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

Goran DURN, Dragutin SLOVENEC and Marta ČOVIĆ

Key words: Terra rossa, Iron, Manganese, Iron oxides, Istria, Croatia.

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 Fe2+/Fe3+ ratio, taken as an index of weathering is 0.7 and reflects quite high degree of weathering of Fe-containing primary silicates. Relatively uniform Fe2+/clay ratios clearly indicate a predominance of co-illuviation of clay and Fe oxides. Low values of Fe2+ point to the low content of poorly crystalline Fe oxides in analysed terra rossa. Fe2+/Fe3+ ratios in the analysed profiles vary. In the upper part of the Pomer, Poreč and Novigrad profiles Fe2+/Fe3+ 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 Mn4+ and clay and Mn4+ and Fe3+ 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-Paleogene 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 affected 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 & TAYLOR, 1976). Iron oxides may occur evenly dispersed throughout the soil, concentrated in particular horizons or in certain morphological features such as mottles and nodules (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 pedogenic 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, lithiophorate 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 Mn4+ at a higher Eh than that at which Fe3+ may be reduced to the more mobile Fe3+ (FANNING & FANNING, 1989). Namely, LOVLEY (1995) stated that at pH 7 and 25°C reduction of Mn4+ begins below a redox of 526 mV, while reduction of Fe3+ 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 Mn4+, and Fe3+ reduction will not begin until Mn4+ 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
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\textsubscript{o} and Mn\textsubscript{o}, while dithionite-citrate bicarbonate extractable iron and manganese are labelled Fe\textsubscript{d} and Mn\textsubscript{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 toposequence 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) recognized 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 (VELIÆ 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, CuKα 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.
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 ferrhydrite 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-
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 Θ = 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 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 prepared 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 Θ = 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 Feₜ, Feₜ and Feₜ are 5.19%, 3.68% and 0.39% respectively (Table 2). The mean value of the Feₜ/Feₜ 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 Feₜ/Feₜ 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 Feₜ and Feₜ 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). Feₜ/clay ratios are relatively uniform (Table 1, Fig. 5) and clearly indicate a predom-

<table>
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<td>0.73</td>
<td>0.14</td>
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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 ($\text{Fe}_d$) and total iron ($\text{Fe}_t$) in terra rossa; $r$ is significant at level $p<0.01$.

Fig. 5 Ratio between the amount of clay fraction ($<2 \mu m$) and dithionite soluble iron ($\text{Fe}_d$) in terra rossa; $r$ is significant at level $p<0.01$.

Fig. 6 Ratio between oxalate extractable iron ($\text{Fe}_o$) and dithionite extractable iron ($\text{Fe}_d$) 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 Feₐ (Tables 1 and 2) point to the low content of poorly crystalline Fe oxides in analysed terra rossa. Feₒ/Feₐ ratios in the analysed profiles vary (Table 1, Fig. 6). In the upper part of the Pomer, Poreč and Novigrad profiles (5YR Munsell hues) Feₒ/Feₐ ratios are higher than in the lower part of those profiles (2.5YR and 10R Munsell hues). Significant positive correlation (r = 0.7) between Feₒ and Feₐ in samples with 5YR Munsell hues was observed (Fig. 7).

Mean values of Mnₒ, Mnₐ and Mnₐ are 1089 mg/kg, 817 mg/kg and 625 mg/kg respectively (Table 2). The mean value of the Mnₒ/Mnₐ 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 Mnₐ and Mnₐ (Fig. 8) points to a clear relationship between Mnₐ and Mnₐ in terra rossa. Values of Mnₐ are lower compared to those of Mn₀ (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 Mnₐ values rather than on Mnₒ values which does not provide any new qualitative information. Consequently, in further texts only Mnₐ values will be evaluated. The lack of positive correlation between Mnₐ and clay (Fig. 10) and Mnₐ and Feₐ (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
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 (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/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/clay 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 and Fe in samples with 5YR Munsell hues, and the higher content of Fe in samples with 5YR Munsell hues (0.137 %) compared to samples with 2.5YR and 10R Munsell hues.
The lack of a positive correlation between Mn\textsubscript{d} and clay (Fig. 10) and Mn\textsubscript{d} and Fe\textsubscript{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).

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