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# Understanding the (paleo)soils: From palaeoenvironmental reconstruction to the role of iron oxides and soil organic matter on the formation of the surface physicochemical properties and the aggregation processes

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A multi-proxy analytical approach (MPAA) in the investigation of (palaeo)soils that involves a detailed analysis of soil micromorphology, soil physics and chemistry, geochemistry, and bulk and clay mineralogy is crucial for the determination of the palaeoenvironment in which they were formed. The determination of the soil mineral composition and their surface properties that control the formation of soils by aggregation processes is necessary to understand their response to environmental changes (BRONICK & LAL, 2005). Soil aggregation is a complex process, which involves rearrangement of submicron- and micron-sized mineral particles into larger clusters by mutual physico-chemical and biological interactions between the mineral surfaces, various organic and inorganic compounds and microorganisms (SIX et al., 2004). Humic compounds are omnipresent in soils and they designate the most important compounds covering the surfaces of the minerals, particularly iron oxides and clay mineral particles (BALDOCK & BROOS, 2012). This lecture aims to demonstrate the significance of MPAA in three different cases, from profile description and palaeoenvironmental reconstruction, to the role of iron oxides and soil organic matter on the formation of the surface physicochemical properties and the aggregation processes. It is based on our previous (DURN et al., 2015; DURN et al., 2017) and current research within the NanoMin project (grant 2504, Croatian Science Foundation).

Case 1: A polygenetic soil formed on Late Glacial Loess on the Island of Susak

The complete polygenetic profile (A-2C1-2C2-3Btb-4Ck) was formed through both normal pedogenesis and erosion/sedimentation-driven pedogenesis, and is a result of the interaction of the sediments (loess) with environmental conditions from the Late Glacial throughout the Holocene (Fig. 1). This profile bears valuable imprints of climate, vegetation, land surface, and land use changes in this part of the Adriatic area for the time period covering the past 16 ka. A high-resolution approach enabled schematic reconstruction of polygenetic formation of the soil profile while the results of clay fraction analysis and micromorphology in particular helped to understand the genesis of the investigated soil at the Susak Island (e.g. inherited vs. pedogenic clay).

Case 2: (Paleo)soils formed in contrasting pedoenvironments (oxidizing vs. reducing) on pure Cretaceous limestones in Istria

Terra Rossa soils formed in an oxidizing pedoenvironment, while Cretaceous greenish-grey palaeosols (GGP) formed in a reducing one. While kaolinites and illitic material are dominant clay mineral phases in the clay fraction of Terra Rossa, the main clay mineral phases in GGP are illitic material and ordered and irregularly oriented illite/smectite mixed layer minerals. Terra Rossa soils are slightly enriched in Co and Pb and significantly enriched in REE compared to GGP. The important difference in the total REE content in analysed Terra Rossa soils can be attributed to the REE content of both parent carbonate rocks (their insoluble residues) and different external materials which have contributed in the genesis of Terra Rossa (loess, flysch, bauxite), modified by weathering processes which favour LREE enrichment. Sequential extraction analysis showed that Mn, Co and Pb, mainly bound to the reducible fraction, are potentially the most mobile trace elements in Terra Rossa. The enrichment of GGP in Cd, Sb, Ni, V and especially in U and Mo is considered typical of reducing environments (Fig. 2). Variation of the total REE content in GGP is much narrower compared to Terra Rossa soils. Total REE content in GGP is dominated by the residual fraction and probably also reflects parent materials (insoluble residue of limestone, aeolian and volcanic dust), modified in an acidic and reductive marshy pedoenvironment which favours HREE enrichment. Cd, Ni and Co, mainly bound to the adsorbed fraction are potentially the most mobile trace elements in GGP.

Case 3: The role of iron oxides and soil organic matter (SOM) on the formation of the surface physicochemical properties and the aggregation processes of the Terra Rossa and the Calcocambisol from Istria

Terra Rossa is the most common type of soil in Istria, an archetypal example of a non-isolated karst terrain that has been affected by karst processes, (neo)tectonic activity and contributions of external materials since the Late Tertiary. Their clay size fraction contains hematite as a dominant, and goethite as a minor iron oxide. The second most important and insufficiently investigated soil type in Istria is the Calcocambisol, a brown soil on limestone and dolomite. In comparison with Terra Rossa, this soil type contains a higher amount of organic matter while goethite was determined as the only well-crystallized iron oxide. The aim was to determine the character and the role of SOM and iron oxides on the formation of the surface physicochemical properties, electrophoretic mobility (EPM), specific surface area (SSA), and cation exchange capacity (CEC) of mineral particles that are main constituents of submicron- and micron-sized aggregates in selected Terra Rossa and Calcocambisol samples from B horizons. Specifically, the ultimate goal is to identify these properties on original soils and on the samples from which the SOM and the iron compounds were selectively removed. This study endeavours to contribute new evidence on the role of SOM and iron oxides in the formation of surface properties of mineral particles and to determine their role in the process of aggregation in these type of soils (Fig. 3).

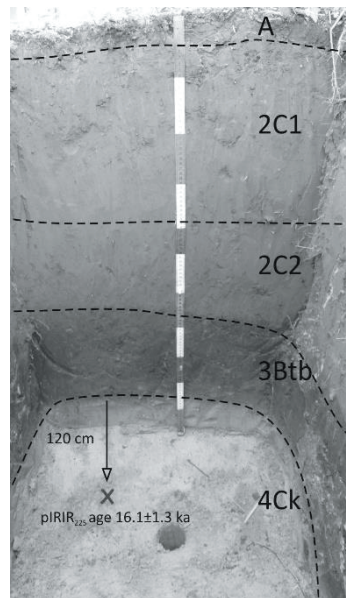


Figure 1. Polygenetic soil profile at the Susak Island (From: DURN et al., 2017).

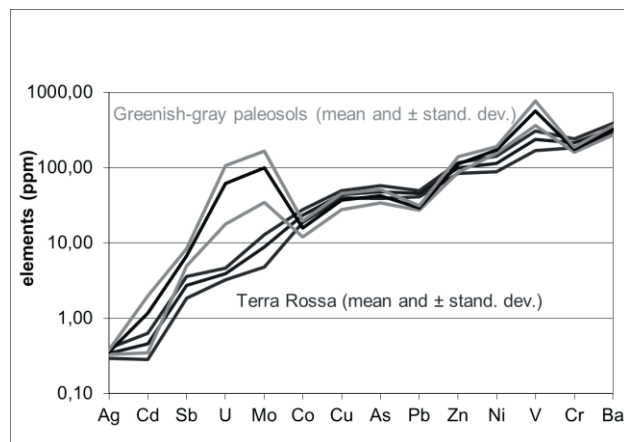


Figure 2. Distribution of trace elements in Terra Rossa and greenish-gray paleosols.

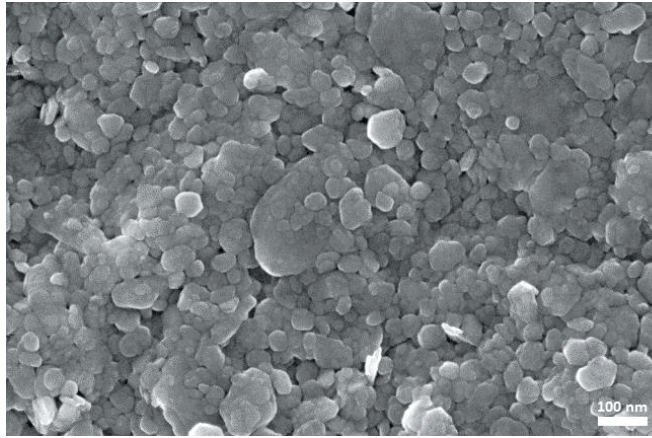


Figure 3. FESEM photomicrograph of Terra Rossa (submicron-sized fraction) after removal of iron oxides. A significant part of submicron-sized fraction appear in nanosized range.

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