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## Integrated study of Red Mediterranean soils from Southern Italy

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## ABSTRACT

Terra Rossa is a typical Mediterranean soil characterized by an association of the Mediterranean climate, high internal drainage (due to the karstic nature of the underlying hard limestone) and neutral pH conditions. The genesis of this soil is a controversial subject in terms of the origin of the parent material, from the residual underlying (carbonate/dolomite) bedrock and/or from external (aeolian dust) contributions. We apply an integrated approach (chemical, physical, mineralogical and geochemical) to nine soil profiles of terra rossa from Apulia region (southern Italy), in order to investigate the main soil properties relating to soil weathering and pedogenetic processes, as well as to acquire knowledge on soil-bedrock relationships and their origin. Results showed that these terra rossa were generally clayey, had colors (moist) ranging from 2.5YR to 7.5YR Munsell hues and a mineralogical composition of mainly kaolinite, illite/mica and Fe-oxides (hematite and goethite). The pedogenetic indices (Feo/Fed, Fed/Fet) exhibited a generally high degree of crystallinity of iron forms and soil weathering. The correlation between illite/kaolinite ratio and pedogenetic indices, as well as that of kaolinite and hematite with the  $Fe_{\alpha}/Fe_{d}$  ratio indicated that weathering processes in the studied environments promoted the formation of both kaolinite and hematite from illite/mica minerals. Since the hematite/goethite ratio was generally higher than 1, rubification processes also occurred in these soils. The comparison of the geochemical composition of terra rossa with that of insoluble residues (obtained from the underlying limestone and dolomite rocks) indicated that a group of elements (such as Ti, Mn, Th) was more concentrated in terra rossa than in the insoluble residues, whereas another group (made up of Fe, K, Ca, Cr, Cu, Zr, Zn, Rb, Ni, As, Sr and Pb) was more concentrated in the insoluble residues than in terra rossa. The two groups of elements were considered to be different as a result of their having different sources, the first being allochtonous and the second mainly authoctonous. The additional correlation of Ti, Mn and Th with terra rossa clay content seemed to support the hypothesis of wind-blown long distance transport for these elements.

#### 1. Introduction

Terra rossa is a reddish, clayey or silty clayey soil, typical of the Mediterranean, characterized with high internal drainage and neutral pH conditions. Terra rossa is found covering limestone and dolomite hard rocks in karst regions as a discontinuous layer that ranges from a few centimeters to several meters in thickness (Durn et al., 1999; Durn, 2003; Merino et al., 2006; Torrent, 2005). The colors, ranging from 5YR to 10R Munsell hues, are an important diagnostic feature of terra rossa and reflect the intensity of the "rubification" process, i.e., the preferential formation of hematite over goethite (Schwertmann and Taylor, 1989). In Soil Survey Staff (1975) Mediterranean terra rossa are classified as Alfisols (Haploxeralfs or Rhodoxeralfs) to Ultisols, Inceptisols (Xerochrepts) and, to a lesser degree, Mollisols (Argixerolls or Haploxerolls). The nature and relationship of terra rossa to underlying limestones is a question that

has been greatly debated over recent decades and which has revealed different opinions regarding parent material and soil origin (Yaalon, 1997). Some authors consider that terra rossa may have developed from dissolution of the underlying carbonate rocks (Ahmad et al., 1966; Bronger et al., 1983; Feng et al., 2009; Ji et al., 2004a, 2004b; Kubiena, 1953; Moresi and Monghelli, 1988; Wei et al., 2013). However, other authors have emphasised that terra rossa cannot have been formed exclusively from the insoluble residue of carbonate rocks, that they have a polygenetic nature and that, depending on their geographic position, they might have received external materials, such as volcanic ash, non-carbonate rocks, and aeolian contributions during pedogenesis (Durn et al., 1999; Durn et al., 2007; Jackson et al., 1982; Liu et al., 2013; Muhs and Budahn, 2009; Yaalon, 1997; Sandler et al., 2015). Finally, other studies have inferred that terra rossa was formed by metasomatic replacement processes (Lucke et al., 2014; Zhu and Li, 2002).

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However, Boero and Schwertmann (1989) state that the formation of terra rossa was related to the rubification process, independently from the source of the primary Fe and the general pedoenvironment. The mineral composition of terra rossa in the Mediterranean area consists of Fe crystalline oxides (hematite and goethite) together with kaolinite, micaceous minerals, vermiculite, quartz and a low amount of feldspars (Torrent, 2005). Fe-bearing smectite and kaolinite are reported for red soils developed from basaltic parent material in Sardinia region (Vingiani et al., 2004; Vingiani et al., 2010), as well as kaolinite in red vitric and non andic soils in Calabria region (southern Italy) (Vingiani et al., 2014). According to Moresi and Monghelli (1988), in addition to the above mentioned minerals it is common to find. Al oxides (boehmite) and hydroxides (gibbsite), and Ti-oxides in the silt and sand fractions of terra rossa from Apulia (southern Italy). Torrent and Cabedo (1986) interpret the distribution with depth of the different forms of iron in terra rossa which developed on calcarenites in southern Spain as a consequence of the soil climate, specifically the drainage and, consequently, the moisture regime of the soils. Boero and Schwertman (1987) suggest that the presence of fractured limestones below terra rossa might promote a "rubification" process with a preferential formation of hematite. These authors found that Fed, Fed/Fet, hematite/goethite ratios are strictly related to the specific pedoenvironment in which terra rossa formed. They suggest that Terra rossa found its specific pedoenvironment in the Mediterranean, where there is an association of dry summer climate, high internal drainage (due to the karst nature of the hard limestone) and neutral pH conditions.

In an attempt to acquire a better knowledge of the main chemical, physical, mineralogical and geochemical properties relating to soil weathering and pedogenetic processes in terra rossa in the Mediterranean environment, an integrated investigation was performed on nine terra rossa soils overlying hard and permeable limestone and dolomite rocks in the Apulia region (southern Italy). The aim of this work was to gain, through the use of geochemistry, an understanding of both soil-bedrock relationships and the origins of these soils in their underlying (carbonate) bedrock and/or external (aeolian dust) materials.

#### 2. Materials and methods

#### 2.1. Geology of the Apulia region

The study area is located in Apulia region (southern Italy), which stretches for 350 km between the Adriatic and the Ionian Seas (Fig. 1). The Apulia region is the emerged part of the foreland domain of both Apenninic and Dinaric orogens, where the thick Mesozoic carbonate sequence is overlain by thin Tertiary and Quaternary deposits. The tectonic stability of the last 330 ky promoted a number of polycyclic landforms along the coastline, mainly caves partly filled by marine/ continental sequences with beach levels, algal rims, and Lithophaga boreholes interbedded with slope debris, colluvial deposits, and flow-stones (Mastronuzzi et al., 2007).

The sites of interest were chosen across the whole Apulia region and present a varied geological environment, from S.M. di Leuca (the most southerly point of the geographical "heel" of Italian peninsula) in Salento to S. Nicandro in Gargano.

The landscape on the eastern coast of southern Salento is dominated by a steep slope extending from about 100 m a.s.l. to about 50 m below sea level. From the village of Santa Maria di Leuca to the village of Tricase, the coastal strip is mainly made up of Messinian sediments (Calcareniti di Andrano and Novaglie Formations) which disconformably mantle the pre-Miocene formations (such as Calcari di Melissano, outcropping at Santa Maria di Leuca). There are a few scattered outcrops of Miocene conglomerate, Lower Pliocene marls and glauconitic biomicrites (Leuca Formation, according to Bossio et al., 2001, and Trubi formation, according to Bossilini et al., 1999). The Paleocene-Oligocene Calcari di Castro (reef and associated

clinostratified slope) mainly crop out between Tricase and the village of Santa Cesarea, while random outcrops of the Pleistocenic "Calcarenite di Gravina" formation (carbonatic biodetritic sediments with spectacular remains of Arctica islandica Linnaeus and Mya truncata Linnaeus specimens) rest on the Oligocene limestone. Along the coast from Santa Cesarea Terme to Otranto is the village of Minervino, where the Cretaceous substratum is disconformably mantled by Upper Eocene Torre Specchia la Guardia limestone (clinostratified slope) which is in turn overlain by the Upper Oligocene Porto Badisco Calcarenite or by Miocene Calcareniti di Andrano. At Corigliano, in the inland areas westwards of Otranto, there is an outcrop of the Dolomie di Galatina Formation, made up of dolomite and dolomitic limestones of the Mesozoic substrate (Cretaceous age), which stretch until northern Salento, also outcropping at S. Michele Salentino. Then, proceeding to the NW, the area possesses all of the morphological-structural features of the Murgian relief (Murgian plateau) and a typical plank with large shelves stretches parallel to the coastline (Azzaroli and Valduga, 1967). Indeed, the morphology faithfully reflects the modeling of the Apulia platform by repeated marine oscillations due to tectonic and climatic events, starting in the middle Pleistocene. Wide outcropping of the Cretaceous Calcari di Bari occurs in the area of Bitetto on the Murgian plateau. Then, to the north, we find the Gargano promontory, an ENE-WSW ridge (De Alteriis and Aiello, 1993) extending into the Adriatic Sea (central Mediterranean Sea) and geologically diverse from the rest of the Apulian Foreland, in terms of relief, inland and offshore seismicity, gravimetric and magnetic anomalies, crustal thickness, etc. The Gargano structural high exhibits an over 4000 m thick sequence of carbonate rocks, ranging in age from the Jurassic to the Middle Miocene. These units display different lithological features brought about by spatial and temporal changes in the depositional environments caused by tectonic events (Masse et al., 1987) and platform dismantling (Bosellini et al., 1993). Late Jurassic Calcari di San Giovanni Rotondo and Formazione di Sannicandro outcrop at S. Marco in Lamis and San Nicandro, respectively.

#### 2.2. Selection and main environmental features of the study sites

The studied sites (Fig. 1) were chosen in order to investigate terra rossa origins and relationships with parent material and bedrock in Apulia. Therefore, site selection does not correspond to specific mapping criteria, but rather aims to identify points where terra rossa can be found.

In this framework, the selection included: 1) four terra rossa in Salento (P1, P2, P3, P4), 2) three terra rossa in the Murge, 3) two terra rossa in Gargano.

In particular, the P1 and P2 profiles came, respectively, from Santa Maria di Leuca and S. Cesarea in the extreme South of Apulia, both close to the sea where lands are uncultivated or at Mediterranean Macchia. Minervino (P3) and Corigliano (P4) are located inland westwards of Otranto, where arable lands and pasture are the main land uses, whereas the sites of S. Michele Salentino (P5 and P6) and Bitetto (P7) are located on the Murgian plateau, where there is extensive olive tree cultivation. Two sites were investigated at S. Marco in Lamis (P8) and S. Nicandro (P9) in Gargano, where a degraded and an undisturbed forest occur, respectively.

Regarding the history of land use, it has been reported (Comel, 1966) that human activity over the last forty years has completely changed the terra rossa sites, substituting the original *Quercus robur* forest with the present day degraded Mediterranean Macchia or olive tree cultivation.

The climatic data, as observed by the Otranto climatic station, show that the average annual temperature is 16.3 °C, with the warmest month being August (25.4 °C), the coldest January (9.4 °C). The mean annual rainfall is 797 mm with a maximum in November (144 mm) and a minimum in July (4 mm). Soil moisture regime, evaluated through the use of the Billaux model Billaux, 1978, is xeric in the studied soils.

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