

## Changes of porosity due to weathering in quartzites and slates of a Raña profile (Montes de Toledo, Central Spain)

*Cambios de porosidad debidos a alteración de cuarcitas y pizarras en un perfil de la Raña (Montes de Toledo, España)*

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### ABSTRACT

Rañas are alluvial fan deposits of Plio-Pleistocene age that form the piedmont platforms around the mountains in the interior of the Iberian Peninsula. They are composed of cobbles, pebbles and gravels of quartzite and some quartz, all embedded within a clayey matrix displaying striking changes in hues due to hydromorphism. Beneath these platforms, the Hercynian basement is consistently deeply weathered. In the profile of the Raña, the quartzite stones located into the clayey horizon have a weathering rind that is whitish to ochre in colour, in contrast to the dark reddish hue of those located within the leaching horizon, just below the land surface. These differences are related to changes in the physical properties (e.g., bulk density and porosity), mineralogy (presence of oxyhydroxides) and weathering processes that have taken place in the profile. Such processes have led to the corrosion and replacement of the quartz grains by the iron oxyhydroxides. The main cause is the dramatic changes in the water regime occurring in the pores at the surfaces of the quartzite stones. Due to weathering the slates outcropping beneath the Raña have undergone important release of matter (ca. 30%), together with changes in the mineral association, with a progressive reduction in the component of the unweathered slates and an increase in new minerals (smectites, kaolinite and iron oxyhydroxides) upwards.

**Keywords:** porosity, weathering rinds, quartzite stones, slates, piedmont.

### RESUMEN

Las Rañas son depósitos de abanicos aluviales del Plio-Pleistoceno que forman plataformas de piedemonte alrededor de las montañas del interior de la Península Ibérica. Están formadas de bloques, cantos y gravas de cuarcita dominantes y algún cuarzo engastados en una matriz arcillosa que muestra importantes contrastes de color causados por hidromorfismo. Bajo estas plataformas, el zocalo hercínico se encuentra profundamente alterado.

En un perfil de Rana se distinguen dos tipos de horizontes: i) el superior, de pocos decímetros de grosor, rico en cantos, gravas, arena y limo, pero pobre en arcilla, y ii) el inferior, normalmente de algunos metros de grosor y rico en arcillas. Dependiendo de su situación dentro del perfil de la Rana, los cantos y gravas de cuarcita situados en el horizonte rico en arcillas presentan una corteza de alteración de tonos ocres a blancos, en contraste con los situados en horizonte de lavado inmediatamente bajo la superficie, que presentan una corteza de alteración de intenso color rojo. Estas diferencias están relacionadas con cambios en las propiedades físicas (p. ej. densidad aparente y porosidad), en la mineralogía (presencia de oxihidroxidos) y en los procesos de alteración que han ocurrido en el perfil y que han llevado incluso a la corrosión y reemplazo de granos de cuarzo por oxihidroxidos de Fe. La causa principal han sido los cambios hídricos ocurridos en los poros de los cantos y gravas de cuarcita. Las pizarras alteradas que aparecen bajo la Rana presentan una importante pérdida de materia (ca. 30%) y cambios en su composición mineral, con una progresiva reducción en sus componentes iniciales y el aumento de otros nuevos (esmeclitas, kaolinita s.l. y oxihidroxidos de hierro) hacia techo del perfil.

**Palabras Clave:** porosidad, costras de alteración, cuarcitas, pizarras, piedemonte.

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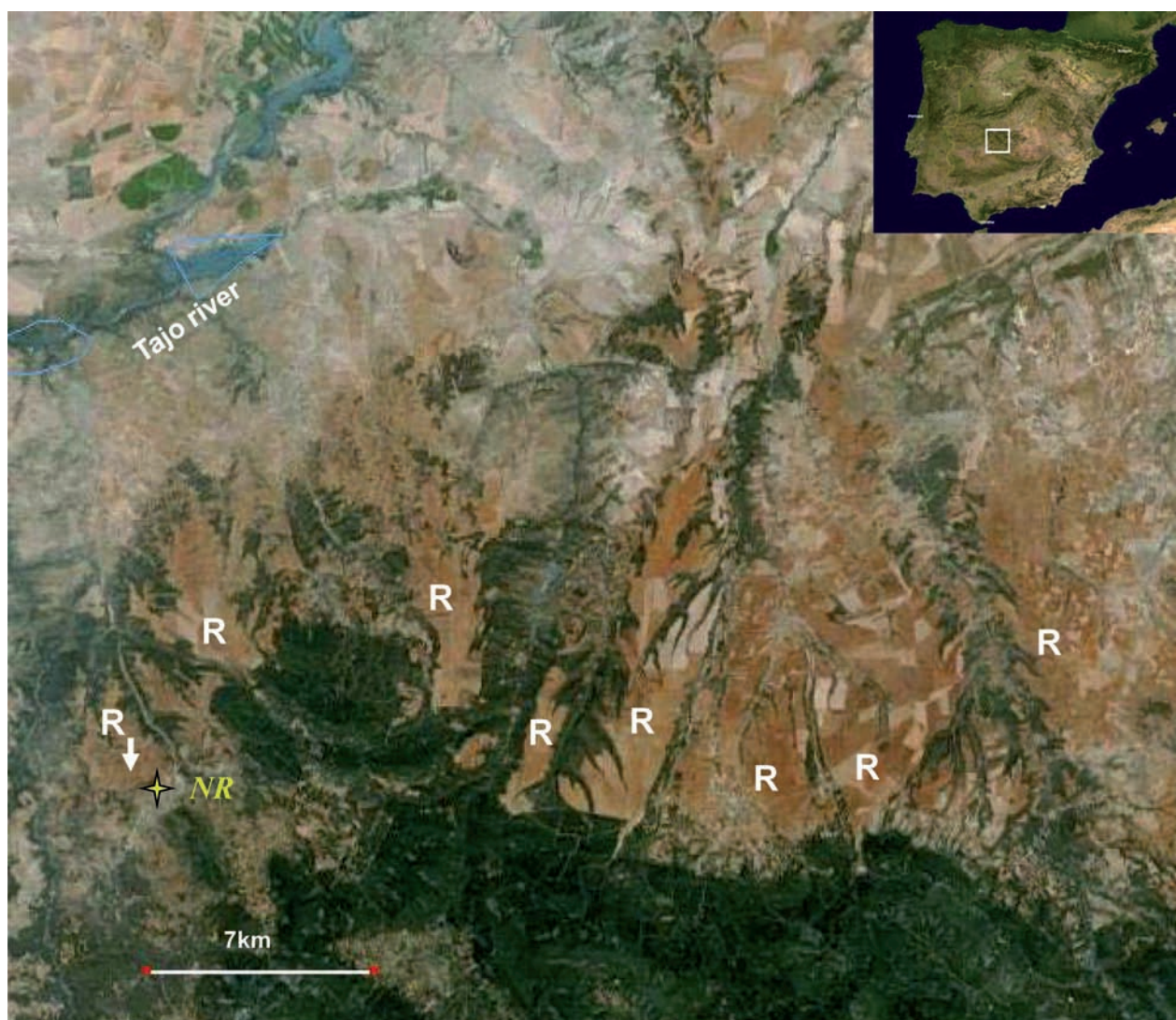


Fig. 1.—Position of the Raña deposits (R) around the Northern piedmont of the Montes de Toledo, in the middle of the Iberian Peninsula. The arrow points to the location of the profile studied. NR is the situation of the village called La Nava de Ricomalillo.

## Introduction

In the interior of the Iberian Peninsula important mantles of detritus materials termed “the Raña” generic are widespread upon different lithologies giving rise to piedmont surfaces gently sloping to the interior of the Tertiary basins. The Rañas are alluvial fan deposits (<25m thick) composed of cobbles, pebbles and gravels of quartzite and some quartz, all embedded within a clayey matrix displaying striking changes in hues due to hydromorphism. Their origins have not been synchronic but an age between the Upper Neogene to the Lower Pleistocene has been attributed (Molina *et al.*, 1991; Matéiz Lope *et*

*al.*, 1995; Borger H. 1997; Clausell *et al.*, 2001). Morphologically, these piedmont platforms are some 150-200m above the current rivers.

Most studies addressing the piedmont deposits have been focused on their age, their lithologies and their sedimentary structures, and their meaning within the morpho-structural and palaeoclimatic evolution of the region in which they are found. On the other hand, some works referring to soil developed over alluvial fans, studied of the weathering processes that these materials have undergone once deposited focus on mineralogical analyses mainly of clays and, in some cases, attending to their micromorphological features.

However, few authors have addressed the role of porosity in these processes.

Many profiles developed on the Rañas have been studied previously, most of them from a pedological viewpoint (Vaudour, 1977; Espejo, 1978, 1987; Gallardo *et al.*, 1987; Ingelmo *et al.*, 1991; Pardo *et al.*, 1993; Vicente *et al.*, 1997; Espejo *et al.*, 2003). In all cases, the soils are old and the profiles are well developed to be made such as luvisols, ultisols, and planosols, displaying a more or less sharp delimitation among horizons. Wherever this cover lays upon the Iberian Hercynian basement its outcrops are always deeply weathered. With regard to this aspect, Molina Ballesteros *et al.* (2011) focused on two profiles of a weathered basement under the Rana cover: one on granite and the other on pre-Cambrian slates. In both profiles, the Rana is some meters thick, whereas the weathering of the basement rocks reaches dozens of meters in depth.

The present study aims to the role of porosity on weathering of the quartzite stones of the sedimentary cover and slates right under this cover, but we also consider the mineralogical changes of both materials.

## Materials and Methodology

### Materials

To accomplish this investigation, samples from a profile located near the village of La Nava de Ricomalillo in the region of the Montes de Toledo, central Spain (Fig. 1), (cord. 39°38'38''N; 4°47'32''W) were selected. Here the Raña deposits remain at an altitude of ca. 735 m a.s.l. over deeply weathered slates and greywackes of pre-Ordovician age. Currently, the region has a Mediterranean climate (mean temperature ca. 13°C) influenced by the nearby mountains with summits at altitudes of 1200-1400 m. The annual rainfall varies between ca. 500 mm/year in the piedmont platform and >900 mm/year at the summits of the mountains, where snow is common for some weeks in winter. The water balance of the soils shows a deficit from June to September/October, and a surplus from January to April (Cuadrado *et al.*, 1987; Ingelmo *et al.*, 1991). However, during some weeks of April and/or May it is common for the soils to become flooded (Fig. 2 A). Accordingly, depending on the water regime along the year, the wilting point is reached in June. The soils are extremely dry ( $pF > 4.2$ ) down to a depth of ca. 30-60 cm in July, August and

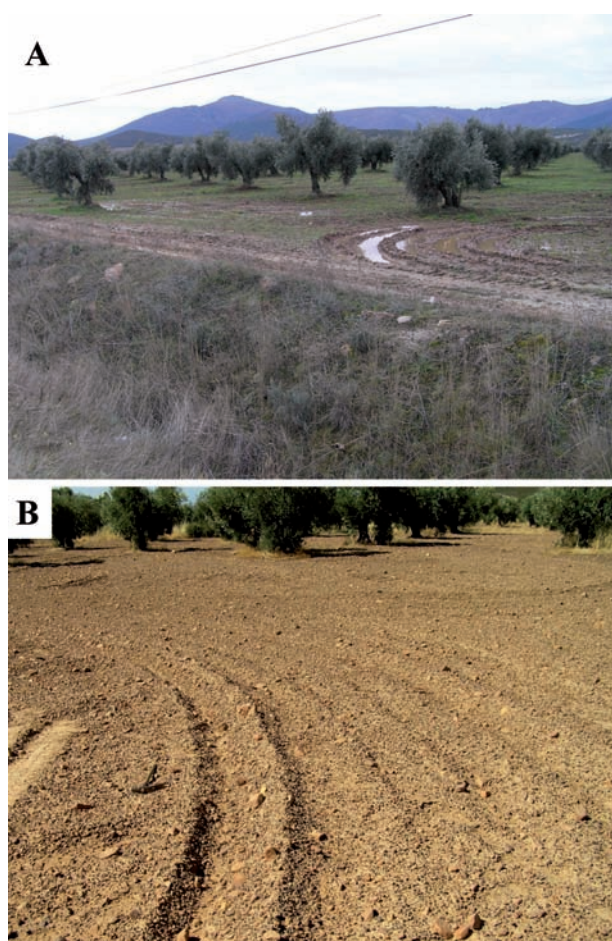


Fig. 2.—The Raña surface during the wet season (A) and at the end of the dry season (B) in the region of the Montes de Toledo.

September (Molina Ballesteros and Cantano Martín, 2002) (Fig. 2 B).

In the profile selected, 5-6 m thick of the Raña deposits (Fig. 3 A) lays on slates whose alteration grades upwards to a compact and reddish clayey mass crossed by a network of whitish weathered fissures and veins composed by kaolinites (Fig. 3 B). Two main horizons can be distinguished in the Raña sediments: a) an upper horizon, immediately below the land surface some 0.3-0.5 m thick, with a sandy to loamy matrix and rich in pebbles and gravels of quartzite (centil ca.8 cm) with dark reddish weathering rind, and b) a lower horizon, some 4 to 5 m thick, rich in clays where the coarse fraction (centil ca.14 cm) displaying drastic changes in hues is embedded. Some gravels and pebbles of quartz are present in this sedimentary cover, but in a percentage < 15% and they do not display weathering rinds.

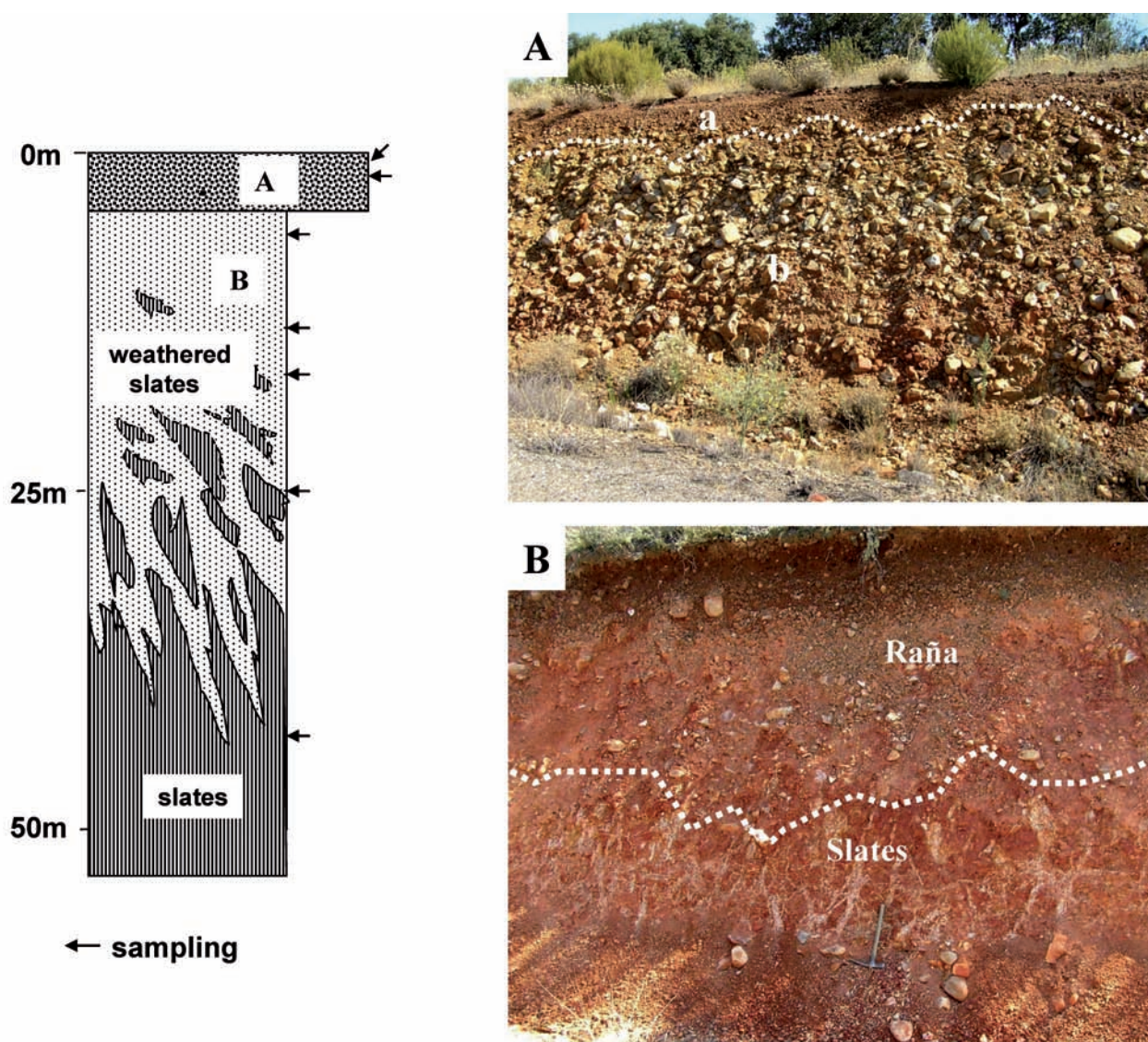


Fig. 3.—Sketch of the profile studied with the situation of sampling. Picture A shows the two horizons (a and b) distinguished at the upper part of the Raña cover. Picture B shows the contact between the Raña and weathered slates, with the bleached fissures and discontinuities.

At the land surface, iron oxy hydroxides appear surrounding the quartzite stones (Fig. 4 A), or as small free nodules some mm in size. A red weathering rind (reddish brown, 2.5YR after Munsell Color System) grades from the outside of stones to the ochre interior (orange 7.5YR to yellow 5Y), the darkest zone being some mm thickness. In the lower horizon, the cobbles, pebbles and gravels embedded into the clayey matrix display a weathering rind some cm thick that is yellow (hues 2.5Y) and/or whitish in colour (Fig. 4 B). Whitish and greys hues (5GY) cross the ochre, the first

being related to fissures and areas of leaching (composed by kaolinites). The ochre-yellowish front of weathering can reach the core of some pebble affecting to the whole rock preserving its morphology while no remove. Wind removes the finest fractions of the upper horizon during the dry seasons, while the clayey mass of the lower horizon remains more or less moist.

In the profiles of the old Rañas the reddish quartzite stones appear related only to the land surfaces, while they can also appear at any horizon into the new profiles of the younger surfaces (e.g.

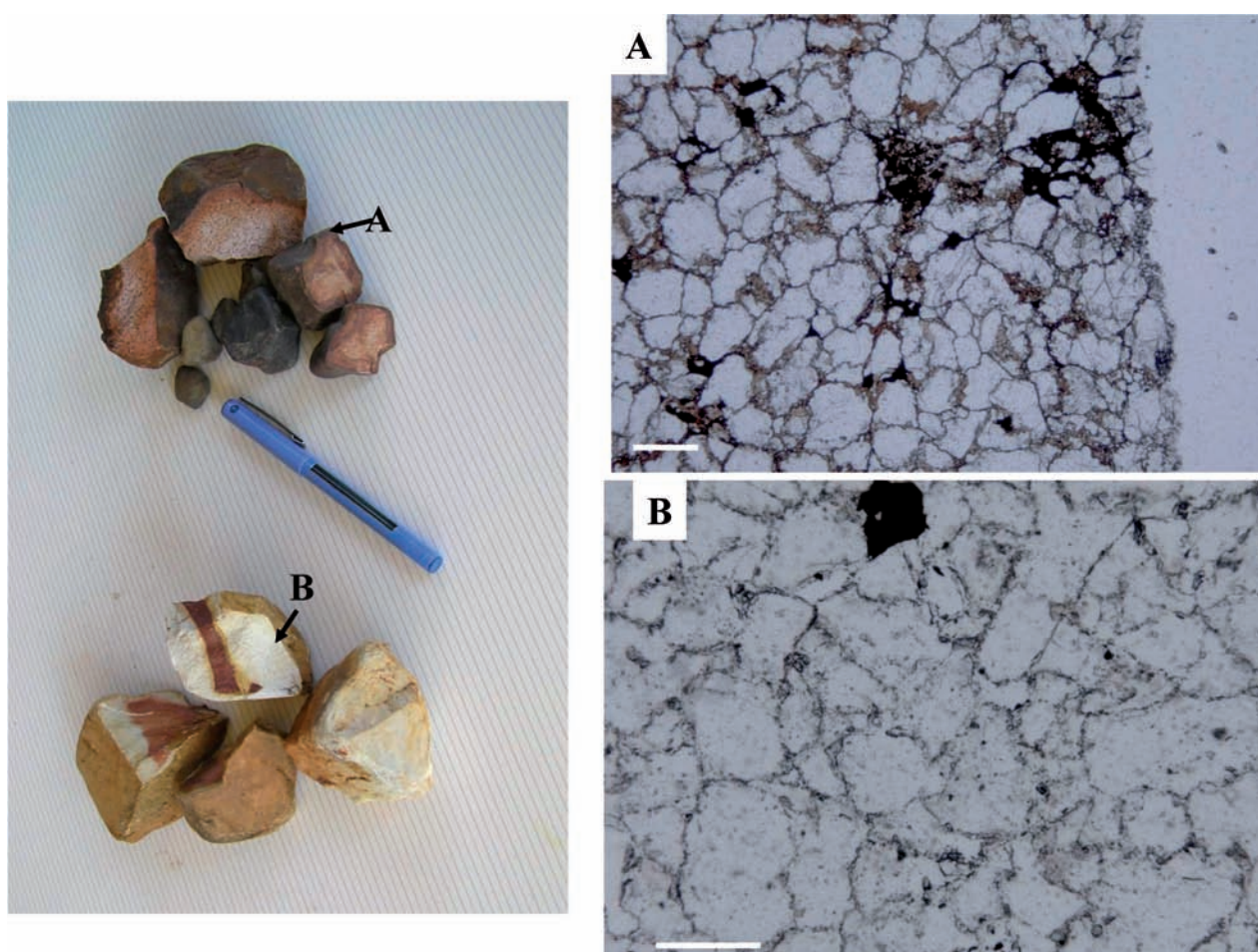


Fig. 4.—Examples of the two types of pebbles from a profile of the Raña. A and B are microphotographs (one nicol) of two thin sections from the reddish and whitish rinds, respectively. Samples A come from the Raña surface while samples B come from ca. 1.5m deep. Scale bars 100 $\mu$ .

new piedmont platforms, old terraces). This points to that i) part of the sediments forming these new deposits come from the Rañas, and ii) many of the stones with whitish and/or ochre cortex are fragile and brittle which led to their disintegration (arenization) during transport.

On slates, the weathering traits are evident down to some 13-15m below the contact with the cover. This weathering has preserved volumes and structures of the parent rock (e.g., it preserves quartz dykes orientations upwards), but it has given rise to slabs whose colour, density and porosity change down the profile. The hues grade from grey (7.5 GY) for the unweathered slates at the bottom to yellowish (2.5 Y), orange (5 YR), and reddish (10 R) for the strongly weathered rock alternated into clayey mass at the top, crossed by whitish and yellowish fissures beneath the cover.

#### *Techniques.*

Mineral and petrophysical techniques were used in this work. Samples of quartzite stones of the Raña cover and samples from the different levels of the weathered slates were collected (Fig. 3). Pieces of the weathered quartzites and of the slates were dried and grained to ca. <math>16\mu\text{m}</math> size. The clay fraction of the slate samples was separated regarding as remaining suspension for 8 h after shaking with water for 24 h.

The mineralogy of the collected samples (weathering rinds and slates) was determined by: i) observation of thin sections using a Leitz polarized light microscope (Leitz Laborlux 12 Pol S); ii) the study of small pieces (3D) of samples using a SEM and microprobes EDX (HITACHI Co. model S4800); iii) X-ray diffraction patterns of powdered

Table 1.—Changes in density and porosity (hydic properties) of pebbles of quartzite from the Raña in the surroundings of Navahermosa (province of Toledo).

Samples		Total porosity (%)	Free porosity (%)	Real density g.cm <sup>-3</sup>	Bulk density g.cm <sup>-3</sup>
Pebble on the Raña surface	Dark-red rind	1.74	1.51	2.67	2.62
	Pebbles (no weathered)	1.51	1.33	2.66	2.63
Pebble into the Raña	Ochre rind	3.82	3.36	2.66	2.56
	Whitish zones	5.83	5.02	2.66	2.51
	Core (no weathered)	1.50	1.35	2.67	2.62

(<16µm) and clay fractions of each sample using the XRD technique (Philips PW-1730 device with a PW-1050 goniometer, a PW-1710 diffractometer control, CuKα tube type).

The physical properties of the samples from the levels of the Raña cover and from the slates (Fig. 3) were studied by: i) hydric determinations according to the French Standard Norms NF B10-503 and 504 (Paris, 1973), which inform on changes in the density and porosity of the three samples from the pebbles of the surface and into the Raña and upper and lower level of weathering slates (Iñigo *et al.*, 1994); ii) the mercury porosimetry injection techniques (Quantachrome Co. PoreMaster PM 60) to determine the pore size distribution of a mixture of small pieces from the reddish and ochre rinds of three selected pebbles.

## Results

### *Weathering of pebbles and gravels of the Raña*

Table 1 shows the mean values for the density and porosity of three pebbles of quartzite with the reddish rind from the upper horizon (20-30cm deep), and another three samples with the whitish/ochre rind from the clayey horizon (*ca.* 0.8-1.5m deep). Moreover, three pebbles of apparently no weathered quartzite from the surroundings of the profile have been tested in order to know their density and porosity. The data were obtained following hydric methods. The rate bulk/real densities suggest a release of matter due to weathering of *ca.* 6% in case of the whitish/ochre

stones, being higher in the whitish than in the ochre zones. Data of the apparently no weathered quartzites are similar to that of the core of the ochre pebbles, and they were used as reference with that of the reddish pebbles. This rate is *ca.* 1-2%.

XR diffraction of powder from samples of the reddish and whitish/ochre rinds (Fig. 5) showed that, apart of quartz and small signatures of 1:1 phyllosilicates (the kaolinite *s.l.* groupe) that of hematite can be identified only in the former. SEM photographs of the reddish rind (Fig. 6 A) show that Fe oxy hydroxides tend to concentrate within the finest pore spaces among the quartz grains, while the quartz grains of the whitish/ochre rind display strong corrosion traits (Fig. 6 B).

Attention should be paid to the fact that the ordinate scale for the reddish rind sample is one fifteenth of that for the ochre rind, indicating that the porosity of the reddish sample is almost negligible.

Whereas the data show that in the ochre/whitish zones the main porosity is centred between 0.1-10 µm (Fig. 7), in the reddish rind the main porosity is finer than 1µm. The data of porosity centred at 0.01µm and between 10-100µm of the reddish rind probably are caused by disruptions during the measurements.

### *Changes in slates of the basement*

The pre-Cambrian slates form the basement of this profile. Two levels of weathering can be distinguished in this basement: i) the lower level, being apparent some 13-15m below the contact with the cover, and ii) the upper level, beginning at

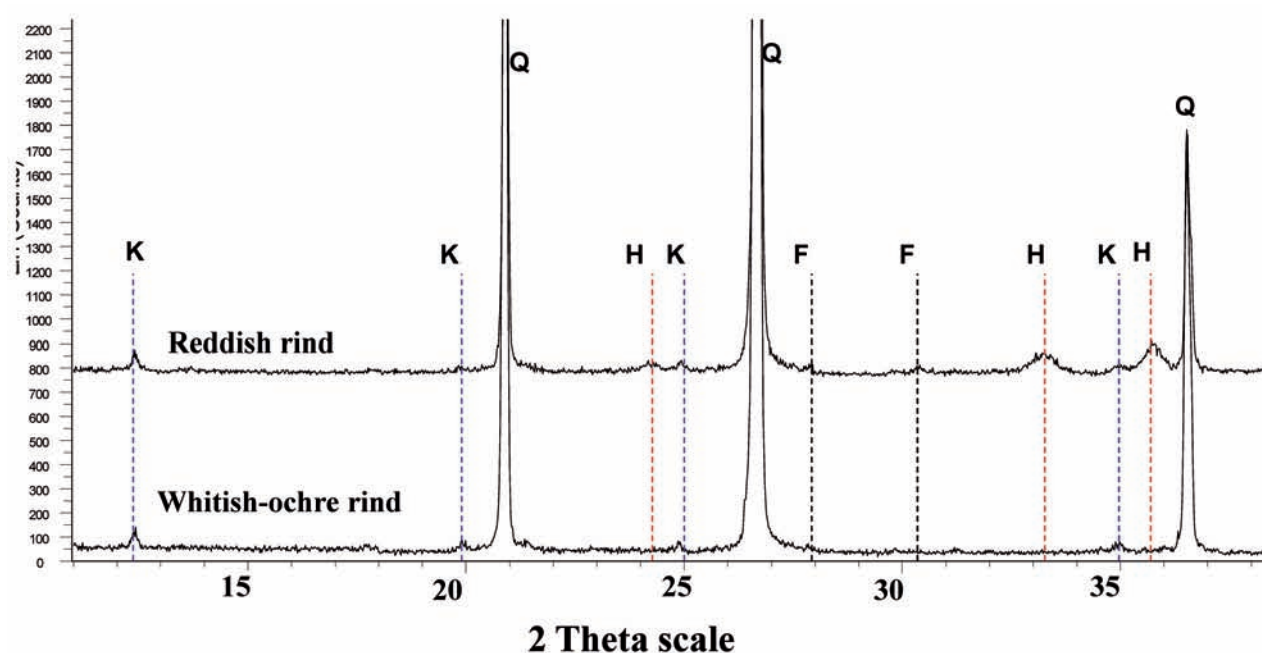


Fig. 5.—XRD diagrams (powder) of the reddish and whitish-ochre rinds of two pebbles of the Raña cover. Apart of the quartz (Q), signatures of the 1:1 phyllosilicates (K) can be identified in both diagrams. By contrast, the signatures of hematites (H) and K-feldspar (F) appear only in the diagram of the reddish rind.

ca. 3-4 meters beneath the contact with the Raña cover. Therefore, sampling was carried out at different depth (Fig. 3), each sample being of ca. 5-10 slabs some cm in size.

At the lower level, alteration of the parent minerals has led to a reduction in feldspar, in some phyllosilicates (e.g. chlorites) (Fig. 8 A, B), and generation of new ones (e.g. smectites *s.l.*) (Fig. 8 C, D). At the upper level, the Fe oxy-hydroxides and kaolinites *s.l.* increase. Oxyhydroxides hamper the recognition of the different clay minerals by XRD techniques. However, once the oxy-hydroxides have been leached out in the bleached zones, both kaolinites *s.l.* and smectites *s.l.* can be identified. Table 2 shows that the real density of the slates does not change along the profile, total porosity is increased by some 14-fold in comparison with the unweathered slates and, since the weathering is conservative in volume, there is a reduction of ca. 30% in the bulk density at the top of the weathered basement.

### Discussion

Over the last thirty years studies of weathering rinds developed on stones of different compositions

have been published, most of them referring to cobbles and pebbles occurring on old piedmont platforms and terraces under different climates. Some authors (e.g. Anderson and Anderson, 1981; Chinn, 1981; Colman, 1981; Colman and Pierce, 1981; Oguchi 2004) consider that the thickness of the rind is indicative of age. Others (e.g. Etienne, 2002, Etienne and Dupond, 2002; Oguchi and Matsukura, 1999) have focused on the role of porosity and the micro-organisms involved in the weathering process.

A somewhat similar problem is found in the development of the weathering rind on the quartzite stones of the Rañas, but in this case age is not the only factor to bear in mind; the facilities for drainage, the presence of carbonates, the sources of the materials, etc. have all influenced the situation (Alcalá del Olmo *et al.*, 1993; Jiménez Ballesta and Ibáñez Martí, 1993; Borger 1997). In general, only the quartzite stones of the Rañas and the highest terraces display some weathering rind and, even then some of them may have been inherited.

According to different authors (Espejo, 1978; Gallardo *et al.*, 1987; Alcalá del Olmo *et al.*, 1993; Pardo *et al.*, 1993), there is a progressive reduction in the development of the catena profiles of soils

Table 2.—Changes in density and porosity (hydic properties) of samples of slates from the profile located close to the village of La Nava de Ricomalillo, Montes de Toledo.

Samples (depth)		Total porosity (%)	Free porosity (%)	Real density g.cm <sup>-3</sup>	Bulk density g.cm <sup>-3</sup>
Upper Level of weathering	7 m	34.8	32.5	2.71	1.75
	13 m	24.8	23.7	2.70	2.18
Lower Level of weathering	18 m	19.7	19.2	2.73	2.20
	25 m	8.5	8.3	2.72	2.52
	42 m	2.5	2.4	2.73	2.67

from the Rañas (the oldest) to the different terrace levels. Taking into account that these surfaces have undergone annual periods of flooding in winter and spring and extreme drought during the summer for a very long time (since the Pliocene?), xerolysis (Chauvel and Pédro, 1978; Chaussidon and Pédro, 1979) may occur in the upper horizons. Close to the land surface, the degree of dryness may be very high during some months of the year leading to alteration of clays and concentration of Fe oxyhydroxides in the finest porosity (Fig. 6 A). By contrast, at the clayey horizon ferrolisis (Brinkman, 1970) and the dissolution of both the silica cement and the corrosion of the quartz grains are the main results of weathering (Fig. 6 B). A sketch of the reactions taking place into these profiles would be:

1. Parent mineral + weathering → Fe<sup>2+</sup> released + oxidation → Fe<sup>3+</sup> + e<sup>-</sup>

2. Fe<sup>3+</sup> + nH<sub>2</sub>O → Fe<sup>3+</sup>(OH)<sub>n</sub> + nH<sup>+</sup> (acidification by ferrolisis)

3. Fe<sup>3+</sup>(OH)<sub>n</sub> ± de-hydration → ± crystallization → new minerals (\*)

(\*) = goethite, maghemite, hematite, etc.

During the extreme drought period, at the top of the profiles:

4. Clay.Fe<sup>3+</sup>(OH)<sub>n</sub> + nH<sup>+</sup> + H<sub>2</sub>O<sub>residual</sub> in pores → clay. H<sup>+</sup> + Fe<sup>3+</sup>(H<sub>2</sub>O)<sub>n</sub>

All these reactions have led to changes in the porosity and density of the cobbles, pebbles and gravels from the Raña cover as seen in Table 1. However, other processes are also driven by these changes (Abreu and Robert, 1987; Morris and Fletcher, 1987; Abreu, 1990): within the fine

porosity, oxyhydroxides may react with the surface of the quartz grains, giving rise to an oxyhydroxide – silica complex of some nanometers thick as the phyllosilicate hisingerite Fe<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>.2H<sub>2</sub>O (Vidal *et al.*, 1993), and leading to a progressive replacement of the quartz grains. Many of these quartz grains, with corroded edges, have been released into the sandy-to-loamy material of the upper horizon leading to a progressive reduction of the size of the stones.

Moreover, these processes could also explain the transformation of the inherited clayey material into hydroxy-interlayered 2:1 and high charged smectite clays as a stage in the alteration of illite leading to the enrichment in kaolinite of these soils of the Raña, pointed out by Aragonese and García González (1991).

According to the SEM images (Fig. 6) and data of the Hg porosimeter (Fig. 7), porosity with a diameter of *ca.* 0.1-10µm of samples from the ochre/whitish rinds seems to be caused by the dissolution of both the silica uniting the quartz grains and the corrosion of grains. By contrast, samples from the reddish rind shows a fine porosity centred at *ca.* 0.1-1µm and two extremes: pores of 0.01µm. Moreover, in a comparison to the ranks of the Hg intruded in both samples, that of the ferruginous rinds is reduced *ca.* 15-fold with respect to that the ochre/whitish rinds.

Under these conditions, diffusion would be an important mechanism of weathering (Pédro, 1993; Meunier *et al.*, 2007). These type of processes depend on the “surface charge” of both the Fe oxyhydroxides and of the quartz (Williams and Crerar, 1985; Walsch and Dultz, 2010), the charges mainly



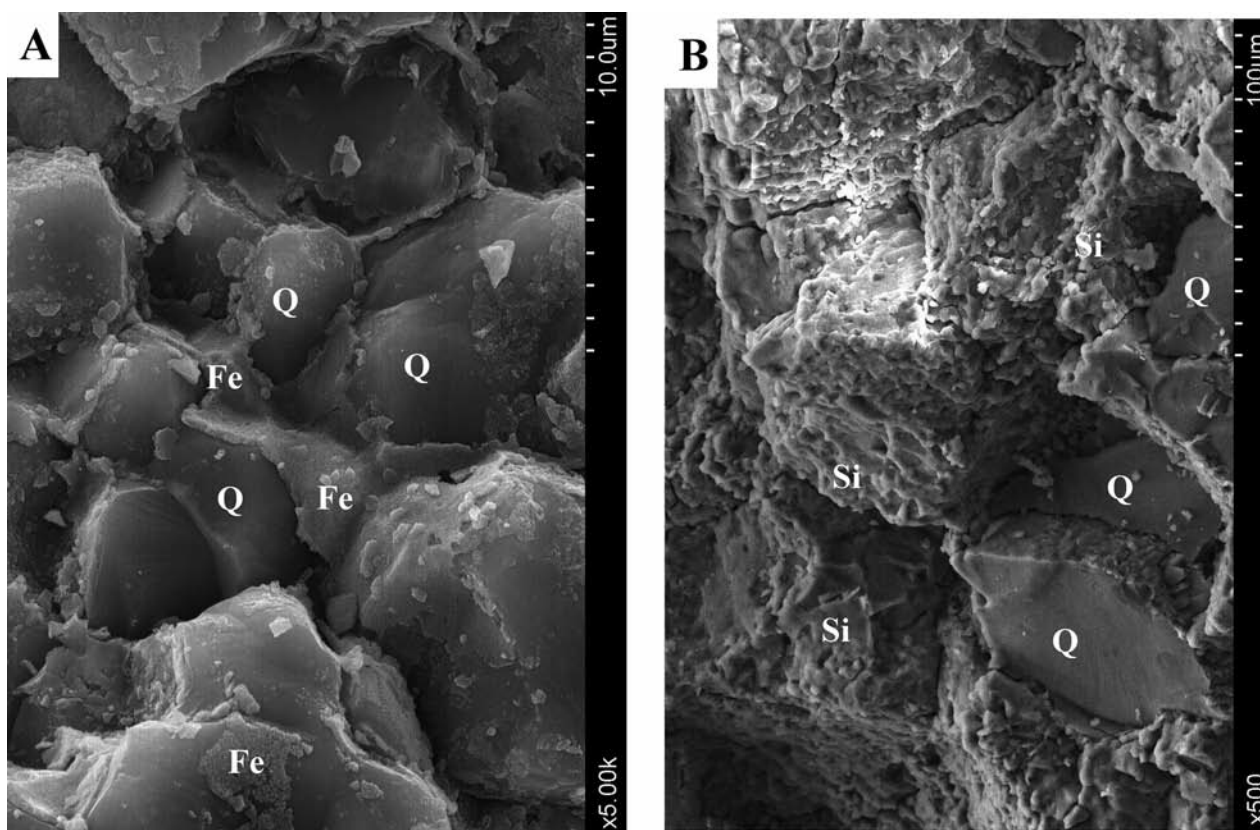


Fig. 6.—SEM photographs of samples from two pebbles of quartzite from the profile studied. Samples A and B belong to the reddish and whitish weathering rinds respectively. In A, the quartz grains (Q) are surrounded by oxy-hydroxides (Fe); in B, the quartz grains are corroded and covered by a jelly-like film of silica (Si).

being controlled by the pH and the presence of ions such as  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{SO}_4^{2-}$ , etc. in the soil solution. Moreover, according to Tardy and Nahon, (1985) and Nahon (1991), among others, the more-or-less dehydrated phases of the oxy-hydroxides develop favourably inside the microsites. By contrast, the coarse porosity in both rinds may be due to the release of the quartz grains that, more-or-less corroded, have been incorporated into the sandy-to-loamy fraction of the profiles. These fractions are dominant at the surface of the Raña landscapes (Fig. 2 B).

As in all profiles of the Rañas, the basement is deeply weathered regardless of the lithology, the degree of weathering increasing upwards towards the Raña cover. At the top of the weathered slates, the fissures and discontinuities define a network of planes by which the oxy-hydroxides attached to the clayey fraction are first hydrated (ochre and yellow hues) and later on leached out from the profile (bleached zones in Fig. 3 B). Leaching is facilitated

by the organic matter coming from the soils profiles developed within the Raña. Table 2 shows that the weathering affecting the slates has brought about a release of matter, with a reduction in bulk density of ca. 30% at the top of the weathered basement.

In previous works addressing profiles outcropping in the region of the Montes de Toledo (Molina *et al.*, 1991; Vicente *et al.*, 1991), the authors posed the question of whether there have been one or two different periods of weathering, the “younger” one would have affected the cover and the “older” one would have affected the slates of the basement. TEM studies carried out on a similar nearby profile located on the southern watershed of the range (Vicente *et al.*, 1997) have revealed that there is a continuum in the mineralogical evolution caused by weathering along the profile. The fact that there is no interruption in this evolution throughout the profile suggests that the hypothesis of the existence of two weathering processes under different climates is

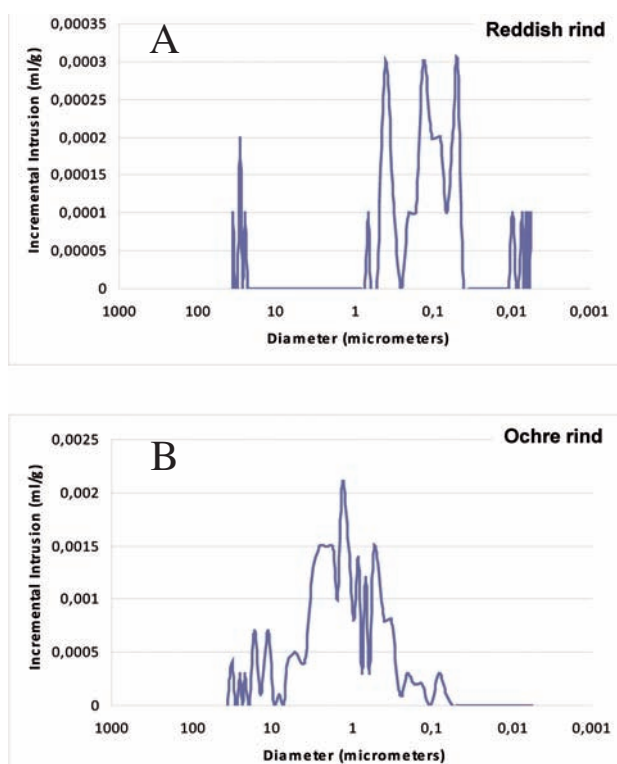


Fig. 7.—A. Hg porosimetry data from the reddish rind of a pebble of quartzite located at the Raña surface in the profile studied. B. Hg porosimetry data from the whitish weathering rind of a pebble of quartzite located within the Raña deposit of the profile studied.

incorrect. Furthermore, taking into account that the Raña deposits display blocks of quartzite that in many places reach up to *ca.*  $\frac{1}{4}$  m<sup>3</sup>, it is difficult to explain how a mantle of deeply weathered rocks, such as slates in this case, could have been preserved unless the weathering affected to both, the basement and the Raña cover, simultaneously.

The study of a similar profile located in the Salamanca province and developed on the same pre Ordovician slates (Molina Ballesteros and Cantano Martín, 2002) showed that the whitish-greyish fissures appearing in both the Raña and in the weathered basement are rich in clay of the 1:1 and 2:1 groups plus vermiculite, micro grains of quartz and some feldspars *s. l.* By contrast, the ochre and reddish clayey masses located at the top of the weathered basement have goethite and hematite, respectively. The dominance of the 1:1 phyllosilicates: i) in the Raña, ii) at the top of the weathered basement, iii) in the bleached fissures and in the whitish clayey masses, and iv) the rearrangement of the Fe oxyhydroxides throughout

the profile, all points to somewhat acid conditions for weathering.

Different works (Clausell *et al.* 2001; Molina Ballesteros and Cantano Martín, 2002; Molina Ballesteros *et al.*, 2011) show that weathering is a combination of processes working together: on the surface (pedological processes) and under groundwater conditions, the latter becoming exposed as the drainage networks is incised. Whereas the pedological weathering leads to the alteration of the structures of the parent rocks, groundwater weathering is more-or-less conservative as regards these structures. Currently, the weathering process continues to be active on the Raña cover, on the old piedmont and terraces deposits, and on the basement. Most parts of these profiles remain more-or-less wet even during the drought period of the year.

## Conclusions

1. On the cobbles, pebbles and gravels of the Raña:

These show weathering rinds whose thickness, colour and porosity depend on their situation in the profile. The origin is either the release of components, mainly silica (whitish/ochre rinds), or the contribution of oxy-hydroxides (reddish rinds) which replace the quartz grains. The main cause of the replacement is the dramatic changes in the water regime occurring in the pores at the surfaces of the quartzite stones, where xerolysis may have long been active.

We found a release of matter of *ca.* 6% in the whitish/ochre rind, while in the reddish one it is *ca.* 2%, the difference being due to new contributions of oxy-hydroxides. This contribution has corroded the quartz grains and has led to a reduction in the mean size of the quartzite stones.

2. On the slates of the basement:

Weathering has had the following effects: i) a large proportion of the parent phyllosilicates have been dissolved and/or have evolved to new ones, and ii) a progressive release in Fe oxy-hydroxides upwards. Immediately below the sedimentary cover, the oxy-hydroxides are more hydrated and leached out, leading to bleached zones along fissures where

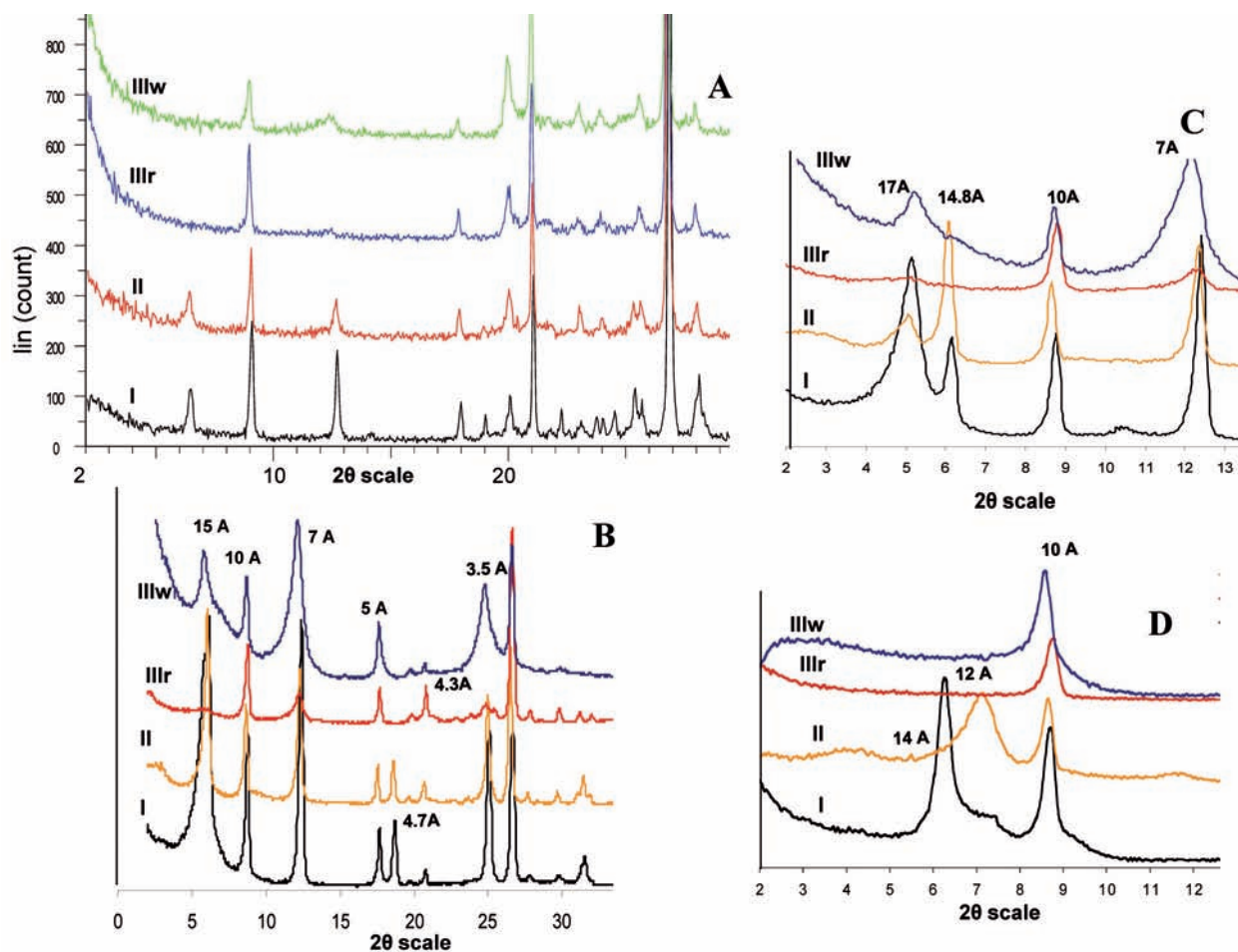


Fig. 8.—XRD diagrams of slates from the profile studied. A: Whole rock powder analysis. B: oriented clay fraction. C: oriented clay fraction after solvation with ethylene-glycol. D: oriented clay fraction after heating at 550°C. The lower level of weathering in the profile: I, no weathered slate and II, ochre weathered slate. The upper level of weathering in the profile: IIIr, reddish weathered slate and IIIw, bleached zones of weathered slate.

the new phyllosilicates (mainly kaolinites *s.l.*) can be identified.

Except at the contact with the cover, the weathering process is conservative in volume along the profile, with a reduction of *ca.* 30% in the bulk density upwards. Although at the top of the weathered slates the total porosity is some 14-fold greater in comparison with that of the not weathered basement, the differences between free and total porosity along the profile are quite limited.

### 3. On the climatic significance.

After these data we cannot specify the climates of this region since the end of the Neogene, but only that the land surface underwent periods of droughts

with strong sunshine, and flood more or less periodically. The processes studied are not only because of climate but also because of drainage that was progressively deteriorated along time due to weathering and re-distribution of matter within the profiles and in the landscape. Without taking this idea into account one can fail in the climatic interpretation of this palaeo-scenery.

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