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Soil formation and mineralogy of a Rhodic Luvisol — insights from magnetic and geochemical studies

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ABSTRACT

Relict *terra rossa* soil from the most south-eastern part of Bulgaria, characterized by transitional Mediterranean climate, has been comprehensively studied by integrating magnetic, geochemical and spectroscopic methods to reveal the origin, pedogenic processes and phases in soil development of this particular soil type. The red colored Rhodic Luvisol is developed on metamorphosed Triassic limestones. Magnetic methods, which include thermomagnetic analysis of susceptibility, isothermal remanent magnetization (IRM) acquisition and thermal demagnetization, IRM component analysis, hysteresis measurements, low-temperature (down to 10 K) IRM behavior, anhysteretic remanence and frequency dependent susceptibility, indicate the presence of three major magnetic phases — maghemite, hematite (Hm) and goethite (Gt). Hematite and goethite are identified also by diffuse reflectance spectroscopy (DRS). Depth variations of the ratio Hm/(Hm + Gt), deduced from the DRS spectra show higher hematite content in the upper soil horizons (A + B), while goethite's contribution is enriched in the lowermost part of the profile. A similar ratio, based on the established magnetic proxies for hematite and goethite, was constructed and its variations were compared with the DRS data. The magnetic proxy for Hm/(Hm + Gt) reflects the variations in the remanence-carrying mineral fraction of hematite and goethite and the obtained difference with the DRS data are ascribed to the presence of the paramagnetic (or superparamagnetic) goethite in the A and illuvial B_{t1} and B_{t2} horizons. The low ratio Fe_o/Fe_d between dithionite (Fe_d)- and oxalate (Fe_o)-extractable iron, and the large proportion of extractable iron with respect to total iron (Fe_d/Fe_{tot}) indicate an advanced degree of weathering. Depth variations of magnetic parameters and ratios (χ_{lf}, χ_{fd}, S-ratio) suggest magnetic enhancement with SP–SD maghemite grains, accompanied by magnetically stable magnetic carriers in the soil, while the parent material is magnetically depleted. Based on grain-size variations of the pedogenic maghemite phase, deduced from a χ_{ARM} vs. χ_{fd} plot, and variations in the content of hematite and goethite in depth, in the uppermost part of the profile, aging of the pedogenic iron oxides is assumed (grain growth from SP to SD and larger), while in the bottom part of B_{t1} and the B_{t2}, changes only in the concentration of maghemite are inferred. The presence of goethite in different parts of the profile and the mineralogy of Fe–Mn nodules are linked to more recent (Holocene) pedogenic changes in the profile. Analyses of trace and rare earth element content and magnetic data suggest possible contributions of aeolian dust flux from Sahara during the soil formation.

1. Introduction

Red soils occur mainly around the Mediterranean sea (Fig. 1a), receiving significant aeolian dust inputs from the Sahara region (Yaalon, 1997; Durn et al., 1999; Durn, 2003; Stuut et al., 2009). These particular types of soils, developed on hard limestones, are characterized by an intense red/brown color due to the high concentrations of ultra-fine pedogenic hematite. The soils are defined as "*terra rossa*" and received much attention in pedological, palaeoclimatic and provenance studies (Yaalon, 1997; Durn et al., 1999; Verheye and de la Rosa, 2005 and references therein) because of their specific properties, composition and evolution under the specific climate conditions.

In Bulgarian territory, only a small limited area in the most south-eastern part of the country is characterized nowadays by transitional Mediterranean climate (Fig. 1a). Under the existing specific conditions, characteristic red colored soils developed usually on the southern slopes of Strandja mountain. They are commonly classified as Chromic Luvisols, but have not been well studied. So far, contradictory opinions about their genesis still exist (Velizarova and Popov, 1999; Ninov, 2002). Moreover, soils developed under more temperate climates in south Bulgaria (Rhodopes mountain, Struma valley, etc.) are considered also under the term "*terra rossa*" (Gjurov and Artinova, 1999; Teoharov

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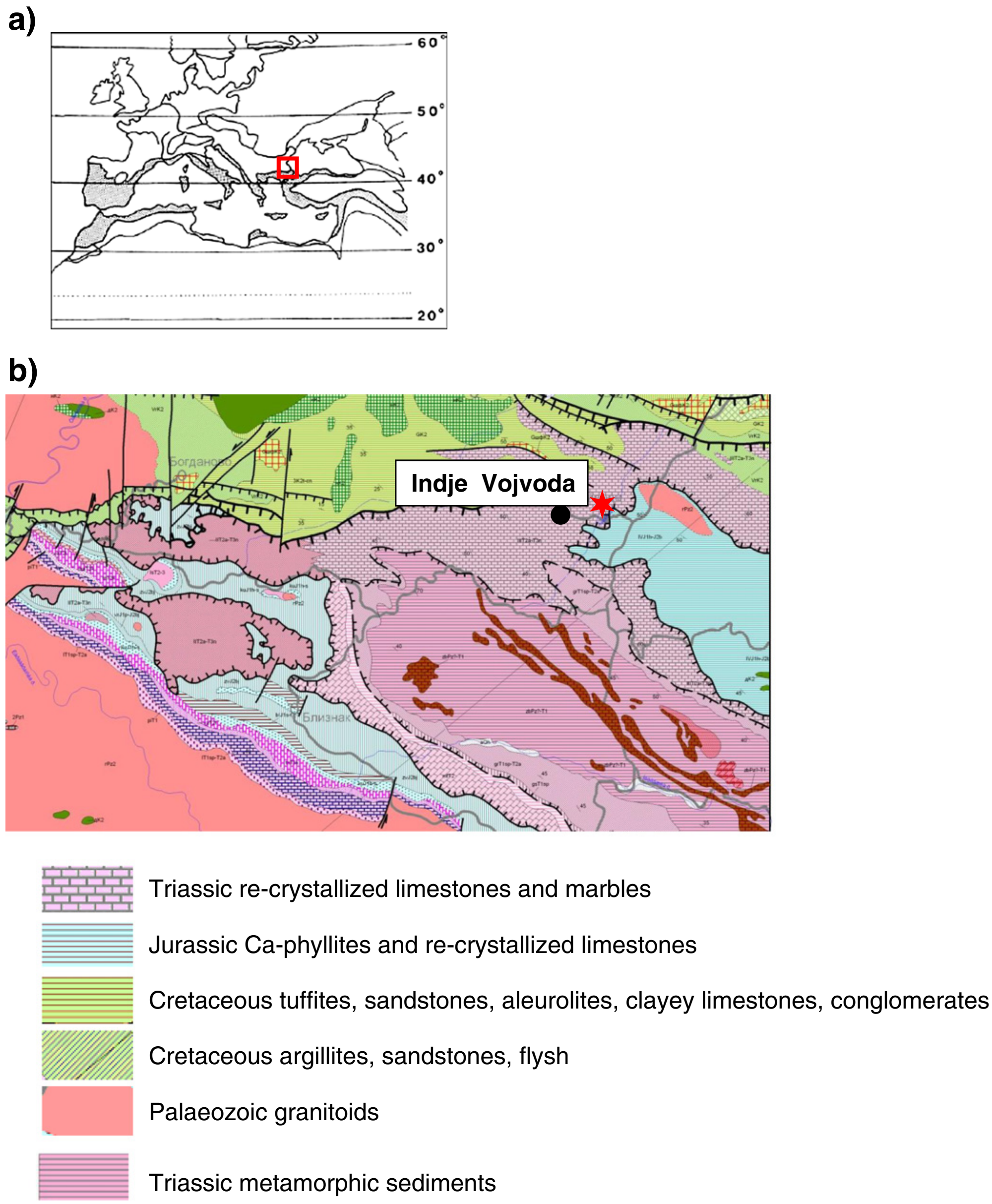

Fig. 1. a) Distribution of *terra rossa* in the Mediterranean area (according to Durn (2003)). The square indicates the sampling area in Bulgaria, and b) geological map of the study area (Strandja mountain) and location of the sampling site (filled star).

and Arsova, 1999). Therefore, it is important to determine whether the studied soil can be classified as Mediterranean type *terra rossa*.

Environmental magnetic methods have been extensively used for revealing genesis and palaeoenvironmental conditions under which the soils have developed. Iron plays an important role in soil formation, and the cycle of this element during pedogenesis is tracked by the transformation of magnetic minerals (Cornell and Schwertmann, 2003). Advances in rockmagnetic techniques for the characterization of natural materials, as well as experimental studies, focussed on deciphering the different pathways of Fe-oxides transformations in various environmental settings (e.g. Maher, 1998; Evans and Heller, 2003; Liu et al., 2012) provide the basis for identification of iron oxides, which in turn supply information about the (palaeo)environmental conditions required for their formation. Magnetic studies on soils from the temperate climatic belt (mainly of Chernozems and similar, well-drained soil types) revealed the dominant pedogenic iron oxide to be nanometer sized magnetite, which subsequently is oxidized to maghemite (Maher, 1988, 1998). Weakly magnetic iron oxides like hematite and goethite are also frequently detected in soils (Maher, 1998; Liu et al., 2004, 2006b).

It is well known that red-colored Mediterranean soils, most of them classified as Luvisols, are rich in hematite, which gives them the specific coloring (Boero and Schwertmann, 1989; Yaalon, 1997; Cornell and Schwertmann, 2003; Durn, 2003). Magnetic studies also have been performed on *terra rossa* soils from Mediterranean (Liu et al., 2010a; Torrent et al., 2010a,b) and red earth from China (Feng et al., 2009; Hu et al., 2009; Feng, 2011; Lu et al., 2012). All of them confirm the predominance of hematite over the other iron oxides.

Rock-magnetic and diffuse reflectance spectroscopy (DRS) characterizations of Calcic Luvisols from Spain (Torrent et al., 2010a) provided evidence for the newly proposed pathway of ferrihydrite transformation in soil (Barrón and Torrent, 2002; Barrón et al., 2003; Torrent et al., 2006) involving hydromaghemite as an intermediate product in the ferrihydrite transformation. A strong correlation between the concentrations of maghemite and hematite has been observed in magnetically enhanced soils of a Xeralf chronosequence in NW Spain (Liu et al.,