	20-35	5YR4/8	41.1	58.3	0.6	4.20	2.78	0.39	0.66	0.14	0.068	1037	909	606	0.88	0.67
2.	35-100	5YR5/6	47.5	51.2	1.4	4.44	2.96	0.39	0.67	0.13	0.062	937	821	646	0.88	0.79
3.	100-145	5YR5/6	49.4	49.1	1.5	4.60	2.89	0.37	0.63	0.13	0.059	999	805	518	0.81	0.64
4.	145-200	5YR5/6	51.8	46.0	2.2	4.68	2.84	0.36	0.61	0.13	0.055	1192	558	330	0.47	0.59
5.	200-225	5YR5/6	54.2	45.3	0.5	5.12	3.22	0.44	0.63	0.14	0.059	1015	1000	839	0.99	0.84
6.	225-265	5YR5/6	53.0	46.1	0.9	4.90	3.34	0.53	0.68	0.16	0.063	984	969	694	0.98	0.72
7.	265-300	5YR5/6	57.1	42.6	0.2	5.29	3.22	0.40	0.61	0.12	0.056	883	800	555	0.91	0.69
8.	300-325	5YR4/6	61.1	38.6	0.3	5.75	3.78	0.60	0.66	0.16	0.062	1185	1100	1093	0.93	0.99
9.	325-335	5YR4/6	59.8	40.1	0.1	5.45	3.80	0.56	0.70	0.15	0.064	875	667	428	0.76	0.64
10.	335-360	5YR4/6	71.7	28.3	0.1	5.92	3.57	0.39	0.60	0.11	0.050	976	494	303	0.51	0.61
11.	360-400	5YR5/6	59.9	39.8	0.3	4.91	3.43	0.48	0.70	0.14	0.057	782	484	302	0.62	0.62
12.	400-450	2.5YR4/6	60.1	39.4	0.4	4.97	3.94	0.62	0.79	0.16	0.066	1084	1020	909	0.94	0.89
13.	450-550	2.5YR4/6	63.1	36.4	0.5	5.22	3.39	0.36	0.65	0.11	0.054	1200	391	251	0.33	0.64
14.	550-650	2.5YR4/6	64.6	34.8	0.6	5.51	3.79	0.31	0.69	0.08	0.059	1386	1173	933	0.85	0.80
15.	650-750	2.5YR5/8	66.4	32.7	0.9	5.51	3.96	0.30	0.72	0.08	0.060	1348	1127	909	0.84	0.81
16.	750-850	2.5YR4/6	62.9	36.2	0.8	5.41	4.00	0.28	0.74	0.07	0.064	1348	1255	1052	0.93	0.84
Profile Kamnik																
19.	10-25	5YR4/6	32.5	65.1	2.4	3.37	1.86	0.29	0.55	0.16	0.057	930	614	532	0.66	0.87
19A	25-50	5YR4/6	35.7	61.9	2.4	3.40	2.03	0.30	0.60	0.15	0.057	852	523	513	0.61	0.98
Profile Pomer																
22.	18-30	5YR5/6	45.1	52.7	2.2	3.74	2.42	0.31	0.65	0.13	0.054	1084	733	655	0.68	0.85
23.	30-62	2.5YR4/8	64.2	34.0	1.9	6.20	4.15	0.47	0.67	0.11	0.065	1084	782	626	0.72	0.80
24.	62-105	2.5YR4/8	71.1	28.0	0.9	6.03	4.11	0.37	0.68	0.09	0.058	1084	817	661	0.75	0.81
25.	105-130	10R4/8	70.2	28.7	1.1	5.60	3.91	0.38	0.70	0.10	0.056	930	662	512	0.71	0.77
Profile Poreč																
53.	15-35	5YR4/6	59.4	39.5	1.1	6.10	4.01	0.46	0.66	0.12	0.054	1240	1093	741	0.88	0.68
55.	35-50	2.5YR5/6	74.1	25.2	0.8	4.70	3.19	0.36	0.68	0.11	0.054	1007	714	490	0.71	0.69
Profile Mondolaco																
60.	12-30	2.5YR5/6	61.3	36.0	2.7	6.57	5.20	0.35	0.79	0.07	0.085	930	897	630	0.96	0.70
61.	30-60	2.5YR5/6	67.7	30.8	1.5	6.70	5.11	0.30	0.76	0.06	0.075	1782	1596	1072	0.90	0.67
Profile Novigrad																
131.	9-20	5YR4/6	55.7	43.2	1.1	4.04	3.19	0.46	0.79	0.14	0.057	1471	956	773	0.65	0.81
132.	20-42	5YR4/6	60.3	38.6	1.2	412	3.64	0.36	0.88	0.10	0.060	1394	946	760	0.68	0.80
133.	42-63	2.5YR4/6	70.1	29.0	1.0	6.07	4.61	0.34	0.76	0.07	0.066	775	543	337	0.70	0.62
134.	63-80	2.5YR4/6	73.1	26.0	0.9	6.12	4.62	0.37	0.75	0.08	0.063	775	676	446	0.87	0.66
135.	80-112	2.5YR4/6	73.5	25.4	1.1	6.20	4.71	0.30	0.76	0.06	0.064	620	395	202	0.64	0.51
136.	112-150	2.5YR4/6	77.2	21.9	0.9	6.51	4.90	0.36	0.75	0.07	0.063	775	477	308	0.62	0.65
Single samples																
42.	5-15	5YR5/6	46.8	47.9	5.3	4.06	2.67	0.52	0.66	0.20	0.057	2401	1956	1900	0.81	0.97
52.	10-30	2.5YR4/8	42.1	55.3	2.5	5.47	3.76	0.30	0.69	0.08	0.089	387	287	87	0.74	0.30
100.	10-25	2.5YR4/8	72.1	26.8	1.1	6.67	5.24	0,47	0.79	0.09	0.073	620	326	275	0.53	0.84
101.	10-25	2.5YR5/8	73.8	25.4	0.8	7.06	5.74	0,48	0.81	0.08	0.078	779	394	201	0.51	0.51
234.	5-15	5YR4/8	35.8	61.1	3.1	3.38	2.30	0.25	0.68	0.11	0.080	1007	749	656	0.74	0.88
235.	5-10	2.5YR4/6	35.1	63.9	1.0	4.13	3.53	0.32	0.85	0.09	0.101	2169	1495	1252	0.69	0.84
236.	5-10	2.5YR4/6	42.1	57.3	0.6	4.33	3.31	0.36	0.76	0.11	0.079	1162	757	549	0.65	0.73
237.	5-10	2.5YR4/6	59.1	40.4	0.5	5.45	3.99	0.36	0.73	0.09	0.068	1084	730	463	0.67	0.63

Table 1 Particle size analysis, total, dithionite and oxalate extractable iron (%) and manganese (ppm) in terra rossa samples (<2 mm). Color (dry) after MUNSELL SOIL COLOR CHARTS (1994). Clay (<2 µm), silt (2-63 µm) and sand (>63 µm); * data from DURN et al. (1999).

SCHWERTMANN & TAYLOR (1989) stated that synthetic haematite crystals produced from ferrihydrite at near-pedogenic conditions generally exhibit a hexagonal morphology. Estimated crystal size of haematite from the XRD and TEM data according to the same authors is 20-50 nm in width and 10-20 nm in thickness. According to TORRENT & SCHWERTMANN (1987) with the increased size of haematite crystals the colour changes from red to purple. In order to establish the colour of haematite in relation to the size of haema-
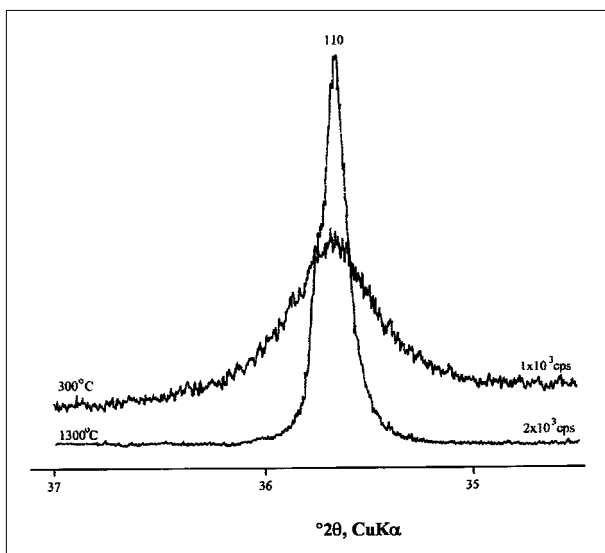
Fig. 3 The profiles of the 110 line of haematite prepared by heating of goethite at 300° and 1300°C.

tite crystals, we prepared several samples of haematite by heating (for 1 hour) fine grained goethite at following temperatures: 300°, 500°, 700°, 900°, 1000° and 1300°C. With the increased temperature of heating, the size of haematite crystals also increased, which resulted in smaller broadening of XRD lines in relation to the instrumental broadening. The profiles of the 110 line at 17.9° for haematite samples prepared at 300° and 1300°C are shown in Fig. 3. The size of haematite crystals in direction <110> was determined from broadening of the 110 line after correction for instrumental broadening. The 110 line of haematite prepared at 1300°C was used as a measure for instrumental broadening. The size of haematite crystals prepared at 300°, 500° and 700°C is about 21, 22 and 28 nm respectively, and their colour (powder) is red (10R4/8). The size of crystals prepared at 900°C is about 45 nm and they are dark red in colour (10R3/6). After heating to 1000°C, crystal size increased to about 75 nm and colour changed to dusky red (10R3/4). The colour of a sample prepared at 1300°C is purple-red (no matching colour with Munsell Soil Colour Charts). We also pre-

pared two homogeneous mixtures with a powder of kaolinite (33 wt.%), mica (30 wt.%), glass (20 wt.%), quartz (5 wt.%), goethite (6 wt.%) and haematite (6 wt.%). Mixture 1 contained haematite prepared at 300°C while mixture 2 contained haematite prepared at 1000°C. Both mixtures matched the average composition of terra rossa clay fraction with two exceptions. The clay fraction of natural terra rossa contains illitic material and amorphous inorganic compound instead of mica and glass. The colour of the clay fraction of natural terra rossa is almost identical to the colour of mixture 1 which contain haematite prepared at 300°C. This matching of colour and broadening of 110 line at 17.9° (Fig. 2) clearly indicate that the size of haematite crystals in analysed terra rossa samples is lower than 50 nm which is in accordance with investigation of BOERO & SCHWERTMANN (1989).

4.2. Total, Na dithionite-citrate bicarbonate and ammonium oxalate extractable iron and manganese

The results of the analysis of total, Na dithionite-citrate bicarbonate and ammonium oxalate extractable iron and manganese are presented in Table 1. Mean values Fe_t, Fe_d and Fe_o are 5.19%, 3.68% and 0.39% respectively (Table 2). The mean value of the Fe_d/Fe_t ratio, which is taken as an index of weathering (e.g. ARDUINO et al., 1984; BOERO & SCHWERTMANN, 1987; BECH et al., 1997) is 0.7 and reflects quite a high degree of weathering of Fe-containing primary silicates. Relatively uniform Fe_d/Fe_t ratios in the analysed profiles (Table 1) are also shown by the high positive correlation coefficient (Fig. 4) and point to a clear relationship between Fe_d and Fe_t in terra rossa. The clay content in analysed terra rossa samples increases with depth in the profiles (Table 1). An exception is the Sjenokoša profile, a colluvial terra rossa complex composed of superimposed features of colluviation and pedogenesis, where the clay content increases with depth within the each superimposed cycle (DURN, 1996; DURN et al., 1999). Fe_d/clay ratios are relatively uniform (Table 1, Fig. 5) and clearly indicate a predom-

	n	x	s	CV (%)	0.95 C.I.
Fe_t*	40	5.19	0.99	19.07	4.88-5.51
Fe_d*	40	3.68	0.89	24.18	3.40-3.96
Fe_o	40	0.39	0.09	23.08	0.36-0.42
Fe_d/Fe_t*	40	0.70	0.07	10.00	0.68-0.72
Fe_o/Fe_d	40	0.112	0.033	29.46	0.102-0.122
Mn_t	40	1089	379	34.80	968-1210
Mn_d	40	817	353	43.21	704-930
Mn_o	40	625	341	54.56	516-734
Mn_d/Mn_t	40	0.74	0.15	20.27	0.69-0.79
Mn_o/Mn_d	40	0.73	0.14	19.18	0.685-0.775

Table 2 Basic statistics for total, dithionite and oxalate extractable iron (%) and manganese (ppm) in terra rossa samples (<2 mm). Legend: n) number of samples; x) arithmetic mean; s) standard deviation; CV) coefficient of variation (%); 0.95 C.I.) confidence interval.
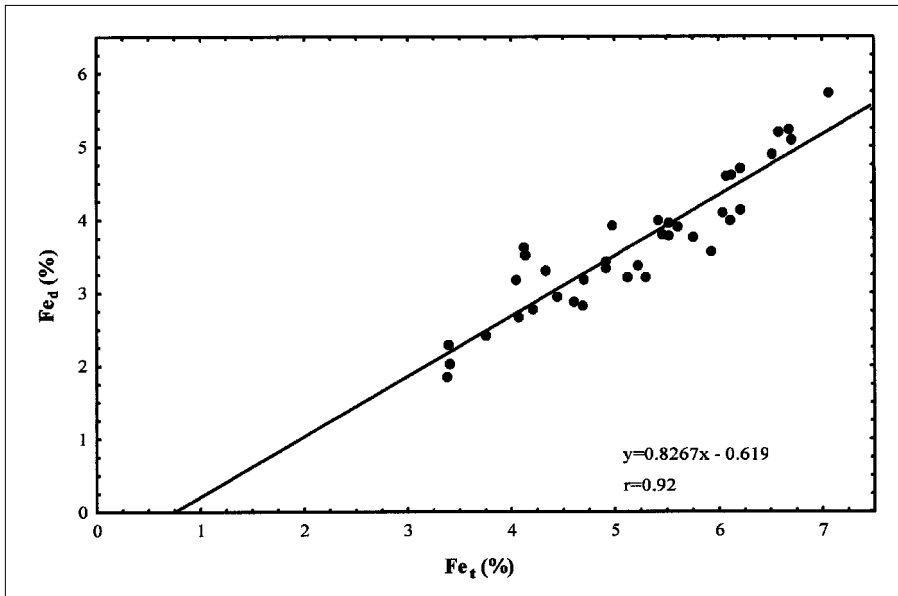
* data from DURN et al. (1999).

Fig. 4 Ratio between dithionite soluble iron (Fe_d) and total iron (Fe_t) in terra rossa; r is significant at level $p<0.01$.
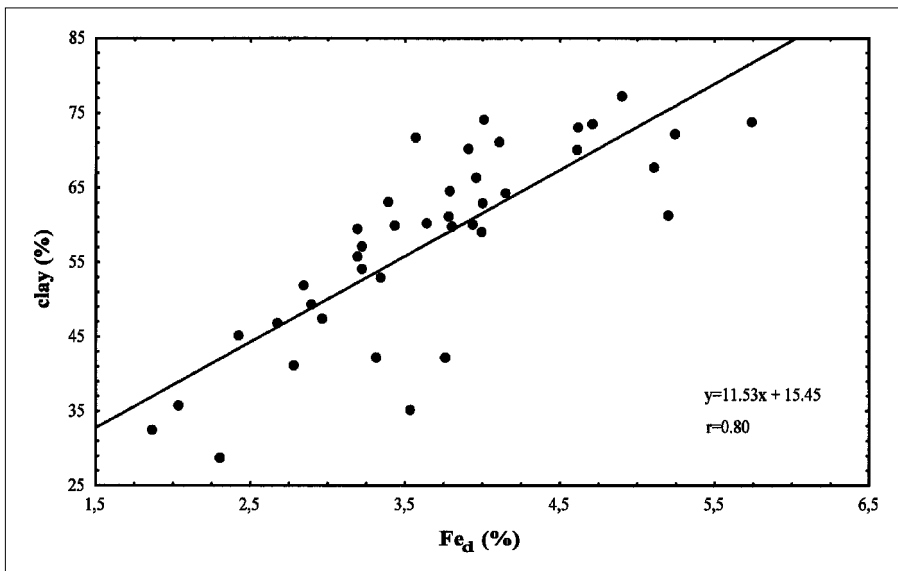

Fig. 5 Ratio between the amount of clay fraction (<2 µm) and dithionite soluble iron (Fe_d) in terra rossa; r is significant at level $p<0.01$.
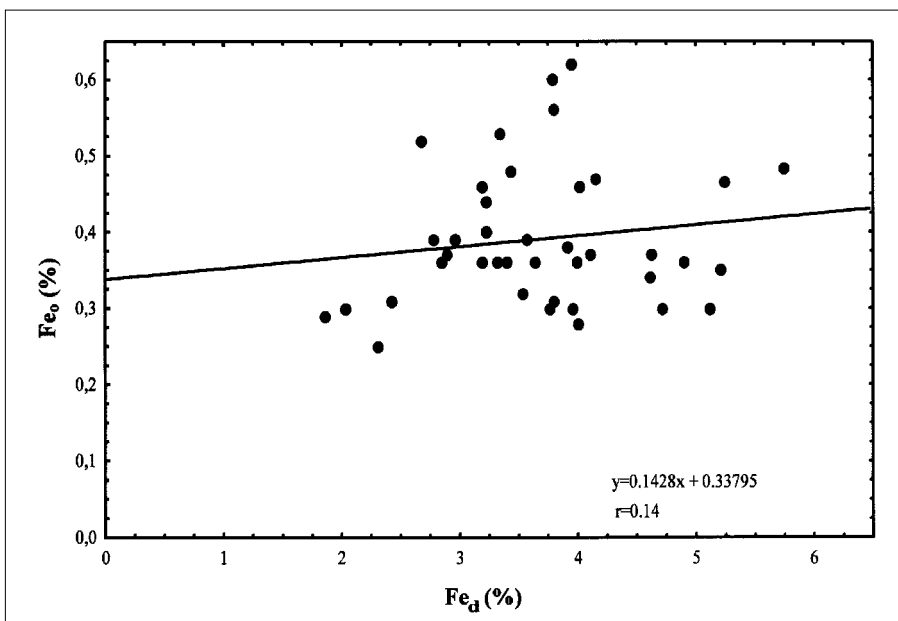

Fig. 6 Ratio between oxalate extractable iron (Fe_o) and dithionite extractable iron (Fe_d) of terra rossa samples; r is not significant at the level $p<0.01$.

inance of co-illuviation of clay and Fe oxides, i.e. connection of Fe oxides with the clay fraction. Low values of Fe_o (Tables 1 and 2) point to the low content of poorly crystalline Fe oxides in analysed terra rossa. Fe_o/Fe_d ratios in the analysed profiles vary (Table 1, Fig. 6). In the upper part of the Pomer, Poreč and Novigrad profiles (5YR Munsell hues) Fe_o/Fe_d ratios are higher than in the lower part of those profiles (2.5YR and 10R Munsell hues). Significant positive correlation (r = 0.7) between Fe_o and Fe_d in samples with 5YR Munsell hues was observed (Fig. 7).

Mean values of Mn_t, Mn_d and Mn_o are 1089 mg/kg, 817 mg/kg and 625 mg/kg respectively (Table 2). The mean value of the Mn_d/Mn_t ratio is 0.74 and indicates that most of the manganese in terra rossa is in the form of Mn oxides and hydroxides. A high positive correlation between Mn_d and Mn_t (Fig. 8) points to a clear relationship between Mn_d and Mn_t in terra rossa. Values of Mn_o are lower compared to those of Mn_d (Tables 1 and 2), and a high positive correlation between them (Fig.

9) is in accordance with the results of BLUME & SCHWERTMANN (1969) who concluded that the presence of Mn oxides and hydroxides in soil should be recognised on Mn_d values rather than on Mn_o values which does not provide any new qualitative information. Consequently, in further texts only Mn_d values will be evaluated. The lack of positive correlation between Mn_d and clay (Fig. 10) and Mn_d and Fe_d (Fig. 11) show that Mn oxides and hydroxides are not connected with the clay fraction and Fe oxides. Namely, they either do not participate in the co-illuviation of clay and Fe oxides, or are remobilized later due to successive processes.

5. DISCUSSION AND CONCLUSION

The association of haematite and goethite as predominantly pedogenic mineral phases, and the rather limited variation of selected Fe oxide characteristics in terra
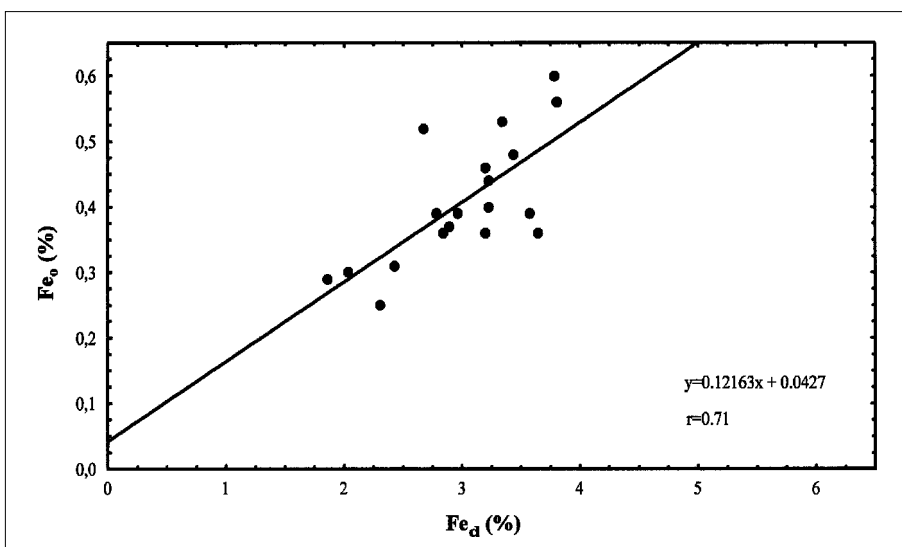

Fig. 7 Ratio between oxalate extractable iron (Fe_o) and dithionite extractable iron (Fe_d) of 5YR terra rossa samples; r is significant at the level p<0.01.
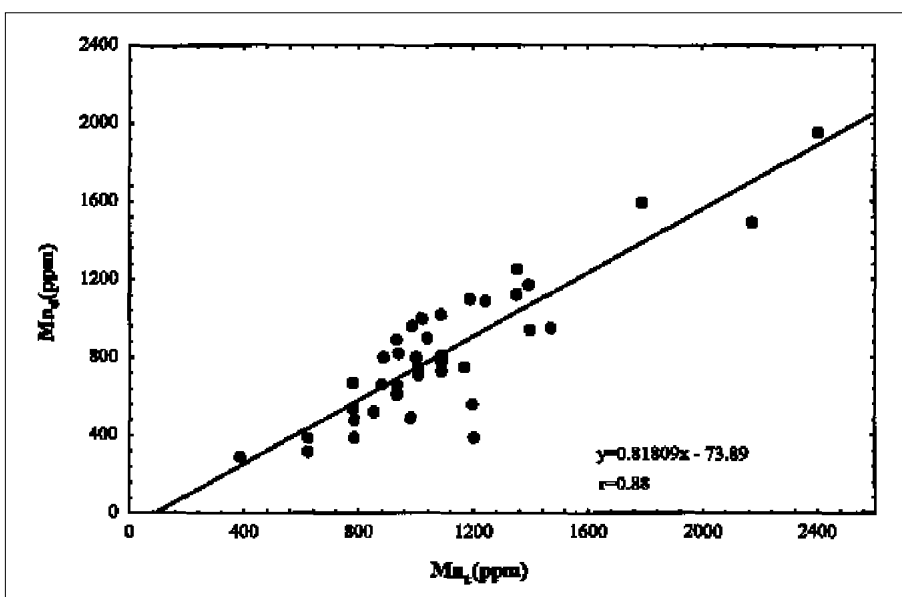

Fig. 8 Ratio between dithionite extractable manganese (Mn_d) and total manganese (Mn_t) of terra rossa samples; r is significant at the level p<0.01.
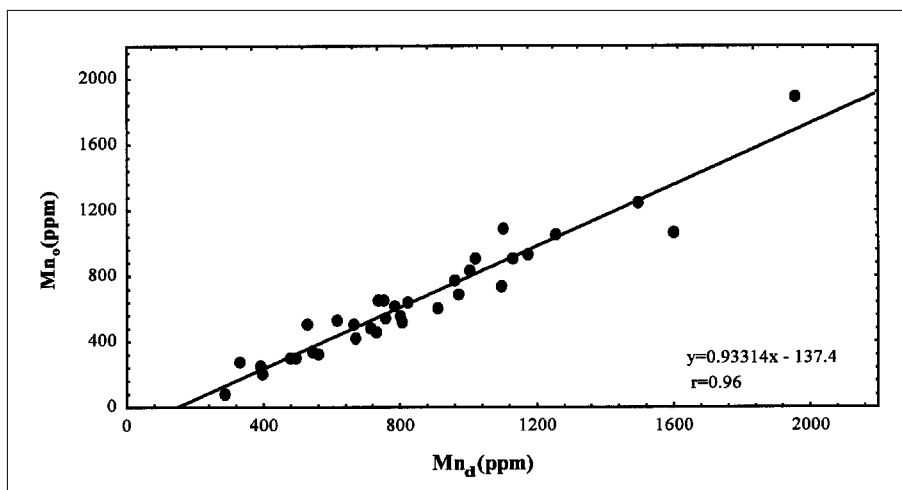
Fig. 9 Ratio between oxalate extractable manganese (Mn_o) and dithionite extractable manganese (Mn_d) of terra rossa samples; r is significant at the level $p<0.01$.
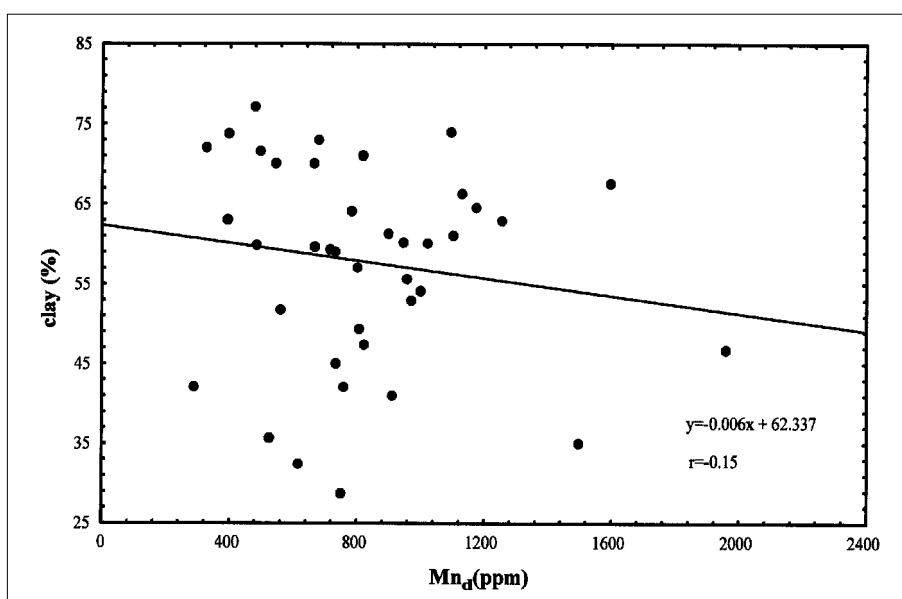

Fig. 10 Ratio between the amount of clay fraction (<2 µm) and dithionite extractable manganese (Mn_d) of terra rossa samples; r is not significant at the level $p<0.01$.

rossa from Istria, indicate specific pedogenic environment in which terra rossa is formed. Our results match those of BOERO & SCHWERTMANN (1989) who concluded that this pedogenic environment is characterized by an association of a Mediterranean climate, high internal drainage and neutral pH conditions. In the 30 samples examined (fraction <2 µm) they also estimated that the haematite/(haematite+goethite) ratios averaged 0.62 ± 0.055 i.e. the content of haematite is higher than the content of goethite in terra rossa. SINGER et al. (1998) interpreted the difference in iron oxide mineralogy between terra rossa (dominated by haematite) and rendzina (dominated by goethite) developed on limestones in Israel as a consequence of soil climate, specifically the moisture regime of two soils.

Poorly crystalline Fe oxides were not detected with XRD in analysed terra rossa. However, low values of Fe_o (Tables 1 and 2) point to their very low (probably ferrihydrite) content. This was expected because most of the Fe-oxides in fersialitic soils are crystallised (BECH et al., 1997).

Relatively uniform Fe_d/clay ratios (Table 1, Fig. 5) clearly indicate a connection of Fe oxides with the clay fraction, as iron oxides are translocated downwards together with clay illuviation. The main pedogenic process which characterises terra rossa in Istria is the accumulation of clay and is manifested through: (1) clay illuviation in the form of coatings and/or (2) microaggregates incorporated in the groundmass due to argilloturbation and soil stress (DURN, 1996). According to FEDOROFF (1997) rubification occurs in upper horizons, then rubified soil material is translocated with clays to depth.

In general, the Fe_o/Fe_d ratio decreases with depth in the Kamnik, Pomer, Poreč, Mondolaco and Novigrad profiles. A decrease of this ratio at depth in profiles was also observed by BECH et al. (1997) in some red Mediterranean soils from northern Spain. Significant positive correlation (r = 0.7) between Fe_o and Fe_d in samples with 5YR Munsell hues, and the higher content of Fe_o in samples with 5YR Munsell hues (0.137 %) compared to samples with 2.5YR and 10R Munsell
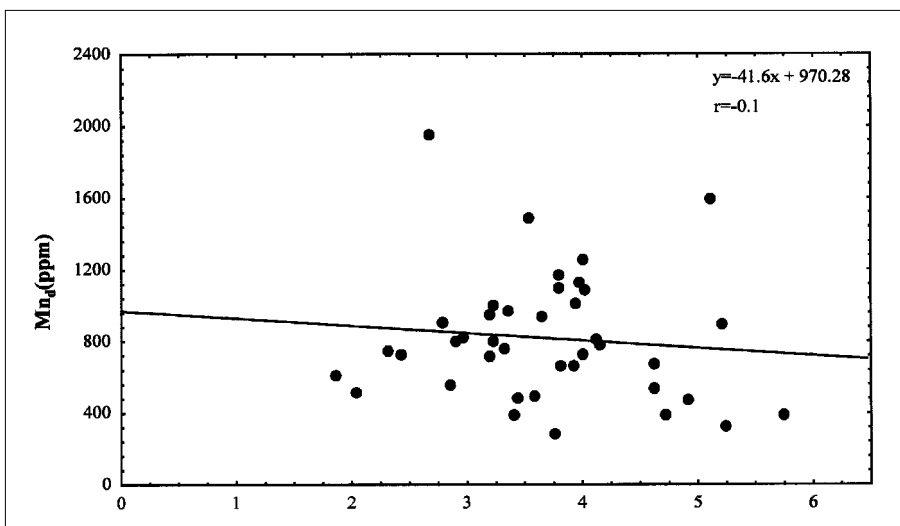
Fig. 11 Ratio between dithionite extractable manganese (Mn_d) and dithionite extractable iron (Fe_d) of terra rossa samples; r is not significant at the level p<0.01.

hues (0.089 %) may indicate a difference between those two groups of samples in respect to their pedogenic environment and/or parent material and, consequently, their content of poorly crystalline Fe oxides. The difference in pedogenic environment can be explained with the higher content of organic material in the upper parts of analysed profiles. BECH et al. (1997) concluded that there is a particular tendency for Fe_o to correlate with organic matter content (r = 0.68). Namely, organic matter in soil inhibits the crystallisation of Fe oxides (BLUME & SCHWERTMANN, 1969). During recent or subrecent pedogenesis a yellowing process might have occurred by preferential dissolution of haematite due to the higher thermodynamic stability of goethite. According to BOERO & SCHWERTMANN (1987), during that process the goethite/haematite ratio increases, Fe_d does not change significantly while Fe_o may increase if inhibitors which prevent its transformation to more stable Fe oxide phases are present. The presence of external materials in the upper parts of terra rossa profiles in Istria was postulated by ŠINKOVEC (1974) and ŠKORIĆ (1979), and confirmed by DURN (1996) and DURN et al. (1999), who found low-charge vermiculite or high-charge smectite in the <0.2 μm fraction of terra rossa samples which are situated bellow or near Upper Pleistocene loess in Savudrija. DURN et al. (1999) concluded that the presence of this mineral in those samples may indicate its aeolian origin because it was detected as one of the main mineral phases in fine clay of the Upper Pleistocene loess in Savudrija which post-dated terra rossa formation. They also discovered that both loess older than that of the Upper Pleistocene age and flysch might have contributed to the genesis of terra rossa.

We interpret the lack of a positive correlation between Mn_d and clay (Fig. 10) and Mn_d and Fe_d (Fig. 11) as a consequence of hydromorphic processes which post-dated co-illuviation of clay and Fe oxides and resulted in the remobilization of manganese. During field work we observed the tendency of manganese

oxides and hydroxides to concentrate as concretions and coatings on different soil features, mainly in the lower part of investigated profiles.

Istria is an example of a non-isolated karst terrain which was affected by karst processes, Neotectonic activity and external material input since the Late Tertiary. Although climatic and biotic factors have changed during the Late Tertiary and Quaternary the pedogenic environment on the hard carbonate rocks of the Jurassic-Cretaceous-Palaeogene carbonate plain of southern and western Istria generally remained suitable for rubification (DURN, 1996; DURN et al., 1999). However, red Mediterranean soils can be affected by eluviation, yellowing and secondary hydromorphy because they have been exposed to various climatic fluctuations (FEDOROFF, 1997).

6. REFERENCES

ARDUINO, E., BERBERIS, E., CANARO, F. & FORNO, M.G. (1984): Estimating relative ages from iron-oxide/total iron ratios of soils in the western Po valley (Italy).- Geoderma, 33, 39-52.

BECH, J., RUSTULLET, J., GARIGÓ, J., TOBÍAS, F.J. & MARTÍNEZ, R. (1997): The iron content of some red Mediterranean soils from Northeast Spain and its pedogenic significance.- Catena, 28, 211-229.

BLUME, H.P. & SCHWERTMANN, V. (1969): Genetic evaluation of profile distribution of Al, Fe and Mn oxides.- Soil Sci. Soc. Am. Proc., 33, 438-444.

BOERO, V. & SCHWERTMANN, U. (1987): Occurrence and transformations of Iron and Manganese in a colluvial terra rossa toposequence of Northern Italy.- Catena, 14, 519-531.

BOERO, V. & SCHWERTMANN, U. (1989): Iron oxide mineralogy of terra rossa and its genetic Implications.- Geoderma, 44, 319-327.

CREMASCHI, M. (1990): The loess in Northern and Central Italy: a loess basin between the Alps and the Mediter-

ranean regions.- In: CREMASCHI, M. (ed.): The Loess in Northern and Central Italy. Centro di Studio per la Stratigrafia e Petrografia delle Alpi Centrali, Editrice Gutenberg, Milano, 15-19.

DURN, G. (1996): Origin, composition and genesis of terra rossa in Istria.- Unpublished PhD Thesis (in Croatian with English summary), University of Zagreb, 204 p.

DURN, G., OTTNER, F. & SLOVENEC, D. (1999): Mineralogical and geochemical indicators of the polygenetic nature of terra rossa in Istria, Croatia.- Geoderma, 91, 125-150.

FANNING, D.S. & FANNING, M.C.B. (1989): Soil, morphology, genesis, and classification.- John Wiley & Sons, New York, 395 p.

FAO (1974): Soil map of the World, 1:5 M, Volume 1, Legend.- Unesco, Paris.

FEDOROFF, N. (1997): Clay illuviation in Red Mediterranean soils.- Catena, 26, 171-189.

LOVLEY, D.R. & PHILLIPS, E.J.P. (1988): Manganese inhibition of microbial iron reduction in anaerobic sediments.- Geomicrobiology Jour., 6, 145-155.

LOVLEY, D.R. (1995): Microbial reduction of iron, manganese, and other metals.- Advances in Agronomy, 54, 175-231.

McKENZIE, R.M. (1989): Manganese oxides and hydroxides.- In: DIXON, J.B. & WEED, S.B. (eds.): Minerals in Soil Environments.- Soil Sci. Soc. Am., Madison, 439-465.

MEHRA, O.P. & JACKSON, M.L. (1960): Iron oxides removal from soils and clays by a dithionite-citrate-bicarbonate system buffered with sodium bicarbonate.- 7th Nat. Conf. Clays Clay Miner., 7, 317-327.

MUNSELL SOIL COLOR CHARTS (1994): Macbeth Division of Kollmorgem Instruments Corporation, New Windsor.

RACZ, Z. (1999): Current global and local issues and problems related to pedological research.- Agriculturae Conpectus Scientificus, 64/3, 231-241.

ROQUERO, C. (1993): Some problems on genesis and classification of red soils in Spain.- Second International Meeting on "Red Mediterranean Soils". Short papers and abstracts, Adana, Turkey, 8-10.

SCHWERTMANN, U. (1964): Differenzierung der Eisenoxide des Bodens durch photochemische Extraktion mit saurer Ammoniumoxalat-lösung.- Z. Pflanzenernähr. Bodenkund., 105, 194-202.

SCHWERTMANN, U. & FANNING, D.S. (1976): Iron-manganese concretions in hydrosequences of soils in Bavaria.- Soil Sci. Soc. Am. J., 40, 731-738.

SCHWERTMANN, U. & TAYLOR, R.M. (1989): Iron oxides.- In: DIXON, J.B. & WEED, S.B. (eds.): Minerals in Soil environments. 2nd ed., Soil Sci. Soc. Am. Book Series, 379-438.

SCHWERTMANN, U., MURAD, E. & SCHULZE, D.G. (1982): Is there Holocene reddening (hematite formation) in soils of oxeric temperate areas?- Geoderma, 27, 209-223.

SIDHU, P.S., SEHGAL, J.L., SINHA, M.K. & RANDHAWA, N.S. (1977): Composition and mineralogy of iron-manganese concretions from some soils of the Indo-Gangetic plain in northwest India.- Geoderma, 18, 241-249.

SINGER, A., SCHWERTMANN, U. & FRIEDL, J. (1998): Iron oxide mineralogy of terre rosse and rendzinas in relation to their moisture and temperature regimes.- Eur. Jour. of Soil Sci., 49, 385-395.

SOIL SURVEY STAFF (1975): Soil taxonomy: a basic system of soil classification for making and interpreting soil surveys. USDA Handbook No. 436, U.S. Gov. Printing Office, Washington.

ŠINKOVEC, B. (1974): The origin of terra rossa in Istria (in Croatian).- Geološki vjesnik, 27, 227-237.

ŠKORIĆ, A. (1979): Two-layer soil profile on the area of terra rossa in Istria (in Croatian).- Zemljište i biljka, 28, 111-131, Zagreb.

ŠKORIĆ, A. (1986): Origin, development and systematics of soil (in Croatian).- Spec. pub. of agricultural scientific meeting, Zagreb, 172 p.

ŠKORIĆ, A. (1987): Pedosphere of Istria (in Croatian).- Project Council of Pedological Map of Croatia, Spec. ed., book 2, Zagreb, 192 p.

TORRENT, J. & SCHWERTMANN, U. (1987): Influence of hematite on the colour of red beds.- J. Sedim. Petrol., 57, 121-125.

VELIĆ, I., TIŠLJAR, J., MATIČEC, D. & VLAHOVIĆ, I. (1995): A review of the geology of Istria.- In: VLAHOVIĆ, I. & VELIĆ, I. (eds.): 1st Croatian geological congress, Excursion guide-book, 21-30, Zagreb.