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Mineralogical and geo-chemical characterization of a diapiric formation in the North of Spain

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Abstract

We have selected seven profiles located in a diapiric formation in the North of Spain. The profiles have been analyzed for the mineralogy and the chemical composition of original materials, soils developed above them and clay fractions. Three soils formed on basic rock of volcanic origin (ophite) and rich in alterable minerals, three others formed on clay marl and one soil formed on gypsiferous marl. Plagioclases, pyroxenes, vermiculites, and biotites are the main minerals found in the soil samples and ophitic rocks. Biotite, smectite, chlorite and interstratified chlorite–vermiculite make up the predominant mineralogical association in the clay fraction of the soils. Calcite, biotite and on top of all chlorite are the main minerals in the marls and the soils developed on them, with gypsum predominant in the gypsiferous marl. The mineralogy of its clay fraction is comprised mainly of chlorite and biotite. The variations in content of Al_2O_3, TiO_2 and Na_2O in the ophites are considered to be associated with the differences in the evolution of the pyroxenes. The variability of the chemical composition of the Keuper sediments and the soils is attributed more to the chaotic disposition of the Triassic materials in the formation of the diapir than to intense chemical weathering. The low concentrations of silica, iron, and aluminum extractable with ammonium oxalate indicate the low proportion of non-crystalline products. Fundamentally, it is the semiarid conditions in the study zone, together with the processes of extrusion and hydrothermal activity affecting the formation of the diapir, that are responsible for the genesis of the minerals.

Keywords: Diapir; Soil mineralogy; Ophites; Mediterranean area

1. Introduction

Diapirs are geological formations that occur when a body of rock rises and pierces through overlying rocky material (Jenyon, 1986). Studies have generally concentrated on analyzing diapir formation in different areas in the world. (Jackson and Talbot, 1986; Weinberg, 1996; Miller and Paterson, 1999; Vendeville, 2002; Jallouli et al., 2005; Pinto et al., 2005).

Among the different forms of diapirism described in the bibliography, the most numerous are those in which salt rock constitutes the mobile material. These are of particular interest as they are to a large extent linked to the geochemistry of hydrocarbons (Ginsburg et al., 1999; Milkov, 2000; Dimitrov, 2002). This same relation was shown by Sassen et al. (2003) on investigation of the presence of hydrocarbons in diapiric formations in the continental plates of the Gulf of Mexico. Following recent studies of diapiric structures in the Tunisian Atlas, Jallouli et al. (2005) relate the importance of understanding Triassic salts and associated structures with mining and oil exploration.

However, although there is an extensive bibliography on diapiric formations from a geological point of view, this is not the case where soil science is concerned. As a consequence of this, considering the environmental interest in such areas, pedologic studies on the characteristics and distribution of soils in complex diapiric formations are essential.

In the present work we study a diapiric zone located in the Miranda–Treviño Depression, in the southern part of the Basque–Cantabrian Basin (in northern Spain). It is made up primarily of clays, marls and gypsums belonging to Keuper

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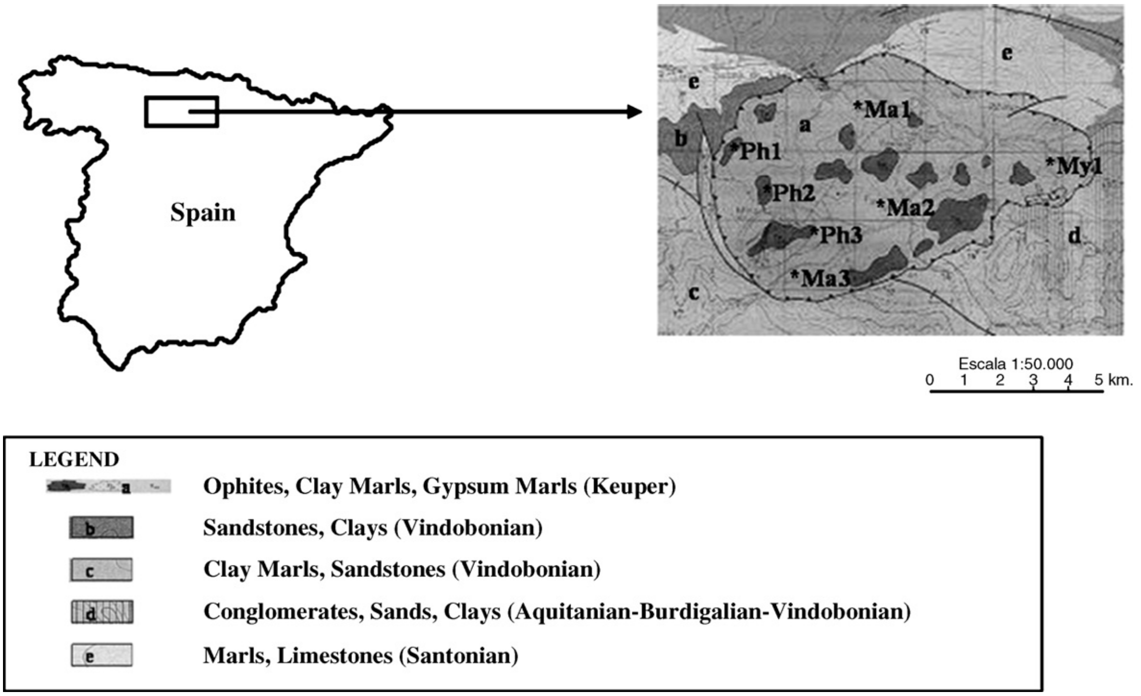

Fig. 1. Localization and simplified geology map of the studied diapiric formation.

facies and rocky igneous outcroppings of ophitic texture, also Triassic in age (López-Lafuente et al., 1999; Pinto et al., 2005).

Ophites constitute a group of basic igneous volcanic and subvolcanic rocks that characteristically display a massive appearance and ophitic texture in which a grid of uniformly sized and distributed mafic crystals can be detected macroscopically. The crystals have no specific orientation and are surrounded by less developed felsic components (Lago and Pocovi, 1980; Sánchez Cela and García Anquela, 1984; Amigó et al., 1985; Desreumaux et al., 2002). Common on the Iberian Peninsula, they are found in association with Triassic materials, mainly with plastic and saline sediments of Keuper facies that facilitate their extrusion (Lago and Pocovi, 1982; Bohoyo et al., 2000).

Although different types of ophites are geologically very similar, petrographic and geochemical field studies point up differences between them. Walgenwitz (1976) demonstrated the presence of magnesium chlorite and on occasion low percentages of illite and kaolinite in Navarre (Spain). Lago and Pocovi (1980) found chlorite, vermiculite, talc, calcite and mica, among other minerals, in the chilled margins of dolerites. Moreno and Íñiguez (1981) described the entire series of minerals at 1.4 nm, from the typical chlorites to vermiculite, including chlorite–vermiculite intergrades. Amigó et al. (1987), analyzing the pargenesis of the chilled margins of the dolerites and of the encasing sediments in the Western Pyrenees (Spain) and paying particular attention to the clay fraction, observed mineralogical associations formed by: talc, smectite, chlorite–smectite regular, interstratified minerals, chlorite, plagioclases and pyroxenes.

On the other hand, and consistent with the literature, encasing sedimentary materials are characterized by the dominant presence of philosilicates as laminate minerals and by calcite, dolomite and gypsum as non-laminate materials (Azaroual et al., 1997; Sánchez et al., 1999). The presence of chlorite in gypsiferous clay materials of Keuper facies in the Eastern and Northern Pyrenees was described by Ruiz Cruz and Lunar (1982) and Amigó et al. (1987). Recently, Owliaie et al. (in press) described the presence of chlorite, in calcareous and gypsum soils and rock in a transect in southwestern Iran. Hamidi et al. (1997) demonstrated the presence of talc as a product of the chemical alteration of triassic basalts en Moyen Atlas, Maroc.

A less studied area has been the geochemistry of the soils developed on diapiric formations (Moreno and Íñiguez, 1981; González et al., 1999; López-Lafuente et al., 2001) and its relationship with the minerals that form them. Thus, the objectives of this study were: (i) to characterize the mineralogical composition of the seven soils developed on diapirs in the northern Iberian Peninsula, (ii) to determine the chemical composition of the said soils, and (iii) to analyze the origin and evolution of the mineral fraction in relation to the weathering processes in a Mediterranean climate.

2. Materials and methods

2.1. Area of study

The soils studied were: three soils derived from ophites, classified according to standard USA procedure specifications (Soil Survey Staff, 1993) as Entic and Typic Haploxerolls

(Ph1, Ph2 and Ph3), three soils derived from clay marls, Typic xerorthents (Ma1, Ma2 and Ma3) and one soil derived from gypsum marls classified as Gypsic Haploxerepts (My1). All the soils were located in the Salinas de Añana diapir (northeastern Spain) at an altitude between 650 and 870 m (Fig. 1). The climate is markedly Mediterranean, with an average annual precipitation of 650 mm and an average annual temperature of 11.5 °C. It is characterized by a dry season (3–4 months) that coincides with a hot season, leading to intense moisture deficit. Precipitation is rare and torrential, especially in the autumn.

From the point of view of bioclimate, the area is part of a lower supramediterranean region with a dry to sub-humid ombroclimate. Two belts of vegetation are distinguished: supramediterranean castilian–cantabric and riojan–estellesen in the basophile of the gall-oak, (*Quercus faginea*), *Daphno latifoliae–Acereto granatensis sigmetum* and supramediterranean castilian–cantabrian and riojan–estellesen in the basophile of the holm-oak (*Quercus rotundifolia*), *Spiraeo hispanicae–Querceto rotundifoliae sigmetum* (Rivas Martínez, 1987). At the present, they only appear in degraded stages, corresponding to dense and degraded thickets, whose main components are ericaceas and cistaceas.

Due to intense mining during the 19th century in the study area, the relief is today greatly altered, its main feature being the artificial terraces constructed to extract salt and quarryable materials, especially gypsum. Hence, the soils are heavily anthropized, with just a few areas of unaltered profiles, located mainly at the base of the diapir. They are AC soils that are extremely gravelly and or stony, with little evolutionary development. The soils formed on ophites have coarse textures (sandy loam) and the soils formed on marls show finer textures (sandy clay loam). The predominant vegetation on the soils conditions the horizontal surfaces, which have a high content in organic matter with

Table 1
Selected physical and chemical properties of a toposequence of the diapiric formation

Profile depth (cm)	Horizon	Texture class	pH H_2O	EC dSm^{-1}	Organic matter g kg^{-1}	C/N	$CaCO_3$ equivalent g kg^{-1}
Ophite soils							
Profile Ph1							
0–10	A1	Loamy sand	6.5	0.08	87.38	14	–
10–40	A2	Loamy sand	7.3	0.04	26.49	11	–
40–80	AB	Loamy sand	7.7	0.04	28.21	10	–
80–100	BC	Loamy sand	7.9	0.04	24.60	–	–
+100	C	Sand	7.9	0.03	3.61	–	–
Profile Ph2							
0–25	Ap	Loamy sand	6.6	0.10	29.76	12	–
25–55	AC	Loamy sand	6.8	0.07	12.21	9	–
55–80	C	Sandy clay loam	6.9	0.09	3.44	–	–
Profile Ph3							
0–35	A	Loamy sand	6.2	0.14	69.14	14	–
35–60	AC	Loamy sand	6.3	0.13	55.38	14	–
+60	R					–	
Marl soils							
Profile Ma1							
0–10	A	Clay coarse	6.5	0.11	30.62	12	25.50
10–25	AC	Clay coarse	6.6	0.09	15.65	9	24.00
25–45	2C	Clay fine	7.8	0.21	7.57	–	46.50
45–56	3C	Clay coarse	8.2	0.19	2.06	–	135.30
56–73	4C	Clay fine	8.0	0.20	1.89	–	153.40
+73	5C	Clay coarse	8.1	0.15	2.58	–	70.60
Profile Ma2							
0–15	A	Clay coarse	7.2	0.31	80.84	13	65.80
15–45	AC1	Clay coarse	7.7	0.18	33.88	12	75.05
45–65	AC2	Clay coarse	7.8	0.17	22.36	11	87.10
65–102	C	Clay coarse	8.0	0.13	11.01	–	91.40
Profile Ma3							
0–15	A	Sandy clay loam	7.6	0.26	79.30	17	179.20
15–40	AC1	Sandy clay loam	8.0	0.18	19.61	10	263.25
40–50	AC2	Sandy clay loam	8.0	0.16	15.99	9	210.80
50–85	C	Sandy clay loam	8.1	0.16	11.35	–	217.10
Profile My1							
0–10	A	Clay coarse	7.5	0.20	32.51	14	19.10
10–30	AC	Clay coarse	7.8	2.04	18.23	13	6.10
30–70	Cy	Loam	7.7	2.33	3.44	–	10.70

values that oscillate between 29.76 and 87.38 g kg^{-1} and C/N relationships that show the presence of a well developed mull type humus. In those soils where the presence of calcium carbonate is high, the type of humus becomes mull carbonate. The pH of the soils is close to neutral, diminishing slightly in surface horizons due to the influence of organic matter (Table 1).

2.2. Laboratory methods

The descriptions of the sampling points, the profiles and the horizons were done following the standard USA procedure specifications (Soil Survey Staff, 1993). Representative soil samples were then collected from the surface horizon and from each underlying genetic horizon. All of the soil samples were air-dried and passed through a 2 mm sieve prior to analysis and all samples were extracted and analyzed in duplicate.

Particle size analyses were conducted following oxidation of organic matter with hydrogen peroxide, dispersion with sodium hexametaphosphate and stirring for 16 h. The sand was fractionated by dry sieving and the clay and silt fractions were determined by the Robinson pipette method. In all cases, salts, carbonates and gypsum were removed in order to preserve the true physical behavior of the soil. Organic C content (C) was determined using the Walkley–Black dicromate acid oxidation method (1974). pH values in H_2O, were determined potentiometrically in a 1:2.5 soil–water ratio (ISRIC, 1993). Electrical conductivity was measured in saturated pastes after a 4 h equilibration. Equivalent $CaCO_3$ was determined using a Bernard calcimeter. Total elements were measured by atomic absorption spectrometry (AAS) (Philips PU9100X) after a nitro-perchloric acid digestion.

Selective dissolutions of aluminum, iron, manganese and silicon compounds were carried out using two chemical reactants. Dithionite-soluble Al (Al_d), Fe (Fe_d), Mn (Mn_d) and Si (Si_d), were extracted using the Mehra and Jackson method (ISRIC, 1993), and oxalate-soluble Al (Al_o), Fe (Fe_o), Mn (Mn_o) and Si (Si_o), according to the Blakemore et al. method (1987). The cations were determined by Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry—(ICP-MS).

The mineralogical composition of the rock and soil samples (fine earth and clay fractions) were examined by X-ray diffraction (XRD) using a Philips X PERTMPD diffractometer with Cu Kα radiation. Soils and rocks were examined on randomly-orientated powders. The clay fraction in air-dried samples after saturation with Mg was calcinated at 550 °C for 2 h and after an ethylene glycol solvation. Semi-quantitative mineralogy of the clay fraction was deduced from peak areas of XRD diagrams after Mg-saturation. Semi-quantitative analyses were performed following the method proposed by Tributh (1991). Petrographic microscopy was used for the study of thin sections to complement the mineralogical characterization of the ophite rock samples.

3. Results and discussion

3.1. Mineralogy of pattern materials

Nine ophite rock samples representing all the profiles were analyzed, with different alteration degrees, by both petrological techniques and by powder X-ray diffraction analyses. Also, eight samples of Keuper sediments that outcrop in the diapir formation were analyzed by X-ray diffraction.

The studied ophites show a great petrological uniformity; analysis of their texture and mineralogical associations reveals an ophitic heterogranular texture with a poiquilolitic tendency.

Predominant components in samples are: clinopyroxenes and plagioclases, and olivine in lower amounts. The clinopyroxene has colorless cores (augite–diopside) and brown titanated edges. Locally, they enclose pseudomorphs of small olivines fully replaced by serpentine. The plagioclase is idiomorphic, tabular and of labradorite–bytownite rock type. Besides this, there are opaque allotriomorphic minerals, which include plagioclases.

Usually, the rocks analyzed show deuteric alteration, mainly concerning olivine and plagioclase. Olivine is fully altered to serpentinic products, while plagioclase is partly altered to sericite–prehnite. The presence of sericite–prehnite as an alteration product of ophitic rocks was first observed by San Miguel de la Cámara (1936); its origin has been under discussion in recent decades. It has been linked to the Pyrenean regional metamorphic process that heavily affects French ophites (Fonteilles and Muffat, 1970), or to late hydrothermal alteration, common in outcropping ophites

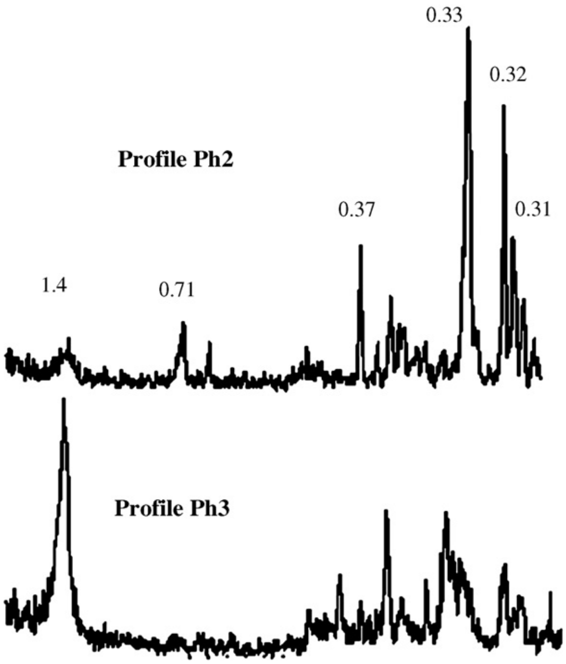

Fig. 2. X-ray diffraction patterns of the randomly-orientated from ophitic rock. Spacings are given in nanometers (Cu Kα radiation).

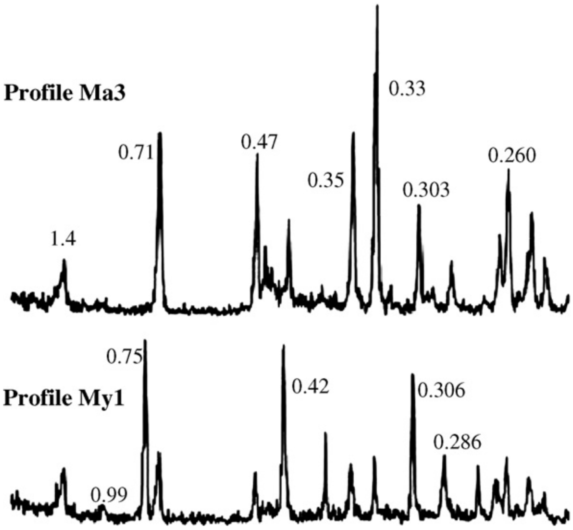

Fig. 3. X-ray diffraction patterns of the randomly-orientated from sediment samples of Keuper. Spacings are given in nanometers (Cu Kα radiation).

deposits of Cantabric–Pyrenean areas, where regional metamorphism is not assessed (Lago et al., 1983).

The X-ray diffraction examinations (Fig. 2) confirm the presence of plagioclase feldspars, olivine and pyroxenes, with a very high proportion of the former as the intensities of the reflections examined at 0.32 and 0.31 nm suggest. The philosilicates at 1.4 nm, vermiculite-type, are the main minerals found in the original material along with small amounts of biotite. These vermiculites are formed by the weathering of biotite. Trioctahedral vermiculites resulting from supergenic alteration or hydrothermal reactions of biotites and phlogopites has been reported by numerous authors (Basset, 1963; April et al., 1986; Moon et al., 1994; Tsirambides and Michailidis, 1999). However, in studies done in diapirs near the study area, the presence of biotite was shown to be the principal mineral in the ophitic rock samples (López-Lafuente et al., 1999), which could reflect a greater degree of alteration in the Salinas de Añana diapir.

The X-ray diffractograms of most of the sediment samples of Keuper age show strong reflections of calcite (0.303, 0.229 and 0.210 nm), quartz (0.426, 0.334 and 0.182 nm) as well as non-laminate minerals. The phyllosilicate materials are made up primarily of chlorites and biotite traces, and illite and talc occasionally appear. Gypsum (0.751, 0.426 and 0.305 nm) is the main constituent of the sediments of the My1 profile (Fig. 3).

3.2. Mineralogy of soils fine earth fractions

Examinations by X-ray diffraction of fine earth fractions (Fig. 4) of the profiles developed on ophitic rock (Ph1, Ph2 and Ph3) indicate, in all cases, higher contents of vermiculite and chlorite, and lower contents of biotite, talc, plagioclases and pyroxenes than in the original material samples. Phyllosilicates appear with clean and symmetrical reflections which show a high degree of crystallinity. Among the plagioclase feldspars albite dominates (0.404, 0.321 and 0.318 nm) with different alteration degrees; andesine is also present as the mean step of the series, with less crystallinity, and anorthite appears (0.470, 0.375 and 0.320 nm), with a greater degree of arrangement. Augite and diopside (0.314, 0.299 and 0.175 nm) are the predominant minerals in the pyroxenes group.

The mineralogy of the fine earth fraction of the soils developed on marl materials is similar to that found in the original materials. Quartz, calcite and chlorite are the minerals present in the samples analyzed, with similar contents in all the profiles. The presence of gypsum alone was detected throughout the My1 profile.

3.3. Mineralogy of clays

The results of the mineralogical analysis of the clay fraction of the selected soils are summarized in Table 2. The clay fractions of all the soils were obtained by controlled sedimentation, previous NH_4OH dispersion and posterior

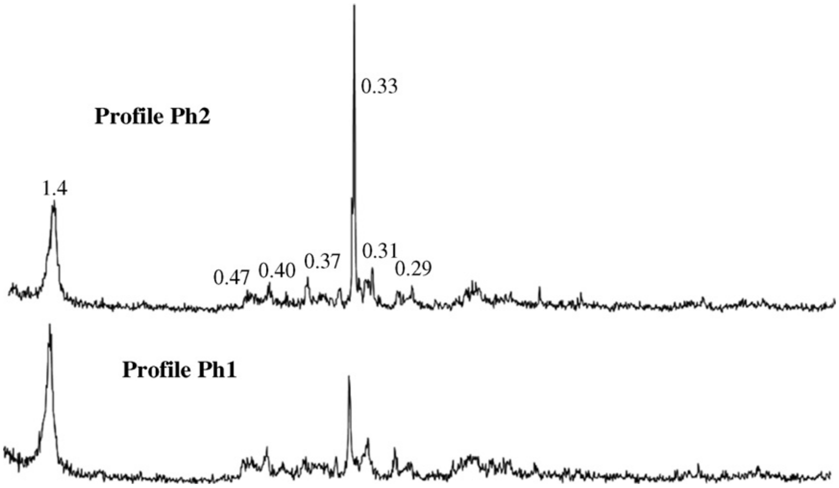

Fig. 4. X-ray diffraction patterns of the randomly-orientated from soil's fine earth fractions formed on ophitic rocks. Spacings are given in nanometers (Cu Kα radiation).

Table 2
Mineral components of selected clay fraction as determined by X-ray diffraction[a]

Profile horizon	Talc	Biotite	Chlorite	Vermiculite	Smectite	Inter.CV[b]	Quartz	Calcite
Ophites								
Pedon Ph1								
A1	−	++	−	−	+	++	−	−
A2	−	++	−	−	+	++	−	−
AB	+	+++	−	−	++	+++	−	−
BC	+	++	−	−	+++	++	−	−
C	+	+++	−	−	++	++	−	−
Pedon Ph2								
Ap	−	+	−	−	++	+	−	−
AC	+	+	−	−	++	+	−	−
C	−	+	−	−	++	+	−	−
Pedon Ph3								
A	−	+	+++	−	−	Trace	−	−
AC	−	+	+++	−	−	Trace	−	−
Marls								
Pedon Ma1								
A	−	++	+++	−	−	−	−	−
AC	−	++	+++	−	−	−	−	−
2C	−	++	++++	−	−	−	−	Trace
3C	−	++	++++	−	−	−	−	Trace
4C	−	++	++++	Trace	−	−	−	Trace
5C	−	++	++++	Trace	−	−	−	Trace
Pedon Ma2								
A	++	++	+++	−	−	−	−	−
AC1	++	++	++	−	−	−	−	Trace
AC2	++	++	++	−	−	−	−	Trace
C	++	++	+++	−	−	−	−	Trace
Pedon Ma3								
A	−	++	++	+	−	−	++	++
AC1	−	++	++	+	−	−	++	++
AC2	−	++	++	+	−	−	++	++
C	−	++	++	+	−	−	++	++
Pedon My1								
A	−	++	+++	−	−	−	−	−
AC	−	++	++	−	−	−	−	−
Cy	−	+	++	−	−	−	−	++

[a] The abundance of components as estimated from X-ray diffraction: ++++, >50%;+++, 25–50%; ++, 10–25%; +, 2–10%; trace<2%.

[b] Interstratified chlorite–vermiculite.

H_2O_2 treatment. In soils developed from volcanic materials, the dithionite–citrate–bicarbonate treatment is habitually employed in order to improve the quality of XRD diagrams. However, it was not used here because of the scarcity of amorphous material in the soils developed on ophite rock. The study of the diffractograms (XRD) of the clay fraction of the Ph1, Ph2 and Ph3 profiles shows the alteration of the phyllosilicate minerals (Fig. 5). Biotite is the main clay material in the Ph1 profile with peaks at 0.99 and 0.33 nm. Smectite is the predominant mineral in all of the horizons of the Ph2 profile, due to the increase in spacing to 1.7 nm (not shown) caused by the solvation of the samples with etilenglycol. The presence of chlorite is noted in profile Ph3, as seen in the reflections at 1.40, 0.70, 0.47 and 0.34 nm in the samples after Mg saturation (Fig. 6). The chlorite–vermiculite interstratifications are especially noted in profile Ph1 (Fig. 5). This mineralogical association corresponds to the minerals detected, both in rock samples and the soil, which are minerals that are common in atmospheres rich in magnesium, like diapiric structures (Azambre et al., 1987; Morata Céspedes, 1994; González et al., 1999; Krupskaya et al., 2004). Plagioclases, pyroxenes and olivines were not detected. They are present, however, in the original material situated immediately beneath the soils. Kaolinite and minerals at 1.0 nm were not detected; its absence probably reflects little leaching.

Examination of XRD patterns of the clay fraction of soils developed from Keuper materials (Fig. 7), permits the identification of distinguishing features of the <2 μm fraction of the soils developed over ophites. Its mineralogy is mostly composed of biotite and chlorite (Table 2), whose total content is much higher than in the first group and does not indicate intense soil alteration. The increase in chlorite is due in part to the contributions of Mg coming from the ophite and in part to associated hydrothermal fluids. The chlorites

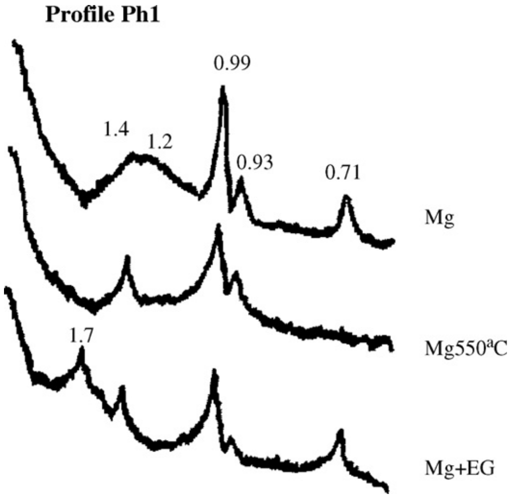

Fig. 5. X-ray diffraction patterns of the orientated Mg^{2+} clays (<2 μm) extracted from the AB horizon of profile Ph1 formed on ophitic rocks. Spacings are given in nanometers (Cu Kα radiation) (EG: ethylene glycol).

are a product of the hydrothermal alteration of the hornblende, biotite and other ferromagnesian minerals (Barnishel and Bertsch, 1989; Lackschewitz et al., in press).

The identification of trioctahedral vermiculite in the Ma3 profile is based on the intensities of the 002/004 basal reflections (Douglas, 1985). Although it is not predominant in soils, it is related with them as a product of a moderate alteration of biotites, talc or chlorite (Ross et al., 1982; Ruiz-Amil et al., 1993; Moon et al., 1994), key minerals in diapiric formation. Bajhernejad (2000) and Khormali and Abtahi (2003) find vermiculite to be one of the dominant minerals in the clay fraction of soils developed in semiarid regions.

The existence of talc in the deepest horizons of the Ph1 and Ma2 profiles is noted. It is commonly present in volcanic environments as a product of the hydrothermal alteration of the original materials (Whitney and Ebrel, 1982; Amouric et al., 2000) and appears in these soils as clay materials inherited from altered volcanic deposits (García-Romero et al., 2005). This mineral was described in soils developed in diapiric environments in the north of the Iberian Peninsula by González et al. (1999) and López-Lafuente et al. (1999), as well as by Tsirambides and Michailidis (1999) when they studied the contact of ultramafic rock with an acid magmatic intrusion in Greece. It is to be noted the presence of calcite as a non-silicated mineral in all soils in varying proportions.

Consequently, we speculate that the origin of the phyllosilicate materials of the clay fraction in all the soils is primarily due to inheritance from the original material. These minerals were produced by hydrothermal alteration of the volcanic rocks and Keuper marls that characterize the diapiric formation. Furthermore, the mineralogical diversity described is due to the variability of the original materials emerging after post-magmatic transformations that modified the initial pargenesis.

3.4. Chemical composition of rocks and soil

3.4.1. Material patterns

The nine fragments of ophitic rock included in the different soil horizons (Ph1, Ph2 and Ph3) are of basaltic origin and show great uniformity in their chemical composition (Table 3). They are basic rocks, non-alkaline, characterized by low silica content (between 35% and 49%), and proportions of between 13% and 24% of Al_2O_3, between 2% and 13% of CaO, around 10% of Fe_2O_3 and 9% of MgO. The remaining oxides are minor components. The variations in Al_2O_3, TiO_2 and Na_2O are associated with essential component minerals of these rocks, in particular with the

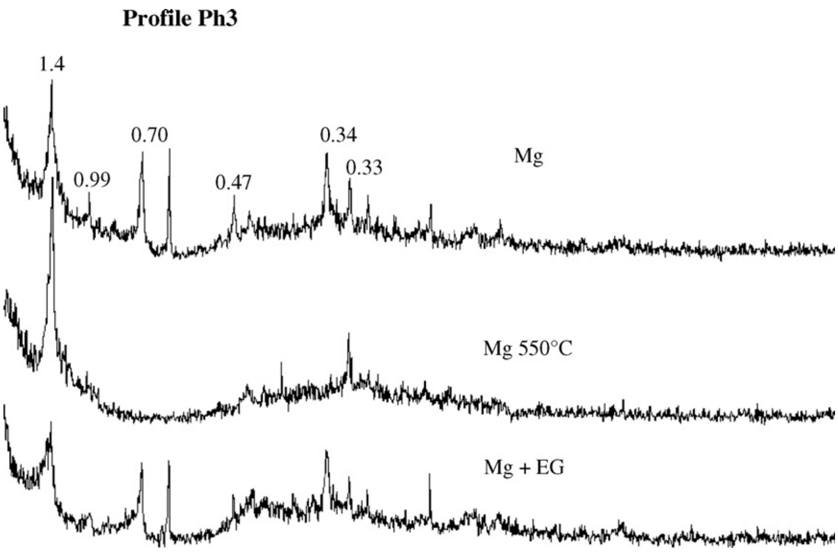

Fig. 6. X-ray diffraction patterns of the orientated Mg^{2+} clays (<2 μm) extracted from the AC horizon of profile Ph3 formed on ophitic rocks. Spacings are given in nanometers (Cu Kα radiation) (EG: ethylene glycol).

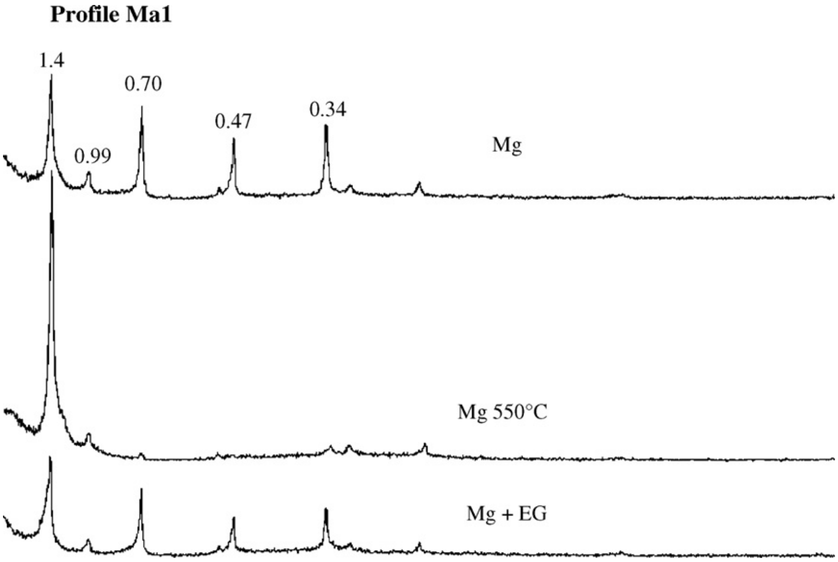

Fig. 7. X-ray diffraction patterns of the orientated Mg^{2+} clays (<2 μm) extracted from the AC horizon of profile Ma1 formed on sediment materials of Keuper. Spacings are given in nanometers (Cu Kα radiation) (EG: ethylene glycol).

differences in the chemistry and evolution of the pyroxenes. Similar results were obtained by Morata and Puga (1993) and Morata Céspedes (1994) in studying the petrology and geochemistry of the ophites of the external areas of the Betic mountain ranges. The percentages of K_2O varied from 0.5% to 4%, which could be due to the presence of sericite in the plagioclases, as demonstrated by Montigny et al. (1982) in studies on the basic magmatism in the Upper Trias of the Pyrenees. The low content in CaO could reflect pyroxenes poor in Ca (Azambre et al., 1987; Lago et al., 1989; Morata and Puga, 1993; Duchesne and Charlier, 2005) and/or a spilitization process by which the calcosodic plagioclases are substituted with albite and the pyroxenes are altered to hydrated ferromagnesian minerals, especially chlorite (Meschede, 1985; I.G.M.E., 1997).

At the same time, Table 3 shows the results of the chemical analysis done on the original materials of sedimentary origin (Ma1, Ma2, Ma3 and My1). Contents in SiO_2 appear in the range 38% to 63%, in general reflecting low quartz content (average of 43%). The oxides of Al_2O_3 oscillate between 4.8% and 21%, in agreement with the differing contents in clays of marls studied (Table 1). The

Table 3
Major element concentrations of rock samples of the diapiric formation

Profile	Depth (cm)	SiO_2 (%)	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	TiO_2	LOI[a]
Ophites											
Profile Ph1	10–40	48.19	14.64	10.86	11.43	9.46	1.37	1.19	0.16	1.70	1.74
	40–80	48.35	13.60	11.52	12.10	9.16	1.37	1.53	0.18	1.56	2.86
	80–100	48.32	14.02	11.10	10.29	9.30	1.37	2.31	0.19	1.84	1.70
	+100	46.02	13.60	11.33	12.84	11.34	1.23	0.56	0.18	1.29	1.84
Profile Ph2	0–25	36.12	22.15	10.25	4.18	9.69	3.55	3.30	0.10	2.58	7.98
	25–55	36.36	22.70	10.25	5.16	9.03	2.35	4.02	0.08	3.14	6.81
	55–80	35.78	23.80	9.47	2.90	8.82	4.57	2.36	0.06	3.43	8.70
Profile Ph3	0–35	37.12	23.53	10.16	4.32	9.28	2.27	4.02	0.09	2.86	6.03
	35–60	35.40	21.88	10.34	6.00	8.77	2.44	4.00	0.07	3.43	7.58
Marls											
Profile Ma1	45–56	41.20	21.05	2.64	5.96	17.96	0.56	0.55	0.02	0.46	9.54
	56–73	29.13	19.67	5.76	13.75	17.98	0.67	0.86	0.03	0.52	11.22
	+73	46.92	19.39	3.42	3.30	15.20	0.54	1.96	0.03	0.44	8.80
Profile Ma2	45–65	41.73	18.57	5.15	6.40	11.40	0.75	1.69	0.04	0.68	13.46
	65–102	42.99	18.57	6.88	6.04	10.17	0.55	2.45	0.06	0.47	11.84
Profile Ma3	40–50	62.59	6.18	2.13	13.95	0.91	0.47	1.16	0.03	0.39	12.54
	50–85	61.96	6.17	2.13	14.07	0.96	0.49	1.14	0.03	0.41	12.71
Profile My1	30–70	38.84	4.79	2.64	25.91	9.51	0.32	0.72	0.04	0.27	17.17

[a] Loss on ignition (LOI).

values of Fe_2O_3 are less than 7% and the total alkalis (Na_2O+K_2O) do not surpass 3%. Content in CaO varies between 3% and 26%. The MgO shows amounts above 9.5%, reaching values of 18%, except in profile Ma3, whose value is <1%. This agrees with the elevated values of equivalent $CaCO_3$ that this soil presents (Table 1) and the presence of calcite (Table 2). The high values of MgO are in agreement with the mineralogy of these marls, rich in trioctahedral phyllosilicates. The LOI values are variable for each of the sediments and are mainly determined by the carbonate contents of the marls. Similar results were described by Kampunzu et al. (2005) when characterizing the geochemistry of sedimentary rocks in the Congo.

The variability found, in the chemical composition of the sediments studied, is a reflection of the chaotic disposition of the Triassic materials produced by the halotectonic processes that took place during the formation of the diapir. These processes were illustrated by Jackson and Talbot (1986) in their study of saline structures.

3.4.2. Soils

Table 4 shows the results for chemical composition for the soils formed on ophitic rocks (Ph1, Ph2 and Ph3). Their chemical nature is essentially the same as the starting material (Table 3). Compared with the original rock, they display a relative liberation of silica, a decrease in aluminum oxides and a slight decrease in the proportions of iron, sodium, potassium and earth alkalines. By extrapolating our data to a SiO_2–Al_2O_3–FeO_3 diagram (Fig. 8), where the results obtained for soils and rock are shown, the great similarity in chemical composition is apparent. This reveals that only slight alterations of the primary materials has occurred (Cheswort, 1973a,b), due principally to the climate conditions in the study area.

The composition of the principal elements formed above marls is shown in Table 4 (Ma1, Ma2, Ma3 and My1). Contents in SiO_2 are found to be between 40.4% and 58.1%, percentages that are very close to those obtained for the original materials. Also, the Al_2O_3 (5%–23%) and Fe_2O_3 (<7.05%) contents are very close to those found in the underlying marls. In general, contents in MgO surpass those of CaO, except in profile Ma3, formed above marl material with high contents of equivalent $CaCO_3$ (Table 1). Notably, contents are higher in K_2O than Na_2O, which agrees with the mineralogy of the soils.

3.5. Selective extraction

Table 5 shows the results of selective extraction with ammonium oxalate 0.2 M, pH 3, (the active or amorphous

Table 4
Major element concentrations of soil samples of the diapiric formation

Profile	Depth (cm)	SiO_2 (%)	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	TiO_2	LOI[a]
Ophites											
Profile Ph1											
0–10	A1	46.14	6.64	9.33	10.66	7.66	1.08	1.05	0.14	1.43	15.72
10–40	A2	52.01	7.16	10.96	8.84	7.42	1.46	1.27	0.17	1.65	8.46
40–80	AB	47.96	8.02	10.77	12.33	7.35	1.35	1.34	0.18	2.11	8.75
80–100	BC	51.64	8.15	11.81	8.52	7.48	1.54	1.50	0.18	1.53	8.28
+100	C	46.42	8.43	11.97	15.64	8.41	1.65	0.96	0.16	1.70	4.98
Profile Ph2											
0–25	Ap	42.22	20.60	9.71	2.08	7.56	1.65	2.31	0.10	2.03	11.64
25–55	AC	42.15	21.05	9.78	2.59	8.11	1.33	2.52	0.10	1.30	10.97
55–80	C	42.45	21.05	9.56	1.79	8.37	1.16	2.69	0.08	1.16	11.58
Profile Ph3											
0–35	A	42.28	18.85	8.01	7.77	6.92	2.23	0.81	0.10	1.16	11.81
35–60	AC	42.75	19.16	8.28	7.74	6.91	2.44	0.73	0.11	1.16	10.67
Profile Ma1											
0–10	A	50.84	19.14	5.68	1.13	9.59	0.60	2.20	0.05	0.23	10.01
10–25	AC	51.96	18.59	5.59	2.59	9.93	0.53	1.94	0.05	0.15	8.10
25–45	2C	41.91	22.43	7.05	1.75	14.63	0.55	2.20	0.04	0.18	8.61
Marls											
Profile Ma2											
0–15	A	40.41	15.83	5.59	7.38	10.67	0.51	1.79	0.04	0.41	18.14
15–45	AC1	43.52	16.91	5.97	6.69	11.12	0.62	1.54	0.04	0.20	12.02
Profile Ma3											
0–15	A	58.11	5.06	1.69	14.24	0.88	0.91	1.06	0.03	0.16	18.15
15–40	AC1	57.89	5.75	1.91	18.01	0.95	0.65	1.06	0.03	0.13	13.61
Profile My1											
0–10	A	47.69	16.64	5.84	3.70	7.46	0.66	1.97	0.06	0.10	15.72
10–30	AC	52.80	17.99	6.10	5.34	6.80	0.67	1.99	0.06	0.11	8.21

[a] Loss on ignition (LOI).

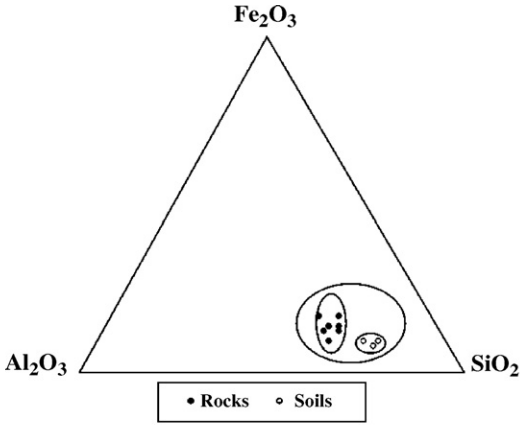

Fig. 8. Average chemical composition of soil and rock samples plotted in Al_2O_3–Fe_2O_3–SiO_2 diagram.

forms Fe_o, Al_o and Si_o) and with a reactive combination of citrate, bicarbonate and dionite (the free forms Fe_d, Al_d, Si_d, and Mn_d), as well as the different relationships of the iron.

The low values found in the soils developed above ophites ($Si_o+Al_o+Fe_o<1\%$), without differences across the profiles, indicates the low proportion of amorphous constituents. The presence of high proportions of organic C stimulates the formation of strong links with Al and Si liberated from subvolcanic materials, which induces the formation of humus-metal complexes at the same time that it inhibits the development of allophanic forms (Tokashiki and Wada, 1975; Mizota and Chapelle, 1988; Shoji et al., 1996; Nizeyimana et al., 1997; Aran et al., 1998).

In these soils the Al_d and the Fe_d present low levels with ranges between 0.45% and 0.86% for the former and between 1.54% and 2.85% for the latter. The higher proportions of Al_d compared with Al_o in all cases indicate that the amorphous clay minerals (allophan and imogolite) are insignificant. However, the fact that the values of Fe_d are also greater than those of Fe_o demonstrates that crystalline iron oxides hematite and magnetite could be present in the soils, although not in high proportions, evidenced in the low proportions of Fe_{do} ($Fe_{do}=Fe_d-Fe_o$) (Nizeyimana et al., 1997). The values of the Fe_o/Fe_d ratio, in every instance lower than 0.35, confirms this fact (Malucelli et al., 1999; Fauzi and Stoops, 2004). On the other hand, the low values of the Fe_d/Fe_t ratio (0.2–0.4 in the ophite soils and between 0.3 and 0.5 in the soils above marls) reflect that all the soils are young with a low degree of mineral alteration.

The content in free and amorphous forms in the soils developed above Keuper materials is, in general, lower than

Table 5
Selective extraction data of soil samples of the diapiric formation

Profile	Depth (cm)	Fe_o (%)	Al_o	Si_o	Fe_d	Al_d	Si_d	Mn_d	Fe_{do}	Fe_d/Fe_t	Fe_o/Fe_d
Ophites											
Profile Ph1											
0–10	A1	0.53	0.23	0.09	1.69	0.63	0.28	0.02	1.16	0.26	0.32
10–40	A2	0.54	0.24	0.11	1.73	0.57	0.25	0.02	1.19	0.23	0.31
40–80	AB	0.49	0.23	0.09	1.71	0.55	0.28	0.02	1.23	0.23	0.28
80–100	BC	0.41	0.21	0.12	1.54	0.55	0.24	0.02	1.13	0.19	0.27
+100	C	0.36	0.16	0.10	1.64	0.45	0.22	0.01	1.28	0.20	0.22
Profile Ph2											
0–25	Ap	0.36	0.19	0.06	2.84	0.85	0.43	0.03	2.48	0.42	0.13
25–55	AC	0.38	0.19	0.07	2.78	0.86	0.45	0.03	2.40	0.41	0.14
55–80	C	0.38	0.18	0.07	2.85	0.81	0.43	0.03	2.48	0.43	0.13
Profile Ph3											
0–35	A	0.53	0.34	0.06	1.68	0.71	0.31	0.02	1.15	0.30	0.31
35–60	AC	0.59	0.33	0.06	1.71	0.68	0.28	0.02	1.11	0.29	0.35
Marls											
Profile Ma1											
0–10	A	0.40	0.15	0.09	1.88	0.55	0.22	0.02	1.47	0.50	0.21
10–25	AC	0.46	0.19	0.09	1.84	0.54	0.22	0.02	1.37	0.51	0.25
25–45	2C	0.17	0.17	0.05	1.83	0.60	0.24	0.01	1.66	0.43	0.09
Profile Ma2											
0–15	A	0.20	0.15	0.05	1.10	0.46	0.22	0.01	0.90	0.38	0.18
15–45	AC1	0.18	0.15	0.05	1.21	0.48	0.21	0.01	1.03	0.31	0.15
Profile Ma3											
0–15	A	0.09	0.06	0.03	0.41	0.18	0.13	0.01	0.32	0.30	0.22
15–40	AC1	0.08	0.06	0.03	0.46	0.20	0.11	0.01	0.39	0.32	0.17
Profile My1											
0–10	A	0.39	0.13	0.05	1.58	0.37	0.19	0.02	1.19	0.40	0.25
10–30	AC	0.43	0.14	0.05	1.75	0.48	0.21	0.02	1.32	0.41	0.25

Fe_o = oxalate-extractable Fe; Al_o = oxalate-extractable Al; Si_o = oxalate-extractable Si; Fe_d = dithionite-extractable Fe; Al_d = dithionite-extractable Al; Si_d = dithionite-extractable Si; $Fe_{do}=Fe_d-Fe_o$.

that presented in soils developed above ophites (Table 5). As in soils developed above ophites, the indexes used are indicative of the predominance of crystalline forms in the iron oxides (Fe_{do}, Fe_o/Fe_d), which is a result of the environmental conditions of the area where these soils developed.

4. Conclusions

The mineralogical and chemical data for the original materials and the soils that make up the diapiric formation, lead to the following conclusions:

1- Plagioclases, pyroxenes, vermiculites and biotites are the main minerals found in the samples of ophitic rocks. These minerals, together with chlorite, dominate the mineralogy of the soils. This result suggests that most of the minerals in the soils are inherited from the ophitic material.

2- Biotite, smectite, chlorite and interstratified chlorite–vermiculite make up the predominant mineralogical association in the clay fraction of the soils, which formed as the result of the transformation of primary biotite under the influence of the hydrothermal activity affecting the formation of the diapir.

3- Calcite as a non-laminate material, biotite, and especially chlorite are the main minerals in the marls and in the soils developed above them. Gypsum predominates in the samples of the gypsiferous marls. The mineralogy of the clay fraction of the soils is primarily made up of chlorite and biotite whose total content is greater than what is found in soils developed above ophites. Heritance is therefore the main process that explains the genesis of the minerals in the clay.

4- The ophites analyzed are basic rocks, non-alkaline, of basaltic nature, in which the variations in Al_2O_3, TiO_2 and Na_2O are associated with the differences in the chemistry and the evolution of the pyroxenes. The chemical nature of the soils is essentially the same as the starting material. The variability in chemical composition of the Keuper sediments and of the soils developed above them is attributed to the chaotic disposition of the Triassic materials in the formation of the diapir, and not to the intense chemical weathering.

5- In spite of the ophitic rocks being of a basic nature, rich in alterable materials and volcanic origin, the low concentrations of silica, iron and aluminum extractable with ammonium oxalate indicate the low proportion of non-crystalline products. These results suggest that the amorphous, liberated compounds evolve toward crystalline forms, due to the semiarid conditions of the area and to sandy soil textures that favor aeration.

6- Processes which play a part in the pedogenesis of soils developed on diapiric formations in the Mediterranean area are conditioned by climatic characteristics and by the original material. The predominance of processes of inheritance over those of transformation is conditioned by the following: (i) the low chemical alteration of the original material, (ii) the insignificant mineralogical differentiation throughout the profiles, (iii) the homogeneity in the content of Fe and Al oxides in soils developed on ophites, and (iv) the presence of $CaCO_3$ in soils developed on marls.

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