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THE ROLE OF HYDROTHERMAL ACTIVITY IN THE ORIGIN OF THE FERROGINOUS CRUSTS IN CALATRAVA (GUADIANA BASIN OF SPAIN): AN APPROACH TO THE PALAEOCLIMATIC CONDITIONS

M. A. POBLETE PIEDRABUENA

Department of Geography, University of Oviedo, Campus del Milán, Avda. Tte. Alfonso Martínez, s/n. 33011 Oviedo, Spain.

mpoblete@correo.uniovi.es

ABSTRACT

Through chemical, mineralogical and geomorphological analysis, the ferroginous crusts in Calatrava are interpreted as Pliocenous and Pleistocenous deposits (alluvial fans, rañas, fluvial terraces, colluviums, accumulative glacis, etc.) cemented by ferrous oxides and hidroxides (hematite and goethite), by a lateral movement of hot springs loaded with dissolved iron, probably under a very extreme Mediterranean Palaeoclimate, which has governed this area since the lower Pliocene until the upper Pleistocene, without any lateriric weatherings being detected in any case.

KEYWORDS

Iron encrustation, hot springs, lateral lessivage, glacis and terrace crusts, Mediterranean Palaeoclimate, Calatrava.

INTRODUCTION

The area in the study can be found in the Campo de Calatrava, to be exact, in the confluence between the rivers Guadiana and Jabalon, forming a tectonic depression situated between the Appalachian landforms of the Montes de Toledo to the North, and Sierra Morena to the South (Fig. 1). It is made of a group of Palaeozoic quartzites mountain ranges with an orientation NW-SE, E-W y NE-SW, which enclose the great La Mancha bowl, alternating with small Tertiary basins full of Pliocenous and Quaternary sediments. Nevertheless, the most important features are, on one hand, the presence of a volcanic relief Tertiary-Quaternary, formed according to Ancochea (1983) and Bergamin y Carbo (1986), from a hot spot and from the lifting of 10 to 20 km of the asthenosphere, which produce the bulge of the crust and the beginning of a failed rift, and on the other hand, the abundance of ferroginous encrustations which could provide valuable information about the Palaeoclimatic conditions prevailing in the central region of Spain during the Tertiary and the Quaternary.

The first reference to ferroginous crusts in the Campo de Calatrava is attributed to Hernandez-Pacheco (1932). In fact, in his study of the central volcanic region of Spain, he points out the presence of quartzite conglomerates cemented by ferroginous cement on the outskirts of some hot springs.

Later Molina (1975) when he analyses the Tertiary and Quaternary sediments of the Campo de Calatrava, interprets as lateritic crust some detritus deposits cemented by ferroginous cement. As far as its chronology, the same author correlates the lateritic crust of Calatrava, genetically and chronostatigraphically, with those found in Zamora, giving them a date between the lower Eocene and the lower Miocene. From a morphogenetic point he considers those laterites as a result of intense mechanisms of chemical alteration under tropical morphoclimatic conditions.

Finally, Crespo (1993) reveals the absence of laterites in the contact between the Paleozoic base and the Tertiary and Quaternary sediments. On the other hand, he no longer mentions laterites but he interprets them as simple ferroginous crusts, which he situates stratigraphically in the ceiling of the Plioquaternary series. He refers to those crusts as of manganese type placed in a subparallel way between phreatomagmatic and sedimentary materials.

Therefore, all these studies manifest the interest stimulated by the ferroginous crusts and at the same time the absence of unanimity in the criteria shown referring to the stratigraphical placing and the chronological dating, and also about the

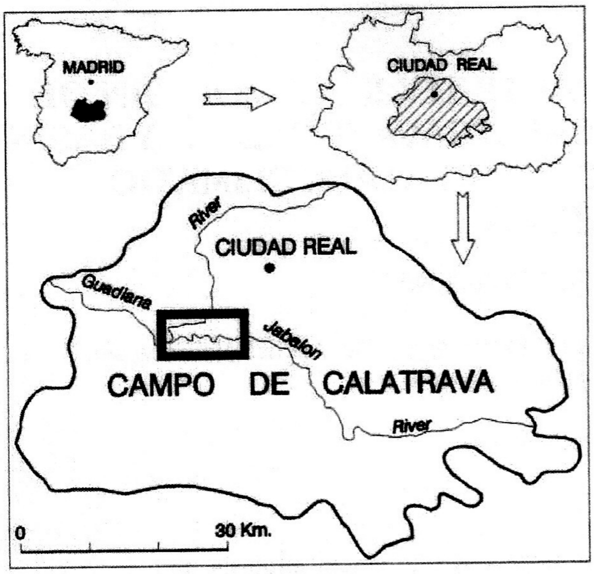

Figure 1.- Location of the study area.

morphoclimatic conditions and morphogenetical mechanisms which intervene in its genesis.

METHODOLOGY

Because the ferroginous crusts of Calatrava are situated near hot springs, it makes sense to hypothesise about its participation in the formation of the ferroginous encrustations. In order to do that, it is necessary to know the composition and the mineralogical content of the solutions and hydrothermal remanents, and to check if these minerals are also the main components of the ferroginous crusts.

With this in mind, we have completed two types of analysis: on one hand, mineralogical analysis (X-ray diffraction) applied to the crusts as well as to the thermal residua; and on the other hand, chemical analysis was done through atomic absorption spectrophotometry to thermal waters.

For the first analysis we took samples of ferroginous crusts representative of the area of study (Sierra de Medias Lunas) and the residua of hot springs, using whole rock analysis for the cemented samples and oriented samples for clays.

The chemical analysis was completed on 16 hot springs to find out the content of metallic components, either dissolved or in suspension, and to identify the minerals of the residua which are deposited in them.

INTERPRETATION

The Calatrava hot springs are well known as "hervideros" (boiling spots), due to its high contents in CO_2 which is released in bubbles and gives a very sour flavour to the waters.

The thermal springs are not situated at random but articulated in a net of well defined alignments, where a dominant direction NW-SE and a subordinate direction ENE-WSW stand out; they coincide with the disposition of the volcanoes, therefore it seems clear the tectonic relation between thermal springs and volcanoes.

The numbers obtained through atomic absorption spectrophotometry reveal that the thermal waters of Calatrava are very ferroginous. The iron contained in the waters, most of it deposited or in suspension, varies between 4.85 ppm in Fuentillejo and 78.86 ppm in San Cristobal, with a media of 24.52 ppm. On the contrary, the soluble iron is minimal being always below 1 ppm. The content of manganese is also very high presented, unlike the iron, in its soluble state. Its values vary between 1.30 ppm in Colodrilla and 0.03 ppm in Fuentillejo, with an average of 0.30 ppm (Table I).

Hot spring	Place	T(°C)	pH	CO_2 (ppm)	In dissolution (ppm)		In suspension (ppm)		Minerals	
					Fe	Mn	Fe	Mn	Main	Subordinate
Fuente Pública	Puertollano	18	5.8	2.000	14.85	0.37	0	0	-	-
Villafranca	Pozuelo de Ctva.	21.5	7.5	35	0.03	0.26	48.06	0.036	G, Q, C, FD	IL, R, L
Chorrillo	Pozuelo de Ctva.	21	7.3	110	0.01	0.15	0	0	-	-
Piedra de Hierro	Pozuelo de Ctva.	18	-	-	0.03	0.10	47.32	0.031	G, Q, FD	F, M, C, D
San Cristóbal	Pozuelo de Ctva.	19	6.1	47	0.03	0.18	78.86	0.044	G	Q, C, D, FD, F, M
Fuensanta	Pozuelo de Ctva.	19	7.4	180	0.02	0.04	24.03	0.028	-	-
Pisada de la Vaca	Pozuelo de Ctva.	17	7.3	95	0.01	0.15	-	-	-	-
Los Baños	Villar del Pozo	28	7.1	80	0.01	0.25	34.01	0.018	A	A
Fuentillejo I	Ciudad Real	18	7.1	-	0.01	0.13	32.98	0.029	Q, G	IL, L, R, C, F
Fuentillejo II	Ciudad Real	-	-	-	0.09	0.03	4.85	0.080	Q, G, C	D, FD, F
Sacristanía	Calzada de Ctva.	17	-	-	0.20	0.13	14.50	0.040	G, Q	IL, L, S, FD, F
Baño del Barranco	Aldea del Rey	17	6.3	-	0.60	0.30	9.20	0.240	Q, G, C	FD, D
Baño de Fontecha	Aldea del Rey	-	6.4	-	0.60	0.45	14.30	0.250	G, SM, Q	C, D, F
Baño Chico	Aldea del Rey	-	-	-	0.70	0.40	21.00	0.050	G, Q	C,D, M, F, FD
Fuente de Colodrilla	Pozuelos de Ctva	17	5.9	340	0.15	0.60	25.03	0.030	Q, G, SM	C, D, R
Charca de Colodrilla	Pozuelos de Ctva	17	5.7	160	0.13	1.30	13.70	0.160	Q, G	FD

A: amorphous
C: calcite
D: dolomite
F: phylosilicate
FD: feldespars
G: goethite
IL: ilmenite
L: lepidocrocite
M: manganite
Q: quartz
R: ramsdellite
S: siderite
SM: siderite with manganese

Table I.- Atomic absorption spectrophotometry and X-ray diffraction of the hot springs' residua of Calatrava.

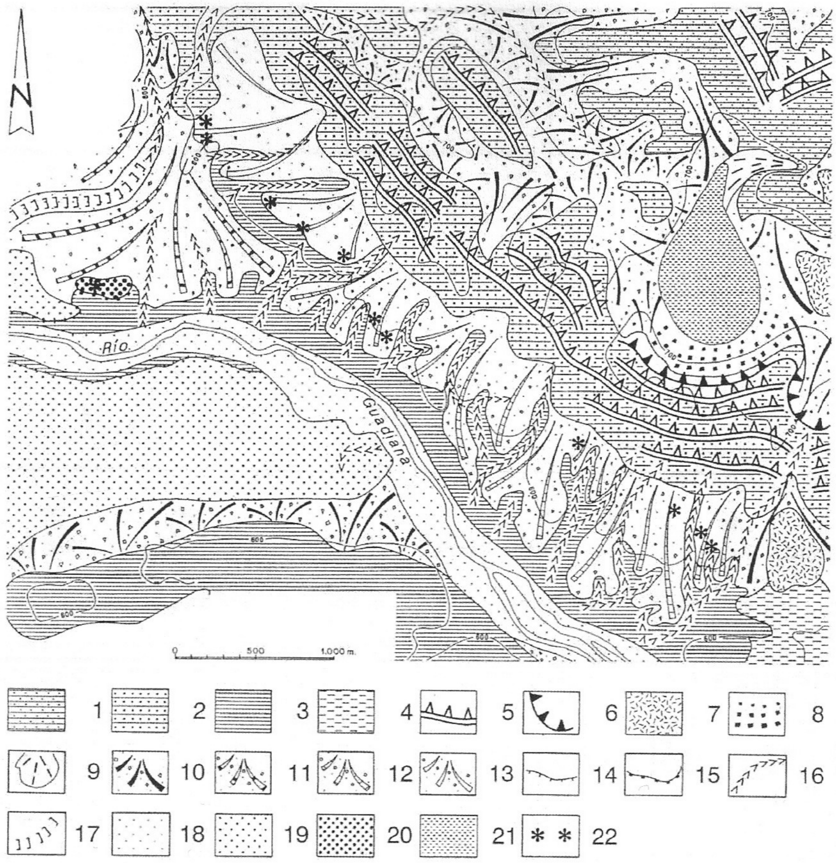

Figure 2.- Geomorphological sketch map of the occidental area in the Sierra de Medias Lunas. 1: Microconglomerates (lower Ordovician); 2: Armorican quartzites (lower Ordovician); 3: Slates and quartzites (medium Ordovician-Silurian); 4: Marl (lower Pliocene); 5: Front of crest; 6: Maar or explosion crater; 7: Lava flows; 8: Debris slope (upper Pleistocene); 9: Alluvial fan (upper Pleistocene); 10: Accumulative glacis (G_1, upper Pleistocene); 11: Accumulative glacis (G_2, medium Pleistocene); 12: Accumulative glacis (G_3, lower-medium Pleistocene); 13: Accumulative glacis (G_4, lower Pleistocene); 14: Smooth terrace border; 15: Steep terrace border; 16: V valley; 17: Flat bottom valley; 18: alluvial bottom; 19: +10 m alluvial terrace (medium Pleistocene); 20: +40 m alluvial terrace (lower Pleistocene); 21: Clay and slime (Holocene); 22: Ferruginous encrusted about several deposits (lower-upper Pleistocene).

The X-ray diffraction of the solid residua has enabled us to determine its mineralogical composition. It is basically goethite, quartz, calcite, and siderite. Amongst the subordinate minerals, ramsdellites and manganites stand out, as well as dolomite and finally, less frequent iron oxides and hydroxides such as ilmenite and lepidocrocite.

The enrichment of such thermal waters with iron and manganese is due to a physic-chemical action of high pressure and temperature, conditions of reduction, a high content of carbonic anhydride and acid pH of the water. All these factors favoured the aggressiveness of the water and, which are able to leach the ferroginous coats of quartzites and slates from the Palaeozoic bases. Therefore, under these limiting conditions and of acidity, the metallic cations leached stay dissolved in such waters. But, when these waters spout into the surface there is a breaking of the physic-chemical equilibrium, due to the lowering of the temperature and of the pressure, and to the transfer to an oxide medium. This facilitates the massive escape of carbonic gas –which increases the pH in the water– and a greater oxidation of the waters which cause the sedimentation of the metallic components, especially of the iron.

Bibliographic references about the participation of hot springs in the origin of ferroginous crusts are very frequents in hydrological litterature. The works of Hernández-Pacheco (1944), Cruz-Sanjulián y García-Rosell (1975), Naboko (1982), Kuhfuss (1984), Chamley (1989) stand up amongst others.

On the other hand, the ferroginous crusts are localised around thermal springs and on the hillsides of the Palaeozoic mountain ranges, as the process of encrustation requires as an essential condition the abundance of iron. For this reason, the best outcrops are in the Sierra de Medias Lunas (Fig. 2).

The ferroginous crusts which are in the foothills of the Sierra de Medias Lunas correspond to four generations of levels of accumulative glacis modelled during the Pleistocene. Those four glacis (G_1, G_2, G_3 and G_4) have their detritic fractions amalgamated by plenty of iron oxide and hydroxide, crystallized as goethite and hematite (Figs. 3, 4, 5 and 6), originating glacis crusts. At the same time, the three fluvial terraces

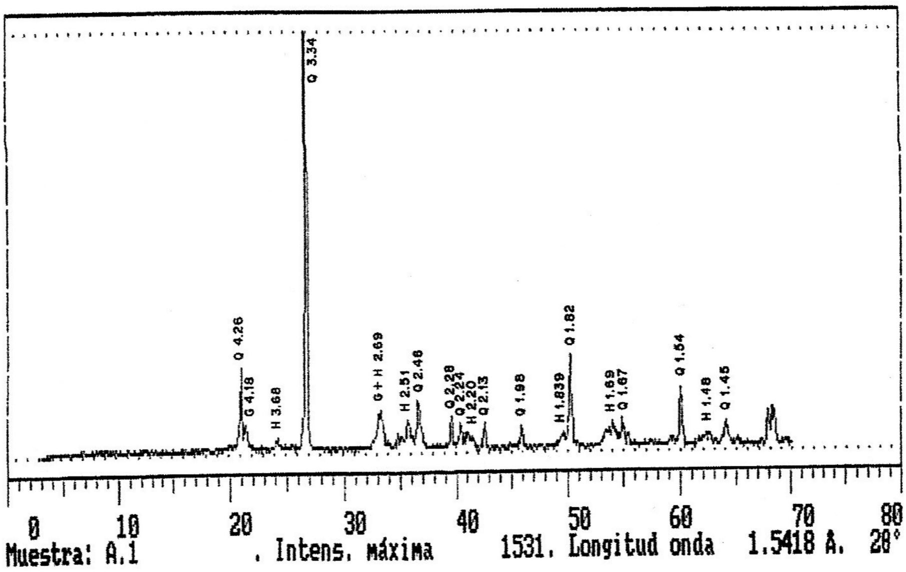

Figure 3.- X-ray diffractogram of the encrusted glacis (G_4) in the occidental area of the Sierra de Medias Lunas.

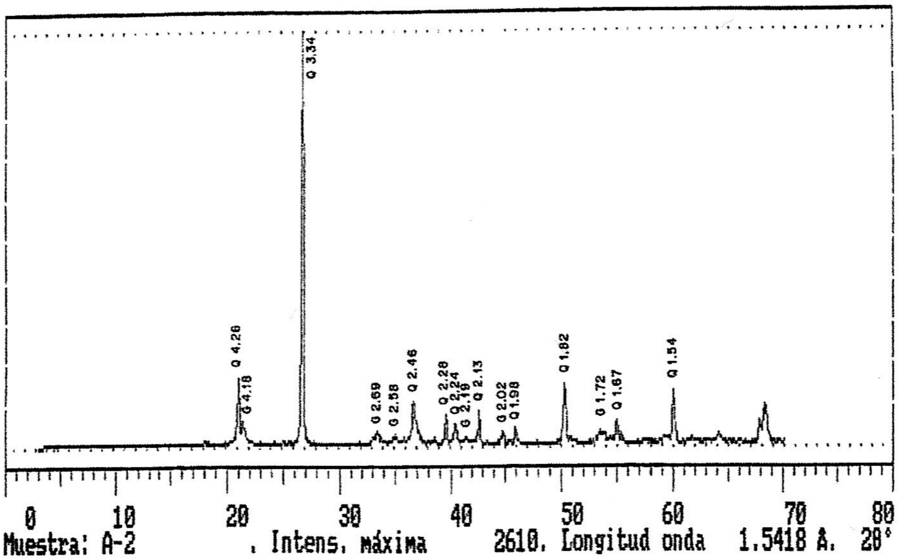

Figure 4.- X-ray diffractogram of the encrusted glacis (G_3) in the occidental area of the Sierra de Medias Lunas.

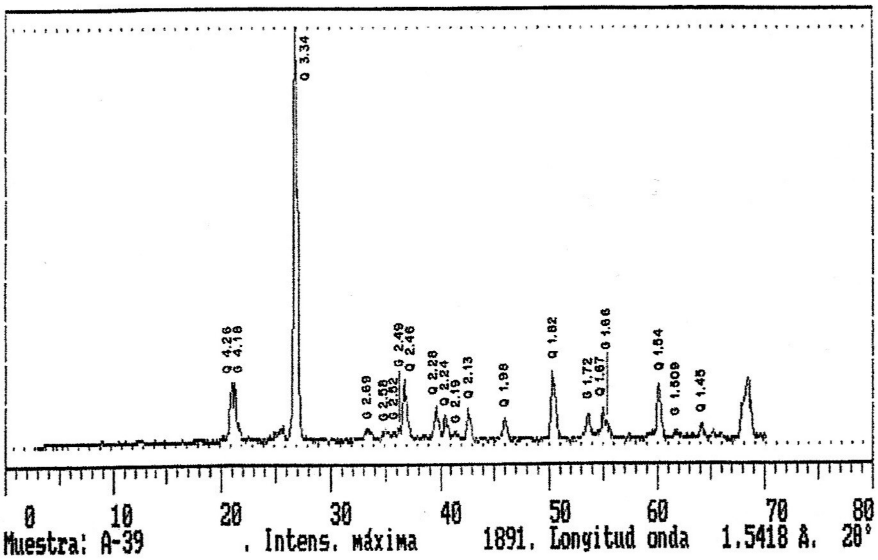

Figure 5.- X-ray diffractogram of the encrusted glacis (G_2) in the central area of the Sierra de Medias Lunas.

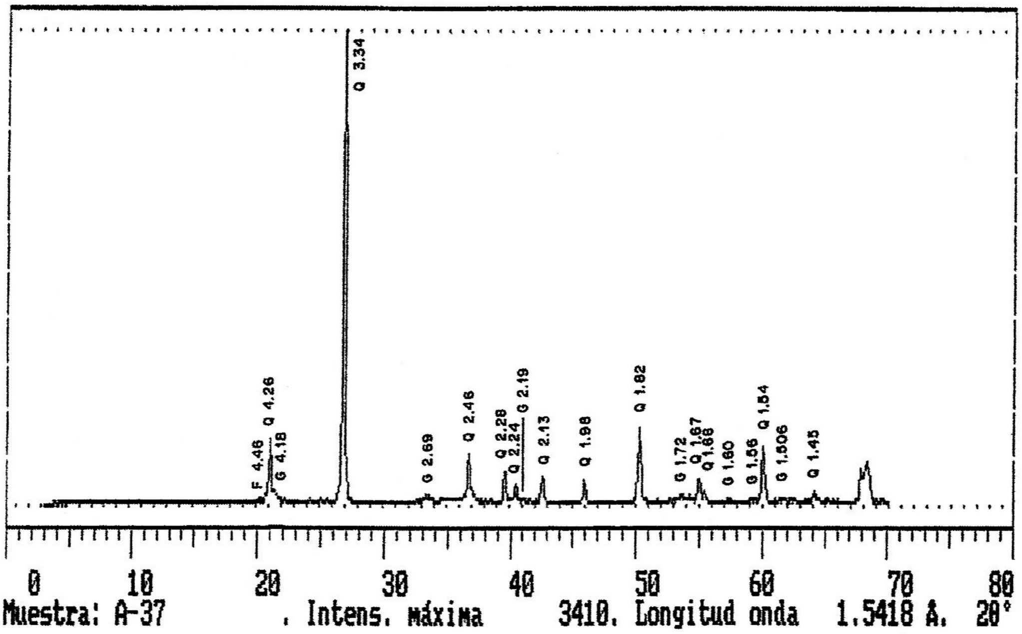

Figure 6.- X-ray diffractogram of the würmian coluvial crust (G_1), Finca Coello, central area of the Sierra de Medias Lunas.

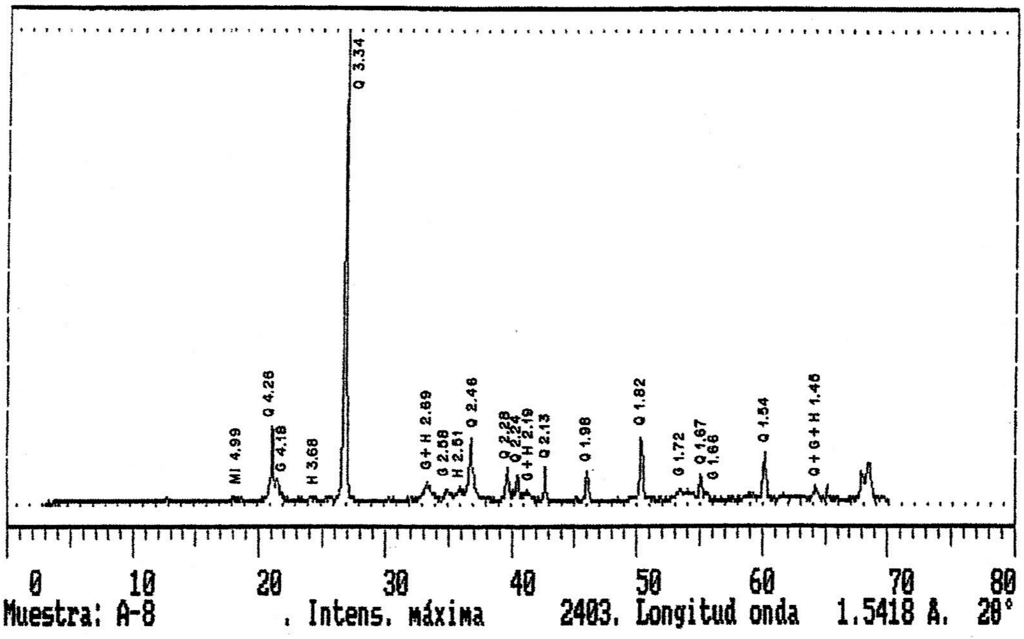

Figure 7.- X-ray diffractogram of the encrusted fluvial terrace +40 m in the Guadiana river (Sierra de Medias Lunas).

of the Guadiana which acted as base level for the elaboration of those accumulative glacis, which are situated in the right bank of the Guadiana, are cemented also by goethite and hematite, establishing three fluvial crusts of conglomerate type. It is the T+40 m, T+10 m and the T+2 m which correspond respectively to the lower, medium and upper Pleistocene. The mineralogical analysis confirm that the components are reduced to quartz, goethite and hematite (Figs. 7 and 8), with a total absence of aluminium oxides and hydroxides which could indicate processes of lateritic weathering.

Therefore, there is a similarity between the minerals which form the crusts'cement and the minerals actually settled in the thermal springs. Therefore it is demonstrated that the hydrothermal activity intervened in the genesis of the ferroginous crusts.

DISCUSSION

The ferroginous crusts of Calatrava are originated by lateral movement of hot springs, affecting shapes and deposits as diverse as alluvial fans, rañas, accumulative glacis, colluviums, fluvial terraces, etc.

This means that the morphogenesis of such crusts is completed by the accumulation of iron sesquioxides from waters full of those substances originating from the Palaeozoic mountain ranges. It is, in fact, a phenomena of lateral lessivage made by thermal waters

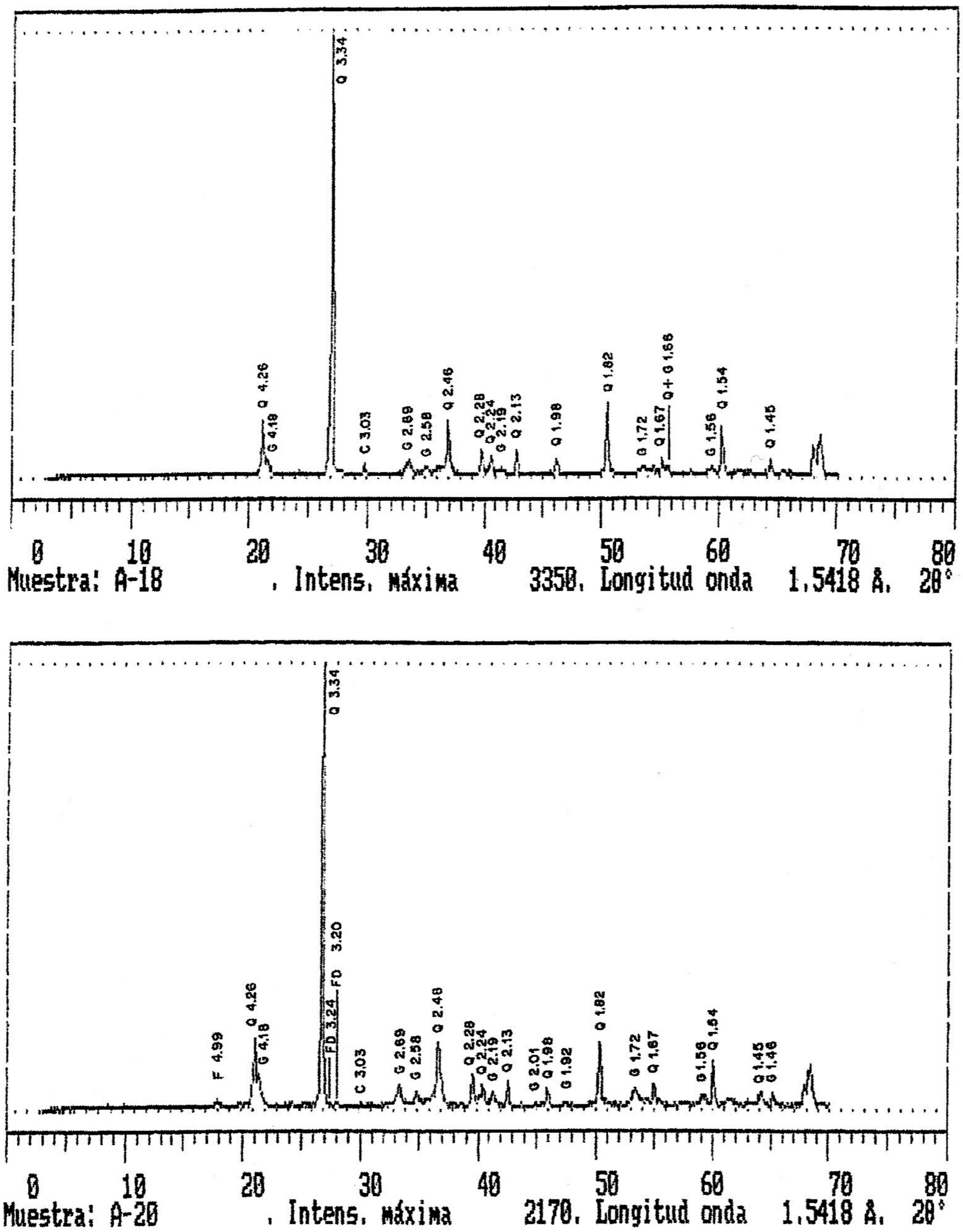

Figure 8-. X-ray diffractograms of fluvial crust +2 m (Upper and lower levels, Guadiana river, Puente de Alarcos, Sierra de Medias Lunas).

which act over very soluble and mobile minerals susceptible to being dissolved and displaced laterally. This fact explains that the crusts are formed by crystallised iron as goethite and hematite.

There are other series of factors which contribute and make possible the precipitation and fixation of ferroginous materials. In the first place, the deposits have quartz detritic fractions which favour the welding or union of iron oxides and hydroxides due to the attraction that the silica (electronegative) has over the iron (electropositive), as well as its porousness which facilitates the iron oxidation. Also the clay exerts a big attraction over the hydroxides molecules, which they adhere easily, in the form of a film, to the clay crystals. Nevertheless, the accumulation and fixation of such elements is not enough, adequate climatic conditions are needed for the compacting and hardening of ferroginous cements.

We know through the affected deposits, whose age dates between the low Pliocene and the upper Pleistocene, that the morphogenesis period of the crusts has been very prolonged in time. This implies that the environmental conditions have been quite uniform, where a Palaeoclimate was ruling, characterised by very contrasting seasons, some very rainy and others dry and probably associated to an extreme Mediterranean Palaeoclimate. We must also take into consideration that Aleixandre (1967) and Monturiol *et al.,* (1970) place the pedogenesis, between the upper Pliocene and the upper Pleistocene, of some Mediterranean red Palaeosoils in this same area.

Finally, it is interesting to verify that the formation of the ferroginous crusts coincides chronologically with the beginning of the volcanic activity, which carries on from the upper Miocene until the upper Pleistocene, therefore we cannot rule out the possibility that this intense and prolonged volcanism could have created morphoclimatic conditions especially favourable to the genesis of ferroginous crusts.

CONCLUSIONS

The ferroginous crusts of Calatrava are Pliocenous and Pleistocenous deposits, cemented by iron oxides and hydroxides (goethite and hematite), which join and harden the detritic fractions of accumulative glacis, fluvial terraces, colluviums, etc.

These ferroginous crusts have been formed from the lateral leaching, produced by stream waters and especially by thermal springs, from the Palaeozoic rocky outcrops rich in iron, probably under very extreme Mediterranean Palaeoclimatic conditions, prevailing with hardly any variation from the lower Pliocene to the upper Pleistocene.

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