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Micromorphology of hydromorphic soils developed in fluvio-marine sediments during the Middle-Late Pleistocene transit in the Gulf of Cadiz (Atlantic South Spain)

Micromorfología de suelos hidromorfos desarrollados en depósitos fluvio-marinos del Pleistoceno Medio-Superior en el Golfo de Cádiz (Atlántico, Sur de España)
Micromorfologia de solos hidromórficos desenvolvidos em sedimentos fluvio marinhos durante o Plistocénico Médio-Superior no Golfo de Cádiz (Atlântico, Sul de Espanha)

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ABSTRACT

This study establishes the controlling factors in the soil development in the ancient coastal plain of the Guadalquivir River along the southern Spanish coast (Huelva) shortly before 100 ka BP. The macro and micromorphological study indicates that a sedimentation hiatus allowed soil formation (extensive clay illuviation) together with the development of widespread redoximorphic features linked to iron oxide depletion and accumulation. Groundwater fluctuations driven by the overall sea-level rise during the onset of the last interglacial period triggered the pervasive occurrence of redox processes, probably acting in the coastal zone from the whole Middle Pleistocene as witnessed in inland outcrops. The resulting redoximorphic pedofeatures show a differential development in the studied zone, which is linked mainly to the activity of the Torre del Loro Fault leading regional differential upwarping of the ancient coastal area as well as local water-escape processes in the fault zone. Petrological, mineralogical and micromorphological data strongly suggest that the occurrence of multiple inheritances of iron-rich pedofeatures from previous Plio-Pleistocene weathering profiles developed under warmer and humid climatic conditions. Several pedofeatures (corroded quartz grains and runiquartz) do not correspond to the temperate oceanic climate prevailing in the zone during soil formation, and are reworked from former stronger weathering conditions. They are included in strongly iron-impregnated opaque domains that can be interpreted as inherited iron-rich nodules or clasts already present in the host sediments. These iron-rich pedofeatures have been subject to subsequent iron mobilization giving place to the iron depletion and accumulation domains observed in the micromorphological scale. Differential iron bleaching is not always linked to the fissure and/or pore-system present in the groundmass, suggesting the occurrence of differential water and sediment vertical fluxes (micro water-escape features) within the soil enhance the redoximorphic features around the fault zone.

RESUMEN

El estudio de paleosuelos hidromorfos desarrollados en la antigua llanura costera del río Guadalquivir (Huelva, España,) con anterioridad a los 100 ka BP, permite establecer los principales factores que controlaron el desarrollo edafogenético. Los rasgos macro y micromorfológicos indican que durante el Pleistoceno Medio final se produjo una importante parada en la sedimentación, que permitió un periodo dilatado de edafogénesis e importantes procesos de redistribución de los óxidos de hierro, prolongándose hasta bien entrado el último interglacial. Las fluctuaciones del nivel freático impulsadas por el progresivo ascenso del nivel del mar desde el comienzo del último interglaciar en la antigua llanura costera favorecieron el desarrollo y la amplificación de los procesos de hidromorfía que probablemente han actuado en la zona durante el transcurso del Pleistoceno Medio, tal y como atestiguan afloramientos de estos materiales en zonas situadas más hacia el interior. Sin embargo, los procesos de redistribución del hierro muestran un desarrollo diferencial ligado a la actividad sin-edafogenética de la Falla de Torre del Loro, que provocó una elevación regional diferencial a lo largo del antiguo sector litoral, así como procesos locales de escape de fluidos en

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las proximidades de la zona de falla. Los datos petrológicos, mineralógicos y micromorfológicos aportados en este trabajo sugieren la existencia de sucesivos procesos de retrabajamiento y herencia de rasgos edáficos procedentes de perfiles de alteración previos desarrollados en las formaciones Plio-Pleistocenas de arenas rojas características de esta zona. Algunos de estos rasgos heredados (runicuarzos y cuarzos corroídos) se desarrollaron en condiciones climáticas previas de tipo tropical responsables de su alto grado de meteorización, diferentes a las condiciones de clima oceánico más templadas en las que tiene lugar el último ciclo edafogenético que afecta a los paleosuelos estudiados. De entre estos rasgos destaca la presencia de cantos armados y nódulos de óxidos de hierro retrabajados que ya estaban presentes en el material original sobre el que tuvo lugar la edafogénesis. La mayoría de los rasgos ligados a la acumulación de los óxidos de hierro han sido afectados por procesos posteriores de redistribución que se manifiestan a nivel morfológico en zonas de extremo empobrecimiento y acumulación de hierro dentro del suelo. Desde el punto de vista micromorfológico, tales procesos no se observan necesariamente ligados a la extensa red microscópica de fisuras y/o poros de los paleosuelos, lo que sugiere la probable existencia de procesos de flujo vertical de fluidos y sedimentos en la matriz arenosa (escape de fluidos a nivel microscópico) que facilitaron la amplificación de los rasgos redoximórficos en las cercanías de la zona de falla.

RESUMO

O estudo dos Paleosolos hidromórficos desenvolvidos na antiga planície costeira do rio Guadalquivir (Huelva, Espanha,) anteriores a 100 ka BP, permite estabelecer os principais factores que controlaram o desenvolvimento pedogenético. Os estudos macro e micromorfológicos indicam que durante o final do Plistocénico Médio-final ocorreu uma importante paragem na sedimentação, que permitiu um período dilatado de pedogénese e importantes processos de redistribuição de óxidos de ferro, que se prolongou até ao último período Interglaciar. Flutuações do nível freático, impulsionadas pela progressiva subida do nível do mar durante o início do último período Interglaciar na antiga planície costeira favoreceram o desenvolvimento e amplificação dos processos hidromórficos que provavelmente actuaram na zona ao longo do Plistocénico Médio, como o testemunham afloramentos destes materiais em zonas mais interiores. No entanto, os processos de redistribuição de ferro mostram um desenvolvimento diferencial associado à actividade sin-pedogénica da falha da Torre del Loro, que provocou uma elevação diferencial regional ao longo da antiga área de costa, bem como processos locais de escape de fluidos na proximidade da zona de falha. Os dados petrológicos e mineralógicos obtidos neste trabalho sugerem a ocorrência de sucessivos processos de reelaboração e herança de características pedológicas procedentes de perfis de alteração anteriores desenvolvidos nas formações Plio-Plistocénicas de areias vermelhas características desta zona. Algumas destas características herdadas (runiquartzos e quartzos corroídos) desenvolveram-se em condições climáticas prévias de tipo tropical responsáveis pelo seu elevado grau de meteorização, diferentes das condições de clima oceânico mais temperadas em que ocorreu o último ciclo pedogenético que afecta os paleossolos estudados. De entre essas características destaca-se a presença de impregnações de ferro opacas que podem ser interpretadas como nódulos de óxidos de ferro herdados do material original sobre o qual teve lugar a pedogénese. A maioria das características ligadas à acumulação de óxidos de ferro foram afectadas por processos posteriores de redistribuição que se manifestam a nível morfológico em zonas de extremo empobrecimento e acumulação de ferro no solo. Do ponto de vista micromorfológico, tais processos não se encontram necessariamente ligados à extensa rede microscópica de fissuras e/ou poros dos paleossolos, o que sugere a provável existência de processos de fluxo vertical de fluidos e sedimentos na matriz arenosa (escape de fluidos a nível microscópico) que facilitaram a amplificação das características redoximórficas nas proximidades da zona de falha.

KEY WORDS
Hydromorphy, clay illuviation, iron-oxides, Last Interglacial, Huelva, Southern Spain

PALABRAS CLAVE
Hidromorfía, argiluviación, óxidos de hierro, último Interglaciar; Huelva, Sur de España

PALAVRAS-CHAVE
Hidromorfísmo, iluviação de argila, óxidos de ferro, último Interglaciar; Huelva, Sul de Espanha

1. Introduction

We present here a micromorphological study of paleosols with redoximorphic features in an ancient coastal-plain environment along the Gulf of Cadiz (southern Spain) developed soon before and during the last interglacial period. The paleosols are exposed at the base of an E-W trending sea-cliff, carved in Late Pleistocene–Holocene aeolian deposits enclosing the present marshlands of the Guadalquivir river estuary (Doñana National Park, Huelva). The Asperillo cliff extends for 28 km, with an average elevation of about 20 m (Figure1). The complete sedimentary succession exposed in this sea-cliff record the Late Pleistocene to Holocene evolution of the littoral sector of the Guadalquivir Basin at the Gulf of Cadiz during the last c. 100 ka, which consists mainly of stacked fluvio-littoral and aeolian sequences burying the studied last interglacial paleosols (Zazo et al. 1999, 2005).

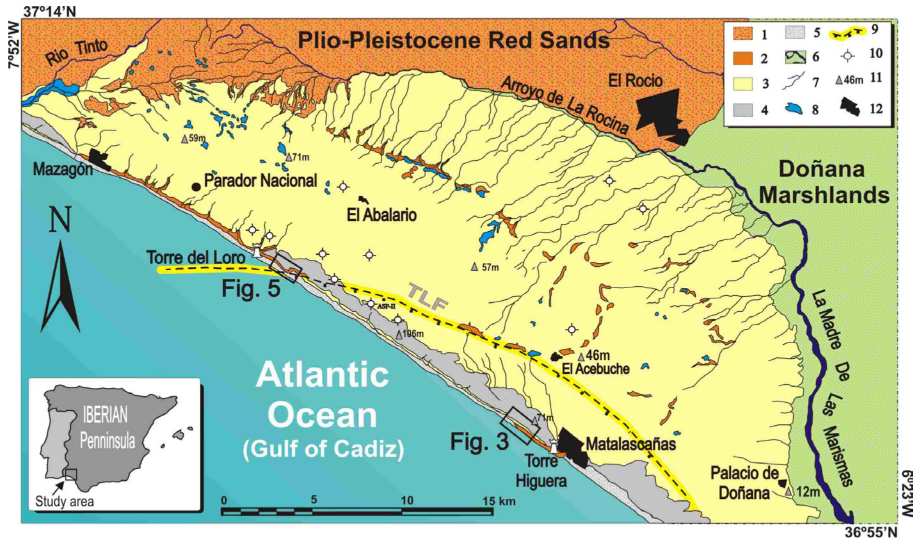

Figure 1. Geology and geomorphology of the El Asperillo Cliff coastal area and the Doñana Marshlands. **1.** Plio-Pleistocene red sand formation; **2.** Fluvio-deltaic late Pleistocene sediments (studied paleosols fringe); **3.** Late Pleistocene aeolian complex; **4.** Late Holocene aeolian complex; **5.** Recent beach deposits; **6.** Doñana Marshlands; **7.** Drainage network; **8.** Small lakes and ponded areas; **9.** Torre del Loro Fault (TLF); **10.** Boreholes (cited in text); **11.** Elevation points; **12.** Main localities in the area (after Zazo et al. 2005). Location of studied paleosols and reference to Figure 3 (PS1) and Figure 5 (PS2) highlighted in the quadrangles.

From the stratigraphic point of view the paleosols studied represent the surface of an ancient fluvio-deltaic coastal plain sequence resulting from the progressive infilling and progradation of Guadalquivir river deposits since the Lower Pliocene (Mayoral and Pendón 1986; Salvany and Custodio 1995). The stabilization of this coastal plain shortly before and during the Last Interglacial sea-level highstands (MIS 5: Marine Isotopic Stage 5) allowed soil development in supra-tidal environments (Zazo et al. 1999).

The underlying fluvio-deltaic sequence cored at various places in the zone, reaches a thickness of more than 20 m in the Asperillo cliff zone, but 70 – 100 m in the Guadalquivir marshlands area (Salvany and Custodio 1995). The paleosols studied display textural, lithological and mineralogical features similar to those reported by several authors for the Plio-Pleistocene fluvio-marine "red sand formations" outcropping along Huelva-Algarve coast, such as the "*Arenas de Bonares fm*" in Spain (Mayoral and Pendón 1986; Torcal et al. 1990; Cáceres 1995); and "*Faro/Quarteira or Ludo fm*" in Portugal (Monteiro et al. 1981; Boski et al. 1999; Chester 2012). Host sediments are mainly siliciclastic silty-sands and sands deposited in an intertidal environment, dominated by quartz and feldspar grains, illite-mica and kaolinite in the clay fraction strongly impregnated by a variety of Fe-oxides (Mayoral and Pendón 1986; Torcal et al. 1990; Boski et al. 1999) which are mainly inherited from the adjacent source area located in the iron-rich Paleozoic "Iberian Pyrite Belt" (Rio Tinto Ore zone; Tornos 2008). The exposed iron-rich materials, both in the Paleozoic substratum and in the subsequent Plio-Pleistocene red sand formations, were subject to deep weathering under past humid-tropical climatic conditions giving place to the development of a wide variety of thick iron-rich weathering profiles, mottled red soils and iron-crusts along the southern Spanish-Portuguese coast (Monteiro et al. 1981; Rodríguez-Vidal 1989; Boski et al. 1999). Paleosols analyzed in this study contain most of the aforementioned features, and in fact they might be considered as the ultimate products of previous Plio-Pleistocene environmental conditions leading to the development of Fe oxides-rich materials in the zone.

Most of the previous works on the Plio-Pleistocene red sand formations deals with the sedimentological and macroscopic description of weathering profiles and host materials, lacking detailed mineralogical and micromorphological analyses. This study focuses on the use of soil micromorphology on argillic horizons developed on top of these iron-rich weathered parent materials from which only macroscopic data were available (Zazo et al. 1999, 2005). This study enhances the role of micromorphological analysis on decoding the inter-relationships between host materials and the variety of pedogenic and geological processes acting in the zone during the eventual soil formation. Additionally these soils are buried by dated fluvio-marine and aeolian sedimentary formations of the Last Interglacial period, providing a preliminary time-period for soil formation during the Middle-Late Pleistocene transition.

2. Geodynamic Setting

The paleosols studied are found in the complex Late Pleistocene-Holocene stratigraphic arrangement exposed along el Asperillo Cliff zone (Zazo et al. 1999). This stratigraphic arrangement is the result of complex interactions of littoral processes, sea-level changes and tectonics on an emergent coastal plain, conditioned by the upwarping of the underlying Plio-Pleistocene fluvio-deltaic sequence of the ancient Guadalquivir River (Salvany and Custodio 1995; Zazo et al. 1999). The progressive upwarping and doming of the Middle Pleistocene coastal plain was related to the escape of over-pressurized fluids, accompanied by dewatering, prior and during MIS 5. Continuous uplift led to the differential emergence of the coastal area favoring soil formation under the humid-warm conditions of the Last Interglacial period. Differential uplift favoured different soil development in permanently emerged areas (East) and partially inundated ones (West) by the pushing sea-level rise prior to c. 100 ka BP. These areas are delimited by the Torre del Loro Fault (TLF; **Figure 2**), which eventually resulted in a large-scale gravitational collapse of the southwestern flank of the emergent dome along the fault (Goy et al. 1994; Zazo et al. 2005) from at least 72-74 ka BP. The resulting mega-scar (c. 20 m high), roughly parallel to the present coastline (**Figure 1**), favoured the accumulation of successive stacked sand dune sequences from the late MIS 5 (< 72 ka BP) to the late MIS 2 (16 ka BP) during low sea-level conditions and an arid-cool climate (Late Pleistocene Aeolian complex; **Figure 2**), burying the basal Plio-Pleistocene coastal plain sequence hosting the soils (Zazo et al. 1999).

After this main period of dune accumulation a major erosive surface fairly leveled the sedimentary sequences at both sides of the TLF correlative to the development of an iron crust-like layer with a thickness of cm sealing the fault (Figure 2). Subsequent sedimentation was again characterized by the development of stacked early Holocene aeolian sequences (Figure 2) and their littoral erosion during Late Holocene and historical times (Zazo et al. 1999, 2005) leading to the development of the present sea-cliff.

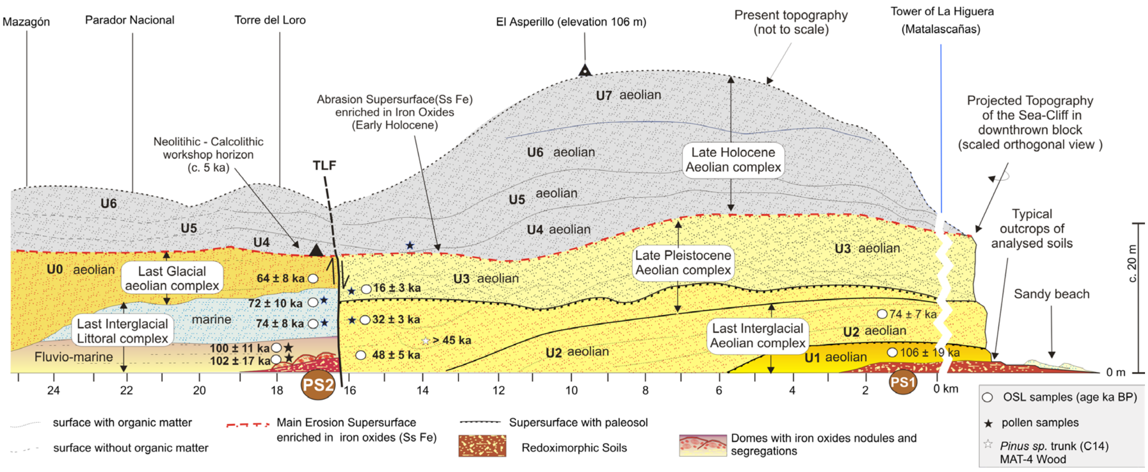

Figure 2. Schematic cross-section parallel to the coast line from ESE (PS1) to WNW (PS2) showing the distribution of sedimentary units and the location of the studied paleosols (Figure 1). The available chronology for the different sedimentary sequences is displayed. Note the strong vertical exaggeration. Distances in km from the Torre Higuera watchtower location (after Zazo et al. 2005).

The paleosols studied are exposed at several sites at the base of the present sea-cliff and are distributed in two clear distinctive outcrop zones located in the downthrown (Torre Higuera; PS1) and upthrown (Torre del Loro; PS2) areas defined by the TLF (Figure 2). These two outcrops are separated several kilometers due to the offset and relative tilting of the sedimentary sequence induced by the fault, so there is no continuity of the studied paleosols along the present sea-cliff. However, the available OSL age data indicate that the littoral fluvio-marine and aeolian sediments overlying the paleosols at both zones have similar ages, around 100 to 106 ka BP (Zazo et al. 1999, 2005), and can be considered to belong to the same Last Interglacial littoral complex showing different environmental conditions in the ancient coastal plain (Figure 2). Consequently, in spite of several distinctive pedological and sedimentological features, the exposed paleosols have to be considered as belonging to same pedogenic cycle acting in the zone prior to c. 100 ka BP during the Middle-Late Pleistocene transition. In fact, the outcrops of the Plio-Pleistocene red sand formation offer good exposures of weathering profiles, but no clear evidence of soil formation as occurs in the zone studied.

3. Materials and Methods

A study of the sedimentary sequence together with a morphologic description of soil profiles was carried out in the field. After surveying several zones along the base of El Asperillo Cliff two sections were chosen for detailed soil study and sampling at the different zones defined by the TLF, named PS1 and PS2 (**Figure 2**). The colours of paleosols are referred to Munsell Soil Color Charts (1990). Due to the difficulty in the definition and differentiation of true soil horizons, the description and analyses of the soils are focused on distinctive morphological, colored and crusted zones identified in the morphological field study. Soil sampling for micromorphological, mineralogical and geochemical analyses was carried out following the same criteria.

The mineralogical composition of samples was analyzed by powder X-ray diffraction on a Philips PW-1710/00 diffractometer using the Cu Kα radiation with a Ni filter and a setting of 40 kV and 40mA. For clayey samples, additional analysis of the fraction < 63 μm was performed by preparing oriented aggregates: air-dried, solvated for 48 hours at 110 ºC with ethylene-glycol, and heated for 1 hour at 550 ºC. Data were collected and interpreted using the XPowder software package (Martín-Ramos 2004; Martín-Ramos et al. 2012).

Geochemical analyses were carried out by a Perkin-Elmer 2380 atomic absorption spectrophotometer (acid digestion, U.S. EPA 1996)

Undisturbed samples were collected for micromorphological study. Vertical thin sections, 9 cm long and 5.5 cm wide, were made from air-dried undisturbed soil blocks and prepared in the University of Lleida (Soil Micromorphology Lab). Thin sections were studied and described by means of a polarizing microscope following the guidelines of Bullock et al. (1985).

4. Results

In this section we describe the macro-and micromorphological features of the paleosols studied in both sectors of El Asperillo Cliff, synthesizing the most outstanding pedofeatures found at the two sectors defined by the TLF. A preliminary interpretation on soil development and related redoximorphic features is provided at the end of each subsection. The exposures of the soil profiles at both sectors are limited by the mesotidal range of the zone. In the Torre Higuera sector (PS1) only low-tide conditions allow the field study, in lowest tidal conditions soil exposure can reach about more than 100 cm (**Figure 3a**), but normal visible exposures are of 30-50 cm (**Figure 3b**). In the Torre del Loro sector (PS2) visible exposures are normally about 90-100 cm above the regular high tide, but in low-tide conditions soil exposure can reach about 150-155 cm (see section 4.2). Additionally, in both cases exposures are normally mantled by the present beach sands. Hence continuous exposures of thickness of more than 100 cm are rarely observed (**Figure 3a**). Host undisturbed sediments never have been observed in low-tide conditions, so the entire soil profiles might presumably reach more than 200 cm, but no data are available below the low tide range. The main mineralogical data of the collected samples are displayed in **Table 1**.

4.1. PS1: Torre Higuera Sector

Paleosol exposures in this sector are restricted to the eastern end of el Asperillo sea-cliff in the downthrown block of the fault close to the locality of Matalascañas (**Figures 1** and **2**). As mentioned before the exposures in this sector are limited by the mesotidal range and visible exposures of the paleosol are normally between 30-50 cm, but with maximum visible soil thickness around 100 cm (**Figure 3**). Preserved exposures of PS1 were truncated before burial by aeolian sediments belonging to the last interglacial (**Figure 2**), consequently the presumed overlying eluvial horizons are not preserved.

Table 1. Semiquantitative mineralogical composition (%)

	Sand fraction		Clay fraction		Fe oxides			
	Quartz	K Feldspar	Illite-Mica	Kaolinite	Hematite	Goethite	Ilmenite	Magnetite
PS1 (7.5YR 5/8)	71	3	5	19	1	<1	1	n.p.
PS1 (2.5YR 4/6)	70	3	6	18	1	<1	1	1
PS2 (10YR 7/1)	68	2	12	14	1	n.p.	1	2
PS2 (10YR 5/8)	74	3	7	13	2	1	n.p.	n.p.

n.p. not present.

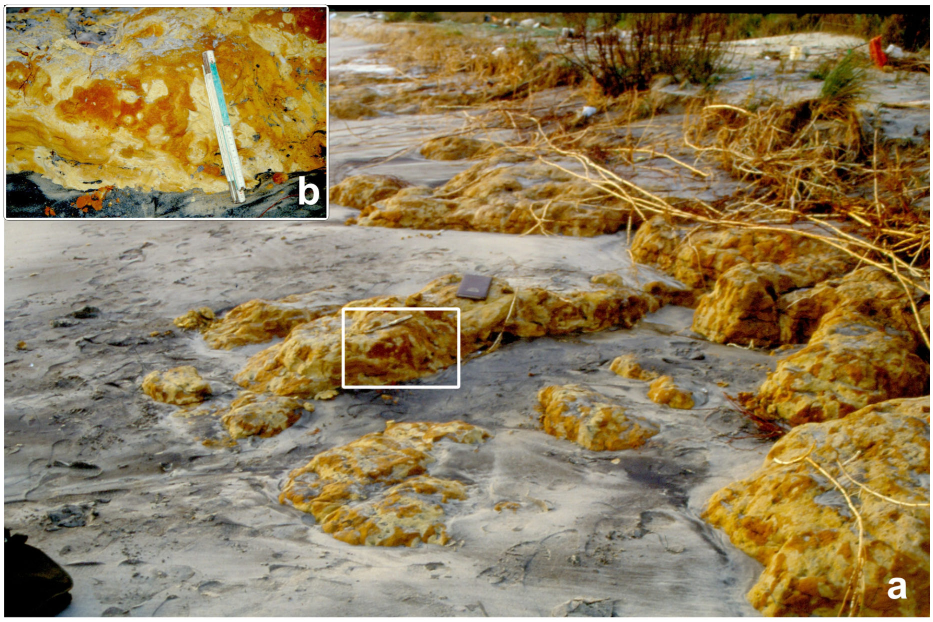

Figure 3. (a) Panoramic view of the paleosol PS1 exposures at the base of the sea-cliff in the Torre Higuera zone in the eastern part of El Asperillo Cliff (Matalascañas). **(b)** Close-up field view of the Paleosol PS1 marked in the white quadrangle in 3a. The schematic cross-section for outcrop geometry and location is provided in Figures 1 and 2.

PS1 is constituted by reddish clayey sands, somewhat plastic and adherent which display strong mottling with large mottles of 10 to 20 cm in diameter (Figure 3a). The dominantly vertically elongated arrangement of mottling suggests a genetic relationship with plant-root activity. In many zones root activity generated clear segregations of concentric structures with a pale-yellow (2.5Y 7/4 m) nucleus grading towards the periphery to yellow-brown (7.5YR 5/8 m) and, eventually to reddish (2.5YR 4/6 m) preserved remains of the original soil matrix (Figure 3b). Mineralogy of brown and reddish zones is very similar, with dominance of quartz and in the clay fraction kaolinite (Table 1).

Thin section analyses indicate that the paleosol is composed of fine-grained sediments, moderately to well-sorted sands, with porphyric or chitonic c/f related distributions. The most common detrital grains are subrounded quartz and k-feldspars, with minor amounts of tourmaline and chert. However some quartz grains have rough boundaries, probably inherited from the previous Plio-Pleistocene red sand formations. Packing voids and channels are the most common voids together with some fissures. Micromass is formed by yellowish, yellowish-red and red clay and iron clay components.

Most common pedofeatures are mainly related to clay illuviation processes and subsequent redox changes due to fluctuating groundwater conditions. Typic and crescent thick clay coatings, usually microlaminated, are very abundant, as well as dense complete microlaminated clay infillings (Figure 4a) where sharp parallel extinction lines (and strong interference colors) point to a strong continuous orientation of fine clay particles (Figure 4b).

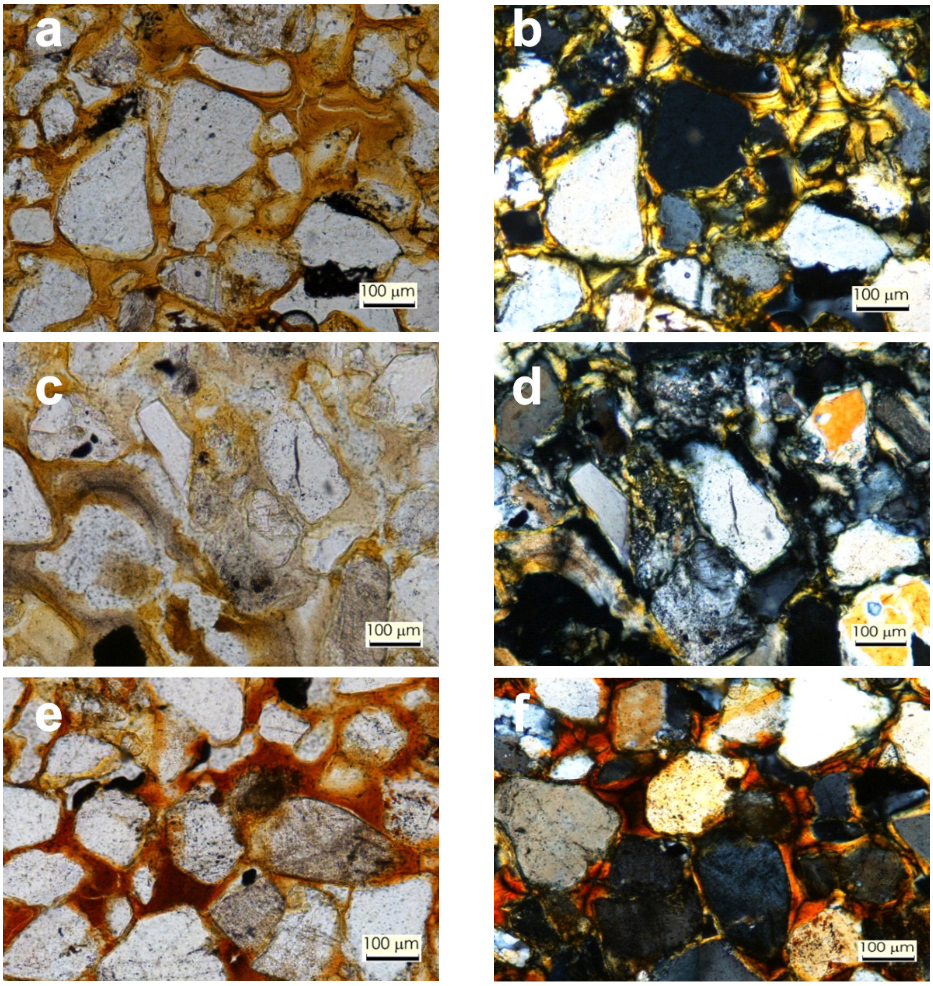

Figure 4. Main micromorphological features of PS1. **(a)** Reddish typic and crescent coatings and dense complete infillings PPL. **(b)** XPL view of a, sharp extinction lines point to strong orientated clay particles. **(c)** Micrograph from macroscale Fe depleted hypocoatings. PPL. **(d)** XPL view of c. Note extinction line in Fe oxide depleted coatings. **(e)** Micrograph from macroscale red domains with preserved clay coatings. Red colour points to hematite presence PPL. **(f)** Strongly oriented clay particles in clay coatings XPL.

Redoximorphic features are mostly related to the mobility of Fe (geochemical analyses confirmed the absence of Mn). The concentric gradation of colour from the bleached nucleus to the periphery observed in the field is presented in thin section as Fe depletion hypocoatings where very light and grayish clay coatings preserve extinction line patterns (**Figures 4c, 4d**) to transitional reddish brown clay coatings and infillings and finally bright red micromass whose colour points to presence of hematite (**Figures 4e, 4f**), probably inherited from reworking of the deeply weathered Plio-Pleistocene parent materials.

The well-developed clay pedofeatures reveal that an intense clay illuviation process took place in PS1 forming an argillic and stagnic horizon at least 90-100 cm thick as revealed by visible exposures of the soil during low-tide conditions. This points to a long period of soil development for this area and is related to a well-developed plant cover living on mature soils. The origin of mottling is related to hydromorphic processes that took place after pedogenic clay translocation, in reducing microenvironments. This mostly occurred in the coarser channels containing decaying roots that favored dissolution and mobilization of Fe, but also randomly within the soil matrix. These features could suggest the occurrence of episaturated or endosaturated conditions (i.e. Vepraskas et al. 1994). Following these authors this pattern of redoximorphic features is difficult to interpret, except to say that redox conditions occurred throughout the soil over the time.

4.2. PS2: Torre de El Loro sector

Sandy sediments at the toe of the cliff show morphological features different from those observed in PS1, linked to the occurrence of large-scale mottling and segregations that suggest stronger redox conditions. In this sector the paleosol PS2 displays a yellowish brown (10YR 5/8 m) matrix, with redoximorphic features, consisting of mottles, 20-30 cm wide and light gray (10YR 7/1 m) irregular segregations with sharp boundaries. Additionally this paleosol displays several interstratified, 2-3 cm thick indurated iron-oxide crusts related to accumulations of subrounded iron nodules, concretions, iron oxide coated clasts and angular crust fragments (**Figure 5**). These anomalous accumulations are discrete (0.8-1.1 m thick and 2-3 m wide), have a planar base, an undulating upper boundary and a domed overall geometry, separated from the overlying sediments and underlying paleosol by the aforementioned iron-oxide crusts (**Figure 5**). These iron-rich domed structures have been preliminary interpreted as relict mud-volcanoes linked to water escape processes near the TLF fault zone (Zazo et al. 2005). In the surveyed sector these indurated domes locally overlie and underlie the studied mottled soil profile (**Figure 5**).

The exposed profile at the base of the sea-cliff is 100-155 cm thick, only visible and accessible under low-tide conditions. In the upper 100-105 cm low-chroma segregations (10YR 7/1) tend to be vertically elongated, but towards the visible lower part (c. 50 cm) they show a more irregular geometry and present a more horizontal arrangement. In addition to these large low chroma segregations, smaller reddish-brown (5YR 5/8 m) or yellowish red (2.5YR 5/8 m) mottles occur in this lowermost zone of the exposed profile. In some places these reddish mottles merge and concentrate in laminated millimeter-thick layers overlying the aforementioned basal undulated iron-oxide crust (**Figure 5**). Mineralogy of the original matrix and discolored segregations are very similar, with a dominance of quartz and kaolinite in the sand and clay fractions respectively as in the case of PS1 (**Table 1**). The main mineralogical difference between the high-chroma matrix and the low-chroma segregations is related to the type and relative abundance of iron oxides. The low chroma mottles contain hematite, ilmenite and magnetite, while the original yellowish-brown matrix contains goethite and a higher amount of hematite (**Table 1**).

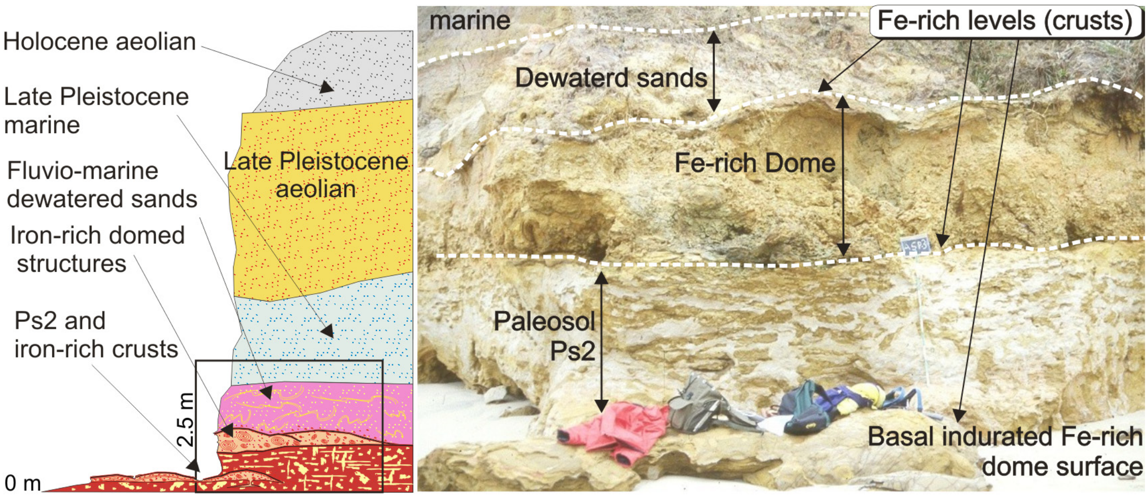

Figure 5. Schematic cross-section of the Paleosol PS2 in the base of El Asperillo Cliff in the Torre del Loro Sector adjacent to the fault zone (see location in Figure 2). To the right frontal field view of the studied outcrop indicating the more representative morphological features.

The PS2 profile consists of moderately sorted fine-grained sands, with a porphyric c/f related distribution, grain size of fine material is 20 µm. The most common detrital grains are subangular quartz and smaller amounts of K-feldspars. Several types of micromass are present in this soil, from a very light yellowish-gray to a dark brown with undifferentiated b-fabric depending on the abundance of iron oxide, and dark red micromass when clay dominates. Channels and planar voids are the most common voids in the groundmass. The groundmass of the original yellowish brown soil matrix (from field description) is more variable. The micromorphological analysis reveals the occurrence of a variety of brown to dark-brown, sometimes isotropic, and reddish domains, where dense, incomplete infillings and thin non-laminated clay coatings are observed (**Figures 6a, 6b**).

Dominant pedofeatures observed in thin sections of low-chroma mottles and segregations (field description) record iron oxide depletion and accumulation, forming complex features composed of depletion hypocoatings and impregnation quasicoatings. They usually develop adjacent to water-filled voids formerly containing organic matter (decaying roots) needed for the microbial reduction of Fe^{3+}. The Fe^{2+} ions migrated from the immediate surface of the void, leaving the observed depletion hypocoatings. Further in the groundmass, they were oxidized forming iron oxide concentrations as quasicoatings (Vepraskas et al. 1994). Depletion hypocoatings occur associated with a dense network of interconnected planar voids and along channel walls, related to a micro-root system.

Iron oxide accumulations also occur as widespread impregnations superimposed upon the groundmass (**Figures 6c, 6d**). The zones displaying a higher degree of iron oxide impregnation commonly constitute large patches with sharp boundaries. They often display internal fissures or cracking, but fissures are also common at the boundaries between the strongly impregnated zones and the depleted matrix. These patches of Fe oxide have a massive internal structure with corroded quartz grains (Beaudou 1972; **Figures 6e, 6f**). Some of the quartz grains show fissures filled with iron oxides, similar to "runiquartz" indicating strong

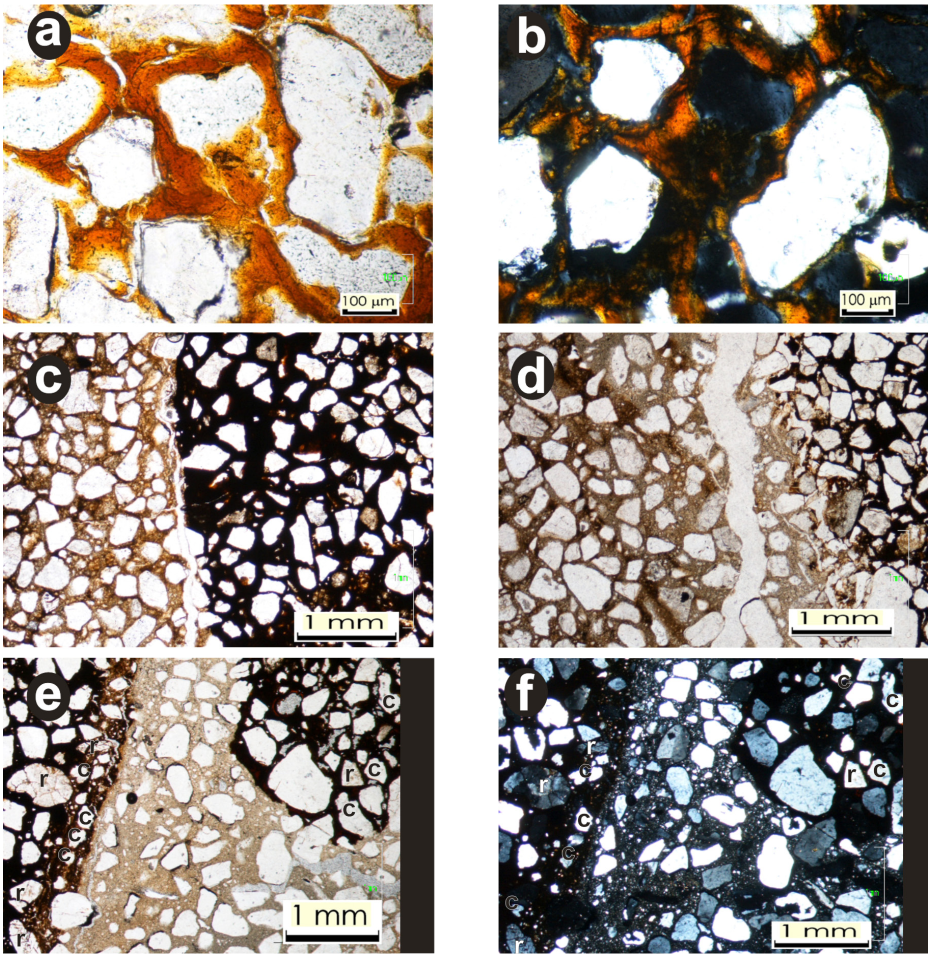

Figure 6. Main micromorphological features of PS2. **(a)** Red clay coatings PPL. **(b)** Same as a XPL. Extinction lines indicate oriented fine clay. **(c)** Fissure at the boundary between strongly impregnated groundmass and depleted matrix. PPL. **(d)** Depletion Fe oxide hypocoating and Fe quasicoating in a greyish groundmass. **(e)** Strongly impregnated Fe oxide domains in a depleted grayish groundmass. Note cracks on the left. PPL. **(f)** Same XPL. Note corroded quartz grains (c) and runiquartz (r) in impregnated domains (e and f), aside poorly sorted depleted infilling related to water escape processes.

weathering (Eswaran et al. 1975). Most of these type of patches are iron-nodules or clasts reworked from previous weathering profiles, present in the sandy sediments before soil formation.

The iron-oxide crusts overlying and underlying the soil show an overall strong iron impregnation similar to the abovementioned patches. In these strongly impregnated crusts the iron oxides nearly mask the former clayey Fe-rich groundmass, giving place to a pervasive undifferentiated b-fabric, often opaque (Figure 7a). In spite of the occurrence of a very dark coloured groundmass, the presence of Mn oxides is ruled out by geochemical analyses. Domains showing a minor degree of iron impregnation allow observation of some preserved clay pedofeatures, such as coatings and infillings, where extinction lines indicate moderate orientation of fine clays (Figure 7b). Where strong impregnation occurs the clay features are masked by iron accumulation. Together with these features light-brownish gray Fe and clay depletion hypocoatings along pores are common (Figures 7c, 7d). The mobilization of Fe makes the clay more prone to dispersion and migration from pore walls. One of the most relevant micromorphological features of the iron crusts is the abundance of corroded quartz grains as well as the common occurrence of runiquartz (Figures 7e, 7f) indicating very strong weathering stages (Eswaran et al. 1975).

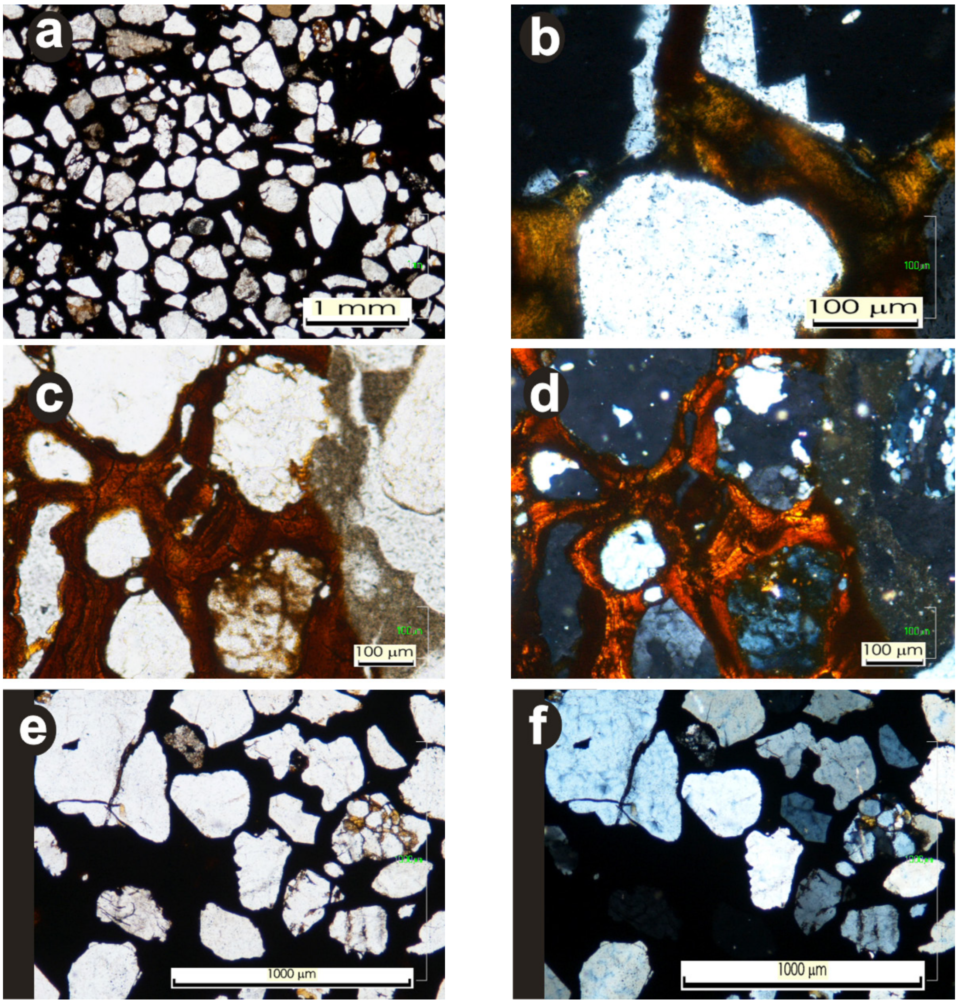

Figure 7. Main micromorphological features of iron crusts in PS2. **(a)** Strongly iron oxide impregnated groundmass. **(b)** Fe oxides on preserved clay coatings and infillings XPL. No sharp extinction lines point to a moderate clay orientation particles. **(c)** Light brownish grey iron depletion hypocoating. Notice contrast with dark red groundmass. **(d)** Same as c XPL. Moderately oriented fine clay coatings and infillings, red-orange colour points to hematite. **(e)** Quartz with corroded boundaries and runniquartz in a strongly Fe impregnated groundmass (PPL). **(f)** Same as e. XPL.

Clay accumulation pedofeatures observed in Torre del Loro sector (PS2) seem to be less developed than those observed in Torre Higuera sector (PS1), possibly indicating a shorter period or lesser intensity of clay illuviation. On the contrary, the overprinted redoximorphic features in PS2 indicate a stronger and presumably longer-lasting influence of epi- or endosaturated conditions forced by water fluctuations and vertical fluxes of water and sediments within the soil in the ancient coastal plain environment near the fault zone. In this sense, the complex association of stronger redoximorphic features with the occurrence of reported water escape processes and mud-volcanism in this sector of the TLF (Zazo et al. 1999) may explain the complex micromorphological assemblages observed in PS2 and absent in PS1 about 14 km away in the downthrown block of the fault (**Figure 2**).

On the other hand, the abundant occurrence of corroded quartz grains and runiquartz in both soil profiles and related iron crusts indicates that these grains are obviously inherited from previous Plio-Pleistocene weathering profiles, and/or iron crusts, present in the materials of the source areas as mentioned in the introductory sections (Rodriguez Vidal 1989; Boski et al. 1999). The presumed Middle to Late Pleistocene temperate humid climatic conditions that occurred before 100 ka BP during the last interglacial and previous interglacial periods (Zazo et al. 1999), does not justify the occurrence of these strong weathering features, usually more common in tropical environments (Eswaran et al. 1975).

5. Discussion

The available OSL dates on the littoral sediments burying the two studied paleosols (**Figure 1**) indicate that the entire coastal plain area was subject to a relevant pedogenic cycle before c. 100 ka BP, including at least the warmer earlier phases (e.g. MISS 5e) of the last interglacial period (Zazo et al. 1999). Analyses performed in this work indicate similar micromorphological and mineralogical features in the two paleosols assignable to the same pedogenic cycle. Differences between the two studied sectors are mainly related to a stronger degree of the macro and micro-redoximorphic features in the Torre del Loro sector (PS2) than in Torre Higuera one (PS1). These differences can be primarily attributed to slight differences in their paleogeographical location within the ancient coastal plain controlled by the activity of the TLF and to geological processes acting near the fault zone (PS2). They can also attributed to the varying distances to the iron-rich source areas of the sandy host materials during the Middle-Late Pleistocene transition.

Differences in the original paleogeographical location are difficult to establish, but the nature of the overlying sediments of the last interglacial littoral complex burying the paleosols studied is clearly distinctive. PS1 is buried by aeolian sediments whereas PS2 is buried by shallow littoral intertidal sediments of similar age deposited after c. 100 ka BP. Therefore supratidal conditions are presumed longer-lasting for PS1 than for PS2. The latter was eventually inundated by the rising sea-level triggering an earlier truncation of the pedogenic cycle in the Torre del Loro sector (PS2), and is in agreement with the relatively weaker degree of development of the observed micromorphological pedofeatures linked to clay illuviation. On the contrary, PS1 is only buried by aeolian sediments (**Figure 1**) and therefore this soil was never under the regional water-table after its formation. In any case the early inundation of the PS2 sector does not justify the more prominent redoximorphic features recorded in this paleosol, which must be linked to the previous supratidal environmental conditions. Additionally, micromorphological study indicates that both paleosols display superimposed Fe oxide impregnation on clay coatings and infillings, suggesting that redoximorphic conditions and processes postdate (PS1 and PS2), or were simultaneous (PS2) with the last stages of clay illuviation.

Diversity in the source area of the host sediments can be ruled out. The mineralogical analysis indicates similar textural and mineralogical features for the sand and clay fractions with the dominance of quartz and kaolinite in both soils (**Table 1**). In addition both soils show a similarly high content of Fe oxides, which is characteristic for the regional formations of Plio-Pleistocene “red sands” existing in the area (Monteiro et al. 1981; Torcal et al. 1990; Chester and James 1995; Boski et al. 1999), derived from the Paleozoic source area, in the Iberian Pyrite Belt (Rio Tinto), and related deep weathering profiles (Tornos 2008). These weathering profiles are affected by deep ferruginous-kaolinitic weathering (Rodríguez Vidal 1989; Torcal 1990; Cáceres 1995; Boski et al. 1999), and acted as one of the main source areas for the sediments studied. The mineralogical data presented in this study are similar to those reported for the formations of Plio-Pleistocene “red sands” by the aforementioned authors. In this sense, the relatively high content of kaolinite in the soils studied can be interpreted as inherited from the Plio-Pleistocene weathering profiles existing in the source area.

There is a remarkable difference between the two studied paleosols related to the relative abundance of rough boundaries and corroded quartz grains and the presence of runiquartz (**Figures 5** and **6**). These features are rarely observed in PS1, but abundant in PS2 located in a former marginal area of the ancient coastal plain, closer to the iron-rich source areas, and adjacent to the TLF fault zone (**Figure 1**). In PS2 corroded quartz and runiquartz are common in strongly iron-impregnated groundmass, and abundant in iron nodules and iron crusts. These strong weathering pedofeatures, are probably inherited from the abovementioned Plio-Pleistocene “tropical” weathering profiles, in which they are frequent (Monteiro et al. 1981; Boski et al. 1999). The widespread occurrence of these pedofeatures in PS2 at micro-and macro-scale can be interpreted as reworked material (iron nodules and crust fragments of varying size), but subject to iron-remobilization (iron crusts, mottling) during the redoximorphic conditions existing in the zone during or soon after the main phases of soil formation.

The occurrence of active geological processes in the sector adjacent to the TLF fault zone (PS2; **Figure 2**) can be considered one of the major factors controlling different observed pedofeatures and different degree of iron mobilization of at both profiles. Both paleosols display evident mottling as a consequence of a progressive shallower and fluctuating ground water level in supratidal environments pushed by last interglacial sea-level rise before c. 100 ka BP. PS1, located in a more stable zone 13-14 km kilometres away from the TLF (**Figure 1**), can be considered to reflect the common environmental endosaturated conditions during soil formation. On the contrary, in PS2 the iron redistribution (depletion and accumulation) was also controlled and enhanced by episodic water-escape processes around the fault zone (TLF) soon after soil formation between c. 100-70 ka BP. The study of PS2 indicates that the combination of iron depletion and iron accumulation is not always linked to the larger pore system, but also occurs randomly within the groundmass, where large zones are differentially bleached. Processes of iron reduction and mobilization –as well as concentration and depletion– of inherited strong weathering pedofeatures, can be reasonably linked to differential artesian flows of water and sediment at microscopic scale (mm to μm) linked to the macroscopic water escape structures described in the area around this exposure (Zazo et al. 1999, 2005). In fact, iron-rich domes bounded by iron-crusts (**Figure 5**), interbedded and overlaying PS2, have been related by these authors to mud-diapirism and eventually mud-volcanism around the fault zone. At present, the existing hydrogeological models (Salvany and Custodio 1995) indicate the occurrence of artesian water flows at the base of the sea-cliff coming from the underlying fluvio-deltaic Plio-Pleistocene red sands and gravels at a depth about 40-50 m. These hydrodynamic conditions lead to the occurrence of many temporary fresh-water springs along the contact of the paleosols and the overlying sediments, especially abundant around the PS2 location on the TLF fault zone. Therefore seasonal endosaturated conditions have also been acting in the sea-cliff since at least the last Holocene sea-level highstand (c. 6.5 ka BP; Zazo et al. 1999), possibly enhancing redoximorphic features described in this paper. Episaturated conditions (perched water levels) could also occur in the zone along the contact of the paleosols and overlying sediments during the sea-level drop of the last glacial period from 70 to 10 ka BP, but no micro or macro evidence allows us to identify this presumed situation. In any case, as stated by Vepraskas et al. (1994), the observed pattern of redoximorphic features is difficult to assign to particular endo- or episaturated conditions, except to say that redox processes occurred throughout the soil in the period following soil formation.

6. Conclusions

Evidence of pedogenesis clearly indicates a pause in sedimentation during the last phases of construction of the Middle-Late Pleistocene coastal plain in the ancient Guadalquivir river-delta, before c. 100 ka BP (Figure 2). Soil formation is evidenced by intense clay illuviation in the paleosols studied, leading to the development of argillic horizons of at least 1.5 m thickness. Repeated hydromorphic processes overprinted on the previous argillic horizon can be related to fluctuations of the water table and seem to represent the onset of new environmental fluvio-marine conditions forced by the uprising sea level from at least the onset of the last interglacial period (MISS 5e; c. 125 ka BP) under humid and warm climatic conditions (Zazo et al. 1999, 2005).

PS1 displays numerous and more strongly developed clay illuviation-pedofeatures compared to those observed in PS2, suggesting that soil formation processes lasted longer in this sector of the ancient coastal plain, as indicated by prevailing subaerial exposure conditions until c. 100 ka BP (MISS 5c). PS1 has to be considered as the soil profile indicating the normal environmental conditions of the ancient coastal plain during soil formation from at least the Middle-Late Pleistocene transition, but probably since older Middle Pleistocene stages. On the contrary, in PS2 soil development was truncated by fluvio-marine sedimentation, and a variety of water escape processes affected the soil profile at both the macro and microscale, favouring water, sediment and iron redistribution, enhancing redoximorphic features, as well as the occurrence of anomalous iron pedofeatures absent in PS1.

Iron depletion and accumulation features in PS2 are not only displayed as domains of iron bleaching and accumulation linked to the larger pore system but also occur randomly in the groundmass, and can be preliminary considered as microscale water-escape features (Figures 6e and 6f) after soil formation. These pedofeatures are also linked to the occurrence of inherited iron-rich elements, such as reworked iron nodules with sharp boundaries including corroded quartz grains and runiquartz (Figures 6e and 6f), which also are dominant in the strongly impregnated domains of the iron crusts (Figures 7e and 7f) but rarely observed in PS1 (Figure 4). These pedofeatures are characteristic of strong deep weathering and are common in the Plio-Pleistocene red-sand formations exposed in this zone (e.g. Boski et al. 1999). They can be interpreted as reworked nodules or crust fragments from the source areas, but their upward emplacement and differential accumulation from vertical fluxes of water and sediment from the underlying Plio-Pleistocene intertidal sands cannot be ruled out, since macroscale water escape features have been reported in the studied exposures related to the activity of the adjacent TLF fault during the last interglacial period (Zazo et al. 2005).

Hydromorphic features observed in both paleosols indicate widespread and long-lasting redoximorphic conditions after soil formation. Groundwater fluctuations linked to the uprising sea-level during the last interglacial period before c. 100 ka BP in PS1 and until c. 70 ka BP in PS2, can partially explain the development of most of the observed features under endosaturated conditions. However, as earlier discussed, perched water tables could also occur during the sea-level drop of the last glacial period allowing subsequent episaturated conditions between c. 70 and 10 ka BP. From this date seasonal artesian fresh-water flows have been presumably acting in the base of the sea-cliff as can be inferred from the existing hydrodynamic models (Salvany and Custodio 1995). In any case, the petrology, mineralogy and micromorphology of the studied paleosols clearly indicate multiple inheritances of iron-rich pedofeatures and the subsequent recurrent mobilization of iron oxides in the zone during and after soil formation. Iron was recurrently transferred from the original weathering profiles on the Paleozoic substratum, to the Plio-Pleistocene "red sand" formations and eventually to the Middle-Late Pleistocene pedogenic cycles in the ancient coastal plain. Subsequent endosaturated, and probably episaturated, environments in the previously formed soils allowed hydromorphic conditions and renewed iron mobilization by redox processes.

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REFERENCES

• Beaudou AG. 1972. Expression micromorphologique de la micro-agrégation dans certains horizons de sols ferrallitiques centrafricaine et dans les sols hydromorphes associés. Cahiers ORSTOM, Série Pédologie 10:357-371.

• Boski T, Moura DM, Machado LM, Bebianno JM. 1999. Trace metals on the Algarve coast, I: Associations, origins and remobilisation of natural components. Bol Inst Esp Oceanogr. 15(1-4):457-463.

• Bullock P, Fedoroff N, Jongerius A, Stoops G, Tursina T, Babel U. 1985. Handbook for Soil Thin Section Description. Wolverhampton: Waine Research Publications. 152 p.

• Cáceres L. 1995. Geomorfología del sector occidental de la Depresión del Guadalquivir. Tesis Doctoral. Universidad de Huelva. 245 p.

• Chester DK. 2012. Pleistocene and Holocene geomorphological development in the Algarve, southern Portugal. Geomorphology 153-154:17-28.

• Chester DK, James PA. 1995. The Pleistocene Faro / Quarteira formation of the Algarve region, southern Portugal. Geomorphology 12:133-149.

• Eswaran H, Sys C, Sousa EC. 1975. Plasma infusion. A pedological process of significance in the humid tropics. Anales de Edafología y Agrobiología 34:665-674.

• Goy JL, Zazo C, Dabrio CJ, Lario J. 1994. Fault-controlled shifting shorelines in the Gulf of Cadiz since 20 Ky BP. In: Abstracts of the 1st Symposium Atlantic Iberian Continental Margin; 1994 Nov; Lisboa, Portugal; p. 24.

• Martin-Ramos JD. 2004. X-powder, a Software Package for Powder X-ray Diffraction Analysis. Version 2004.03. url: http://www.xpowder.com.

• Martín-Ramos JD, Díaz-Hernández JL, Cambeses A, Scarrow JH, López-Galindo A. 2012. Pathways for Quantitative Analysis by X-Ray Diffraction. In: Aydinalp C, editor. An Introduction to the Study of Mineralogy. InTech. Available from: http://www.intechopen.com/books/an-introduction-to-the-study-of-mineralogy/pathways-for-quantitative-analysis-by-x-ray-diffraction.

• Mayoral E, Pendón JG. 1986. Icnofacies y sedimentación en zona costera. ¿Plioceno Superior?, litoral de Huelva. Acta Geol Hisp. 21-22:507-513.

• Monteiro M, Sánchez Furtado A, Cardoso JL. 1981. Testemunhos de couraças ferruginosas quaternárias no Sudoeste de Portugal. Bol Soc Geol. Portugal 12:417-420.

• Munsell Soil Color Charts. 1990. Baltimore, Maryland: Macbeth Division of Kollmorgen Instruments Corporation.

• Rodríguez Vidal J. 1989. El inicio de la red fluvial cuaternaria en el sector occidental de la Depresión del Guadalquivir. AEQUA Monografías 1:27-31.

• Salvany JM, Custodio E. 1995. Características litológicas de los depósitos pliocuaternarios del Bajo Guadalquivir en el área de Doñana: implicaciones hidrogeológicas. Rev Soc Geol España 8:21-31.

• Torcal L, Zazo C, Marfil R. 1990. Caracterización mineralógica y cronológica de los depósitos arenosos neógenos y cuaternarios del litoral de Huelva, España. (Area: Rio Tinto-Rio Guadalquivir). Estudios Geol. 46:153-164.

• Tornos F. 2008. La Geología y Metalogenia de la Faja Pirítica Ibérica. Macla 10:13-23.

• U.S. Environmental Protection Agency. 1996. Microwave assisted acid digestion of siliceous and organically based matrices. Method 3052. Offce of Solid Waste and Emergency Response, Washington, DC: U.S. Government Printing Offce.

• Vepraskas MJ, Wilding LP, Drees LR. 1994. Aquic conditions for soil taxonomy: concepts, soil morphology and micromorphology. In: Ringrose-Voase AJ, Humphreys GS, editors. Soils micromorphology: Studies in Management and Genesis. Developments in Soil Science, Vol 22. Amsterdam: Elsevier. p.117-131.

• Zazo C, Dabrio CJ, Borja J, Goy JL, Lézine AM, Lario J, Polo MD, Hoyos M, Boersma JR. 1999. Pleistocene and Holocene aeolian facies along the Huelva coast (southern Spain): climatic and neotectonic implications. Geologie en Mijnbouw 77:209-224.

• Zazo C, Mercier N, Silva PG, Dabrio CJ, Goy JL, Roquero E, Soler V, Borja F, Lario J, Polo D, De Luque L. 2005. Landscape evolution and geodynamic controls in the Gulf of Cadiz (Huelva coast, SW Spain) during the Late Quaternary. Geomorphology 68:269-290.