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SEDIMENTARY
GEOLOGY

Sedimentary Geology 116 (1998) 159–176

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Received 20 March 1997; accepted 23 September 1997

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Abstract

During the Middle–Late Eocene, Oligocene and Miocene a non-marine succession, about 5000 m thick, was deposited in the western Ebro Basin. In the northern and southern margins of the basin, conglomerate deposits of alluvial fan origin were deposited. Towards the centre of the basin there is a lateral change to flood plain sandstones and mudstones and finally carbonate and evaporitic lacustrine deposits. Two types of saline lakes, where evaporitic precipitation occurred, can be distinguished: central saline lakes of high salinity, and marginal saline lakes, located near the southern margin, with lower salinity than the central ones. X-ray diffraction, TEM, SEM and EDX analysis were carried out on mudstones from central and southern deposits. The clay minerals identified were illite, chlorite, kaolinite, Mg-rich smectite, palygorskite and mixed-layers illite–smectite and chlorite–smectite. Apart from clays, carbonates (calcite, dolomite and magnesite) and other silicates (quartz, plagioclase, K-feldspar and analcime) were recognised. The palygorskite, Mg-rich smectite, analcime, dolomite and magnesite are of diagenetic origin. The other minerals are detrital, and derived from the surrounding mountain chains. The clay mineral assemblage of each environment is related to the diverse various source areas (Iberian Range and Pyrenees) and their compositional variation through time, as well as to diagenetic processes. On the basis of clay mineral distribution, the detrital clay mineral assemblages are preserved in the alluvial fans, the flood plain without saline influence, and the central saline lakes. In the saline flood plains and marginal saline lakes diagenetic palygorskite and Mg-rich smectites were formed. In the marginal saline lakes the formation of magnesium clays prevailed but in the central saline lakes, where no clay mineral diagenesis is observed, the magnesium precipitated as dolomite and magnesite.

Keywords: lacustrine sedimentation; clay minerals; mudstone; evaporites; paleogene; Ebro Basin

1. Introduction

Mudstones are the most abundant lithology in the Tertiary deposits of the western sector of the Tertiary Ebro Basin. They are present as thick, pure sequences of flood plain deposits or as single layers interbedded within both lacustrine and alluvial fan deposits. These mudstones are made up mainly of clay minerals, together with carbonate, sulphate and other silicate minerals. The great majority of these minerals are of detrital origin, coming from

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PII S0037-0738(97)00112-7

the denudation of the surrounding chains. The other minerals are formed within the basin. Previous studies (González and Galán, 1984; Mata et al., 1989; Salvany, 1989a; González López et al., 1992) have shown that the mineral associations in these mudstones vary according to the age and type of the sedimentary formations. However, these authors made no sedimentological interpretations of these mineral associations, nor did they study their regional significance.

The aim of this paper is to describe the mudstone mineralogy of the more representative alluvial and lacustrine formations of the southwestern Ebro Basin and to establish the relationship between this mineralogy and both the source area and the sedimentary environments. Preliminary results were given by Inglès et al. (1994). The regional stratigraphic and sedimentological framework supporting this study was provided by Pérez (1989), Salvany (1989a,b), Muñoz (1992), Salvany et al. (1994) and Muñoz-Jiménez and Casas-Sainz (1997).

2. Geological setting

2.1. General

The western sector of the Ebro Basin (Fig. 1) is made up of alluvial and lacustrine deposits of non-marine origin, deposited during the Middle Eocene to Late Miocene, with a total thickness locally reaching 5000 m. This sector is bordered on the north by the Pyrenees (Pamplona Basin and Cantabrian chain) and on the south by the Iberian Range (Cameros and Moncayo chains). Both ranges are in contact with the non-marine deposits along large reverse faults with hundreds of metres of slip which overlie a part of the proximal deposits.

The non-marine deposits show a decrease in the grain size from the margins towards the centre of the basin. The marginal deposits close to the Pyrenees and the Iberian Range are mainly conglomerates of alluvial fan origin. Towards the centre of the basin these conglomerates gradually change to flood plain sandstones and mudstones. The basin centre of the basin is occupied by lacustrine deposits of evaporitic or carbonate composition.

The evolution of the sedimentary basin is directly controlled by the uplift of the marginal ranges, mainly by the Pyrenees. According to these tectonics, the following three broad sedimentary cycles can be recognised (Fig. 2).

(1) *Middle–Late Eocene.* The western Ebro Basin was opened to the ocean through the present south Pyrenean domain (Pamplona Basin). The alluvial fan deposits of the Turruncún Formation (700 m thick) were deposited on the Iberian margin, while the south Pyrenean zone was filled by marine carbonate and evaporitic sediments (Guendulain Formation, more than 1000 m thick, including the Pamplona marls and the Navarra potash). The link zone between both alluvial and marine domains is unknown because it does not outcrop, and no subsurface data are available. During the terminal Eocene, the Pyrenean uplift caused marine regression and the basin became closed until the present.

(2) *Oligocene and basal Early Miocene.* This is the main filling cycle of the basin, with 2000 m of proximal alluvial deposits in the Iberian margin and more than 4500 m of lacustrine and distal alluvial deposits in the centre of the basin. During the Early Oligocene the central lacustrine sedimentation took place on the present northern margin of the basin (Puente La Reina Formation, 400 m thick). Then the southern basin was covered with a large alluvial system related to the Iberian Range. Its proximal deposits are represented by the lower part of the Arnedo Formation while the distal ones are the Mués Formation (more than 2000 m thick). During the Late Oligocene and the Early Miocene, as a result of the continuous Pyrenean uplift, the lacustrine sedimentation shifted progressively toward the south (Falces and Lerín Formations, 1000 and 600 m thick, respectively). The lacustrine displacement was associated with the retreat of the Iberian alluvial domain (upper part of the Arnedo Formation). During the Early Miocene, Pyrenean compression caused the folding of the previously deposited sediments. The folds show an E–W to ESE–WNW trend.

(3) *Top of the Early Miocene and Middle–Late Miocene.* As a result of the folding structure the western sector of the Ebro Basin became divided into minor subbasins located on the main synclines. The sedimentation was predominantly detrital (Fitero, Yerga, Alfaro, Tudela and Borja formations) with local lacustrine zones of evaporitic (Ablitas and Ribafrecha gypsum units, in the Alfaro Formation) and

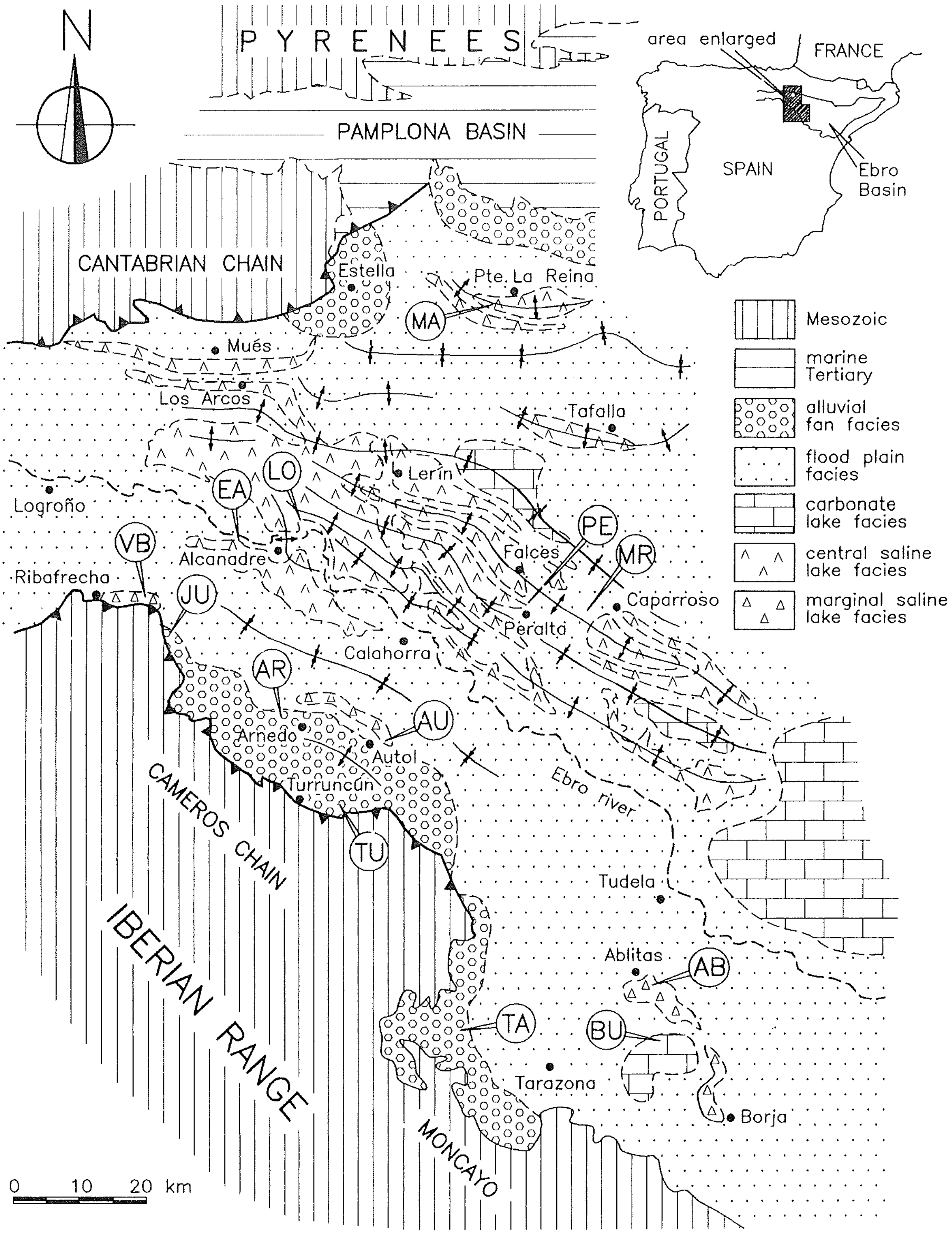


Fig. 1. Geological map of the western Ebro Basin showing locations of studied sections, referred to Fig. 2.

carbonate (Muela de Zaragoza and Muela de Borja formations) sedimentation.

Stratigraphic studies based on tectono-sedimentary analysis have divided the non-marine Tertiary succession of the southwestern Ebro Basin into nine genetic units (Pérez, 1989; Muñoz, 1992; Muñoz-

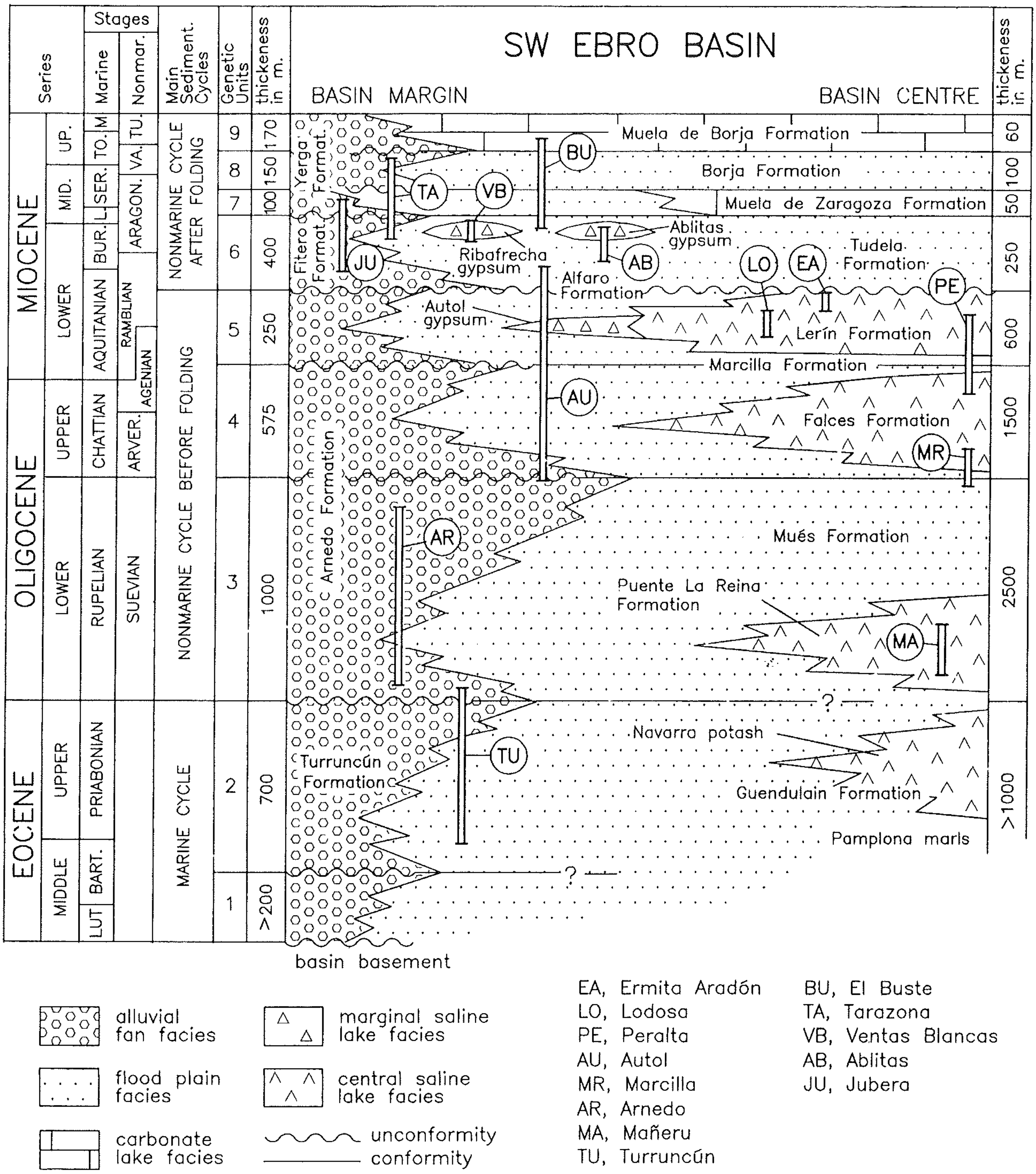


Fig. 2. Stratigraphic pattern of the Tertiary deposits of the southwestern Ebro Basin and locations of studied sections.

Jiménez and Casas-Sainz, 1997), delimited by sedimentary breaks; four are Palaeogene and the rest are Miocene (Fig. 2). The sedimentary breaks are the result of tectonic activity that affected the western sector of the Ebro Basin. They are manifested as angular unconformities on the Iberian margin of the basin and as changes in direction of the sequential evolution in the more central areas.

2.2. Source areas

The Moncayo and Cameros chains (Iberian Range) were the main source area of the southwestern Ebro Basin. The Moncayo chain is made up of Triassic rocks of detrital (Buntsandstein), carbonate (Muschelkalk) and evaporitic (Keuper) composition, forming a sequence about 500 m thick. The Buntsandstein strata are mainly quartzitic conglomerates and sandstones, and red mudstones. The Muschelkalk contains limestones and dolomites, and the Keuper calcium sulphate (gypsum/anhydrite) and halite. The Keuper facies also contain mafic volcanic and subvolcanic rocks (dolerites and olivine basalts, Lago et al., 1988). The Cameros chain is made up of Jurassic and Cretaceous carbonate and detrital rocks. The carbonate facies are related to the Jurassic (300 m thick) and Late Cretaceous (450 m). The Jurassic carbonates, together with Keuper evaporites, form the contact fringe between the Cameros chain and the Ebro Basin, whereas the Late Cretaceous outcrops predominantly to the south of the chain. Most of the Cameros chain is made up of Lower Cretaceous detrital deposits (Alonso and Mas, 1993). These are quartzitic conglomerates and sands, and clays of the Weald facies (more than 8000 m thick) and quartzitic sands and kaolinitic mudstones of the Utrillas Formation (150 to 200 m thick).

The Pyrenean composition is more varied. Besides Mesozoic detrital, carbonate and evaporitic rocks, it also includes a large number of Palaeozoic igneous, sedimentary and metamorphic rocks, as well as the thick Palaeogene marine deposits of the Pamplona Basin (Puigdefábregas, 1975).

The great number of palaeogeographical studies describing the sedimentary evolution of the western Ebro Basin made it possible to identify the source area of the detrital deposits of the various sedimentary formations (Riba and Pérez-Mateos, 1962; Salvany, 1989a,b; Muñoz, 1992; Villena et al., 1996; Muñoz-Jiménez and Casas-Sainz, 1997). The Iberian Range was the only source area for the alluvial fan deposits of the Arnedo, Fitero and Yerga formations, the flood plain deposits of the Mués and Alfaro formations, and the interbedded distal alluvial deposits within the Ribafrecha, Ablitas and Autol gypsum units. Both the Iberian Range and the Pyrenees were the source areas for the lacustrine deposits of the Falces, Lerín, La Muela de Borja and La Muela de Zaragoza formations, and the flood plain deposits of the Marcilla, Tudela and Borja formations. The detrital materials interbedded within the evaporitic deposits in the Puente La Reina Formation are predominantly of Pyrenean origin.

2.3. Depositional environments

2.3.1. Alluvial systems

The alluvial systems are related to the Iberian and Pyrenean margins. Both show two main sedimentary domains: alluvial fans and flood plains.

In the southwestern Ebro Basin two types of alluvial fans can be distinguished (Muñoz, 1992). The first is an alluvial fan dominated by fluvial processes. It shows a good development of the various sectors with gradual transitions between them. The sediments are well sorted and the active segments show predominance of channel processes. It presents a gentle slope and great longitudinal extension (between 20 and 25 km). The second type of alluvial fan shows a smaller extension (10–15 km), mainly occupied by the proximal and distal sectors. It is dominated by gravitational processes in the proximal sector and the sheet floods in the distal one. There are rapid lateral changes of facies between the sectors. The two types of alluvial fans are represented by the Turruncún, Arnedo, Fitero and Yerga formations.

Toward the centre of the basin the alluvial fan deposits change laterally to a broad muddy flood plain. Their sediments were clays, silts and sands, deposited mainly from sheet flood streams and fluvial channels. In the centre of the basin the distal flood plain changes transitionally to saline or carbonate lakes. There, the flood plain shows a strong lacustrine influence and fine detrital deposits alternating with diagenetic evaporites and carbonate horizons (Marcilla and Tudela formations, and the distal facies of the Arnedo Formation). Lacustrine systems occasionally developed in other sectors of the basin. Then the flood plain covered the whole of the western Ebro Basin from the Iberian alluvial fans to the Pyrenean ones (Mués and Borja formations).

2.3.2. Saline lake systems

Two types of saline lakes can be distinguished: central and marginal lakes.

The central saline lakes were large playa-lakes (up to 100 km long) that developed at the depocentre of the basin and were subject to frequent expansion and contraction. They show three concentric subenvironments: an inner lacustrine zone where laminated facies of gypsum and halite (also possibly polyhalite) were deposited; an intermediate zone with laminated gypsum containing diagenetic anhydrite and glauberite; and a marginal zone with diagenetic nodular anhydrite (sabkha environment), gradually giving way to the distal flood plain (Salvany, 1989a; Salvany and Ortí, 1994). During stages of expansion and dilution of the brines, subordinate carbonate horizons (from 1 to 10 cm thick) were deposited. The original calcite muds were replaced by dolomite or magnesite during subsequent stages of water concentration. The magnesite formed in the intermediate and inner lake zones, mainly associated with the glauberite–polyhalite deposits, whereas dolomite extends from the inner zone to the surrounding flood plain. The central saline lake deposits constitute the Puente La Reina, Falces and Lerín formations (the first one does not include glauberite–polyhalite horizons).

The marginal saline lakes were smaller and less saline than the central ones (Salvany et al., 1994). They developed on the flood plain deposits of the Iberian margin with a maximum length of a few kilometres. Their sediments were calcium carbonate and gypsum, together with diagenetic anhydrite and minor amounts of celestite. The carbonate deposits were bioturbated muds containing aquatic plant fragments (mainly charophyte stems), peloids, ostracods and gastropod fragments. In these horizons the original mineralogy (calcite) and components have been preserved (sometimes locally replaced by dolomite). Large diagenetic chert nodules (up to 1 m in length) replace both gypsum and carbonates and are a characteristic feature of these lacustrine facies. The development of marginal saline lakes took place contemporarily with, although independently of, that of the central ones. Their deposits are represented by the Autol gypsum unit (contemporary with the Lerín central saline lake) and the Ribafrecha and Ablitas gypsum units (contemporary with the Zaragoza central saline lake, outside the area studied).

2.3.3. Carbonate lake systems

The carbonate lake systems were restricted to the Middle and Late Miocene. They are interpreted as stable lakes that developed at the basin depocentre without any relation to the saline lakes described above. Two main sedimentary subenvironments are recognized: a marginal palustrine and an inner lacustrine zone. The first one is made up of carbonate bioturbated muds with evidences of almost constant vegetation cover. The inner zone is characterized by massive bioclastic muds with charophytes, gastropods and ostracods. A characteristic feature of these carbonate deposits is the occurrence of diagenetic chert nodules. These lacustrine deposits constitute the La Muela de Zaragoza and La Muela de Borja formations, which are each several tens of metres thick (Pérez, 1989; Pérez et al., 1989).

3. Analytical procedure

A total of 115 samples of mudstones were collected from eleven surface sections. During the sampling the diversity of the sedimentary environments was taken into account. Samples represented alluvial fan (21 samples), flood plain (28 samples), carbonate lacustrine (12 samples), marginal evaporitic lacustrine (18 samples), and central evaporitic lacustrine (36 samples) environments. In the discussion of the results, consideration was given to the mineralogical data of sections EA (7 samples) and MR (10 samples) reported by Salvany (1989a) in an earlier work. The locations of the sections are shown in Figs. 1 and 2.

A portion of each sample was dispersed in distilled water and washed until deflocculation occurred. The fraction of <2 μm was separated by centrifugation of the suspension. Oriented mounts of the fraction of <2 μm were prepared for X-ray diffraction by gravity settling on glass slides. Clay mineralogy was determined from diffraction patterns obtained using samples that were air-dried, solvated in ethylene glycol and heated to 550°C for 2 h. Chlorite and kaolinite were distinguished using a slow scan record between 24 and 25.5°2θ (Biscaye, 1965). Interstratified clay minerals were identified by a low, broad diffraction peak, at 4.5° to 7°2θ which changed to lower angles after solvation with ethylene glycol. This peak indicates the presence of a mixed-layer expandable clay mineral. When several reflections were present it was possible to identify it as of the illite–smectite type.

Another portion of each sample was powdered in a tungsten carbide ring mill to provide fine-grained material for whole-rock mineralogy. All X-ray diffraction analyses were carried out on a Siemens D500 X-ray diffractometer using a CuKα radiation.

A number of 29 representative samples of the various environments were further studied by transmission electron microscopy (Hitachi H-800 MT with H-8010 STEM and SEM system and KEVEX EDS microanalyser) and scanning electron microscopy (Hitachi S 2300 and JEOL JSM 840 equipped with an AN-10.000 LINK energy dispersive X-ray microanalyser) in order to determine the qualitative composition of smectites and interstratified minerals and also to identify the non-clay minerals in the <2 μm fraction.

The semiquantitative estimation of calcite and dolomite was carried out on the bulk powdered sample by a volumetric method measuring the volume of carbon dioxide released in two steps by the acid decomposition of calcite and dolomite. The apparatus used for the determinations was a Geoservices Manocalcimeter.

4. Results

The clay minerals identified in the <2 μm fraction were illite, chlorite, kaolinite, palygorskite, smectite and interstratified illite–smectite and illite–chlorite. Apart from clays, other silicates (quartz, plagioclase, K-feldspar and analcime), carbonates (calcite, dolomite and magnesite) and sulphates (gypsum and celestite) were identified.

4.1. Clay minerals

Illite and chlorite. Both minerals are very widespread. Illite is ubiquitous but chlorite, recorded in 88% of the samples, is absent from the Eocene and Lower Oligocene alluvial deposits. TEM observations revealed that both minerals occurred as irregularly shaped plates.

Kaolinite. Kaolinite is mainly found in the Eocene and Lower Oligocene alluvial deposits, decreasing markedly towards the centre of the basin.

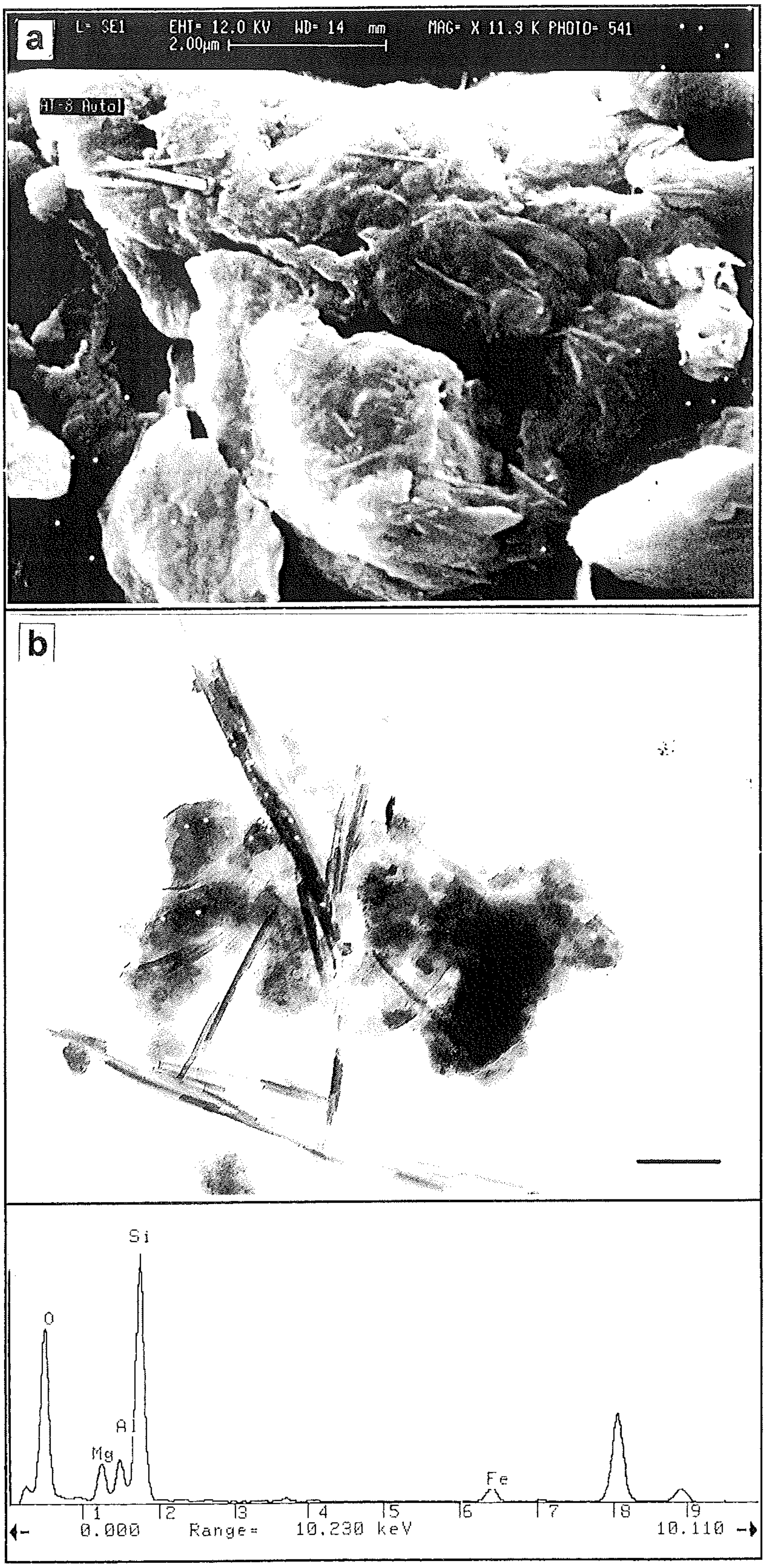
Palygorskite. Palygorskite occurrences are restricted to the marginal saline lakes and the flood plain with saline influence around them. The mineral was positively identified by X-ray diffraction in samples interbedded in the Autol gypsum unit and the flood plain related to it. In the flood plain, short fibres (<1 μm) (Fig. 3) coexist with longer ones. Although abundant, fibres are scattered and rarely form mats or bundles. On the other hand, in Autol gypsum, fibres are longer and form mats and bundles (Fig. 4). TEM observations revealed the presence of palygorskite fibres (short and very scarce) in the mudstones interbedded in the Ablitas and Ribafrecha gypsum units.

Smectite. This mineral is found exclusively in the marginal saline lake mudstones of the Ribafrecha, Ablitas and Autol gypsum units. A reflection between 1.522 Å and 1.520 Å indicates the trioctahedral character of the smectites.

In the mudstones interbedded in the Ablitas gypsum, TEM and SEM observations reveal a great abundance of minerals displaying a fibrous habit (Fig. 5) but neither sepiolite nor palygorskite is recorded in the X-ray diffraction patterns. The STEM energy dispersive X-ray spectra of fibres show a variable magnesium/aluminium peak height ratio ranging from equal heights to high magnesium/low aluminium values as depicted in Fig. 5. Platy clay minerals coexist together with the fibres (Fig. 6), with similar variable ratios of magnesium to aluminium.

The X-ray diffraction information and the qualitative chemical composition enables the interpretation of these fibrous minerals as magnesium-rich smectite or mixed-layer illite–smectite with a high proportion of smectite layers. The presence of Mg-rich smectites in the Ablitas gypsum has been recorded previously by González and Galán (1984). Morphologies similar to those shown in Fig. 5a have been attributed to smectites and mixed-layer illite–smectite (Welton, 1984; Turner and Fishman, 1990).

Mixed-layer clay minerals. Mixed-layer expandable clay minerals occur in Upper Oligocene–Miocene samples of lacustrine carbonate and alluvial environments and in the mudstones interbedded within the gypsum in the Puente La Reina Formation (Lower Oligocene) where all samples contain small quantities of mixed-layer illite–smectite. In addition,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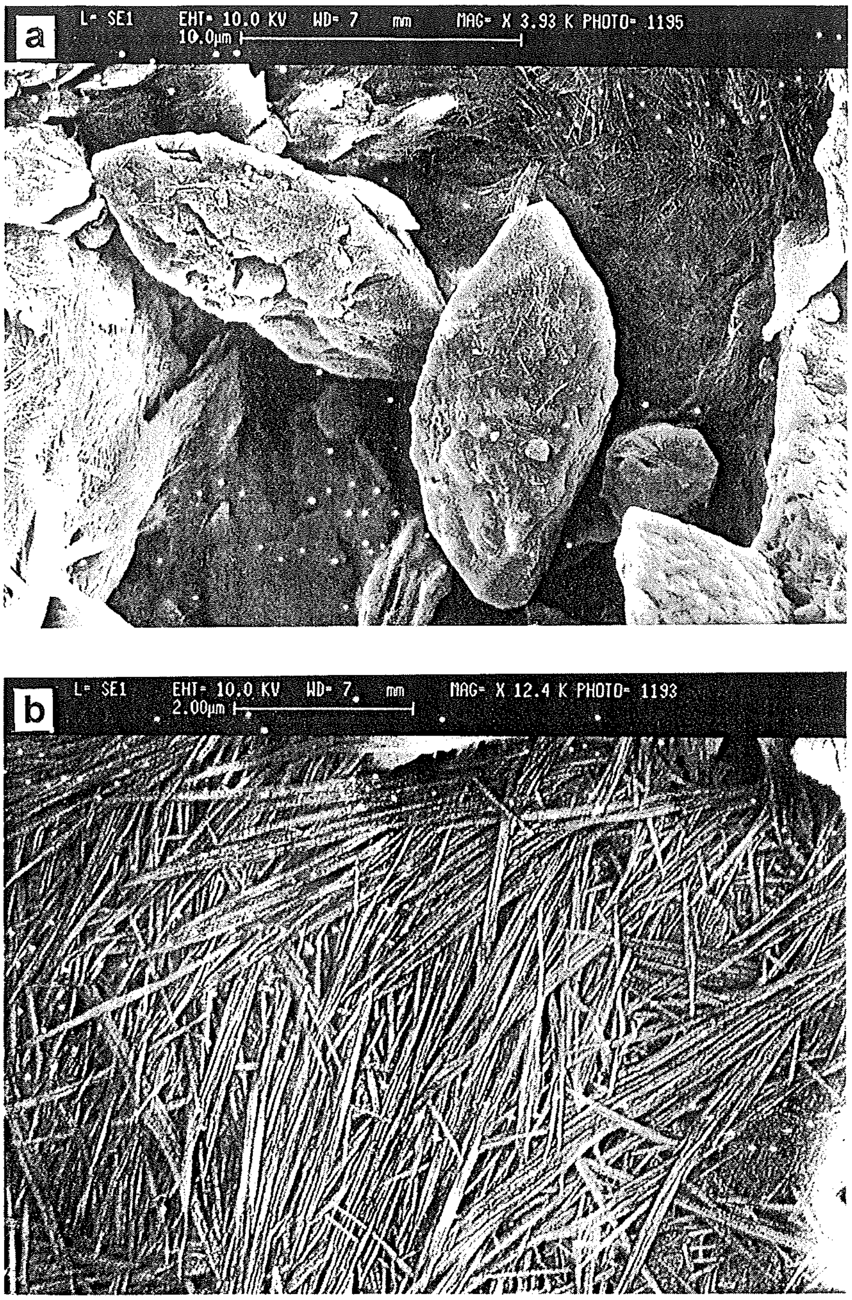
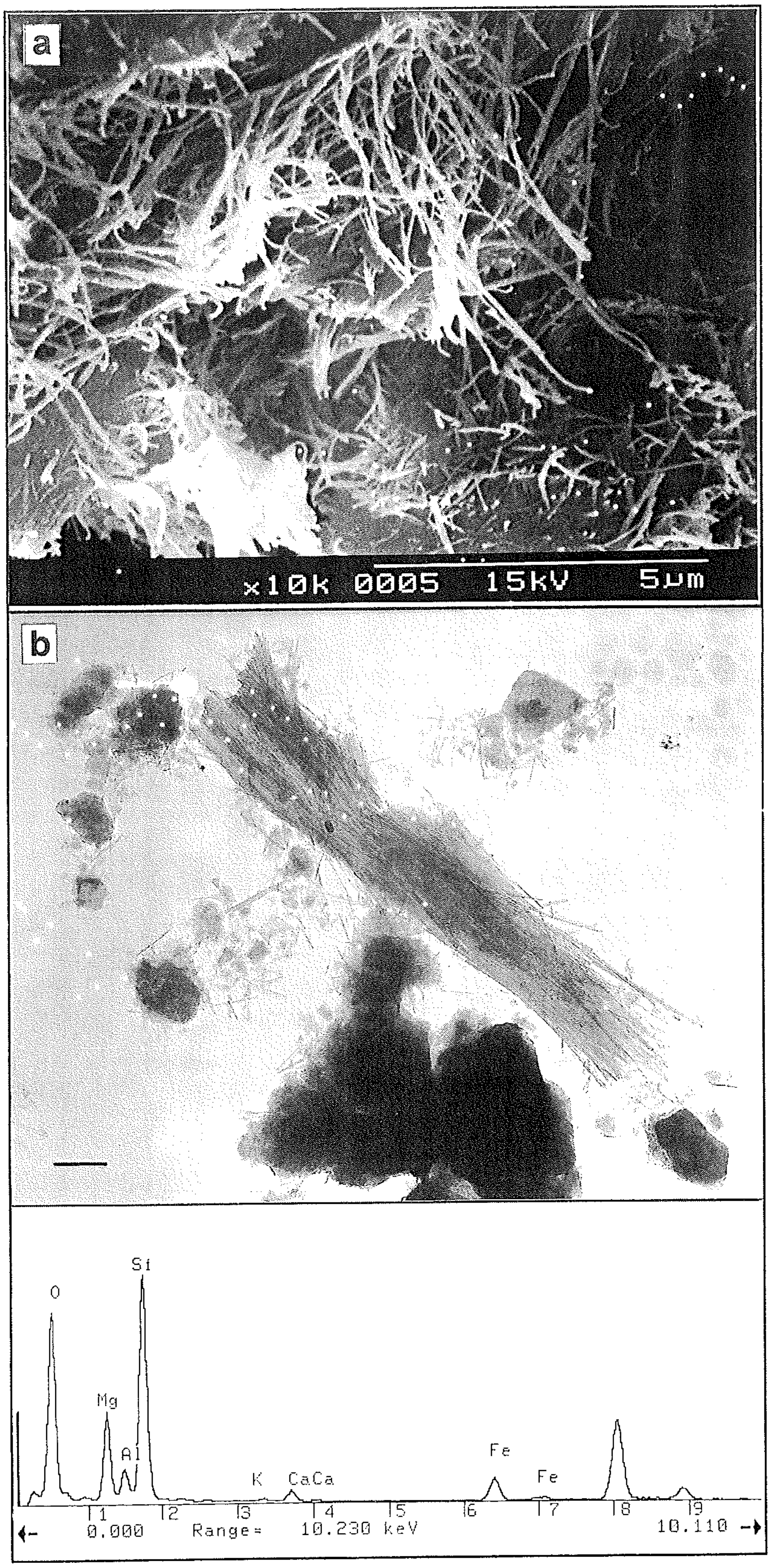


Fig. 4. Scanning electron micrographs of palygorskite from a marginal saline lake sample (AU section). (a) Mats and scattered fibres coating lenticular gypsum. (b) Close view of palygorskite mats.

Fig. 3. Scanning (a) and transmission (b) electron micrographs of short palygorskite fibres from a sample from saline flood plain (AU section). In (b) scale bar is equivalent to 0.5 μm. The energy dispersive X-ray spectrum depicts a representative composition of palygorskite. The analysis was performed on a STEM. Unlabelled peaks correspond to copper and carbon of the support grid and coating. Vertical scale bar is equivalent to 1000 counts.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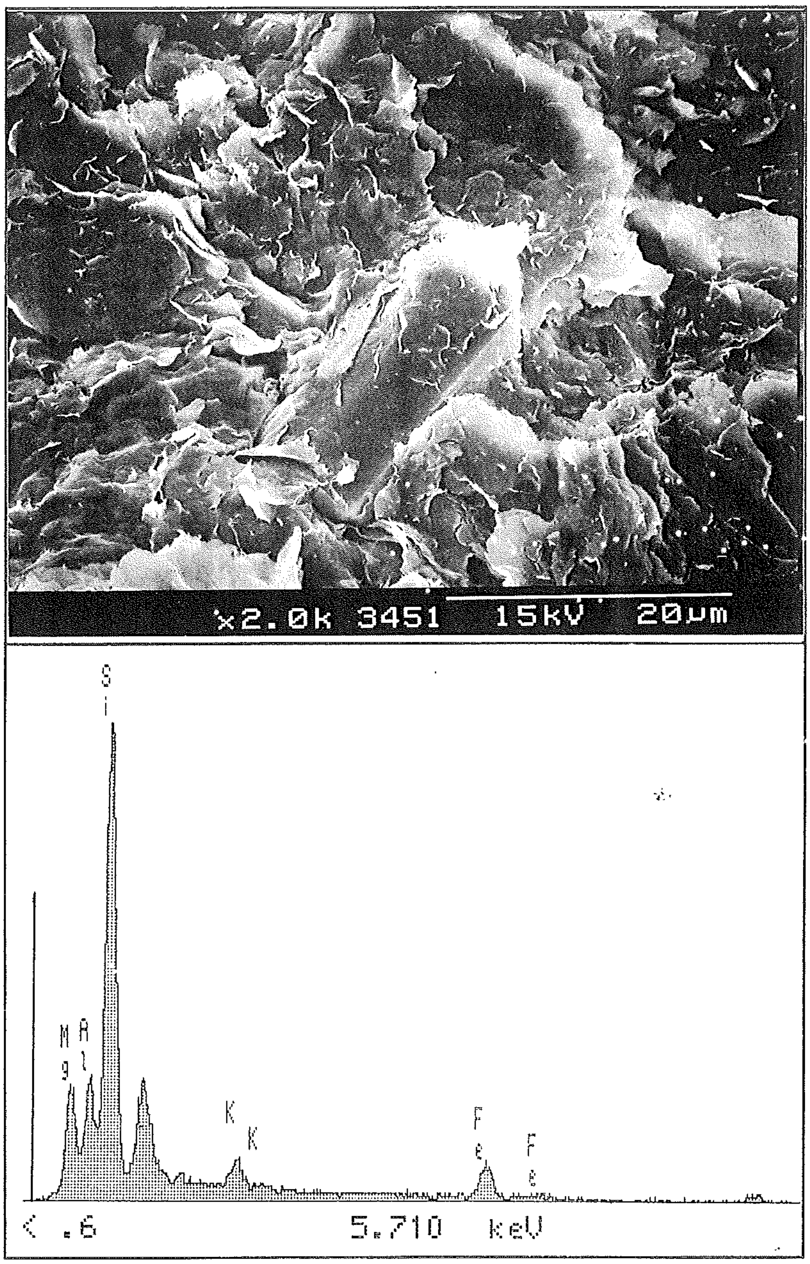


Fig. 6. Scanning electron micrograph of a smectite (AB section). The euhedral grain is celestite. In the EDX spectrum, the vertical scale bar is equivalent to 1000 counts. Unlabelled peaks correspond to gold of the coating.

in the alluvial deposits of the Miocene (Yerga and Fitero formations), interstratified illite–chlorite minerals are recorded in a few samples.

4.2. Non-clay minerals

Silicates. Quartz is ubiquitous. Small amounts of plagioclase and/or K-feldspar are present in the major-

Fig. 5. Scanning (a) and transmission (b) electron micrographs of Mg-rich smectite from a marginal saline lake (AB section). In (b) scale bar is equivalent to 1 µm. The EDX spectrum depicts a representative composition of fibres. The analysis was performed on a STEM. Unlabelled peaks correspond to copper and carbon of the support grid and coating. Vertical scale bar is equivalent to 1000 counts.

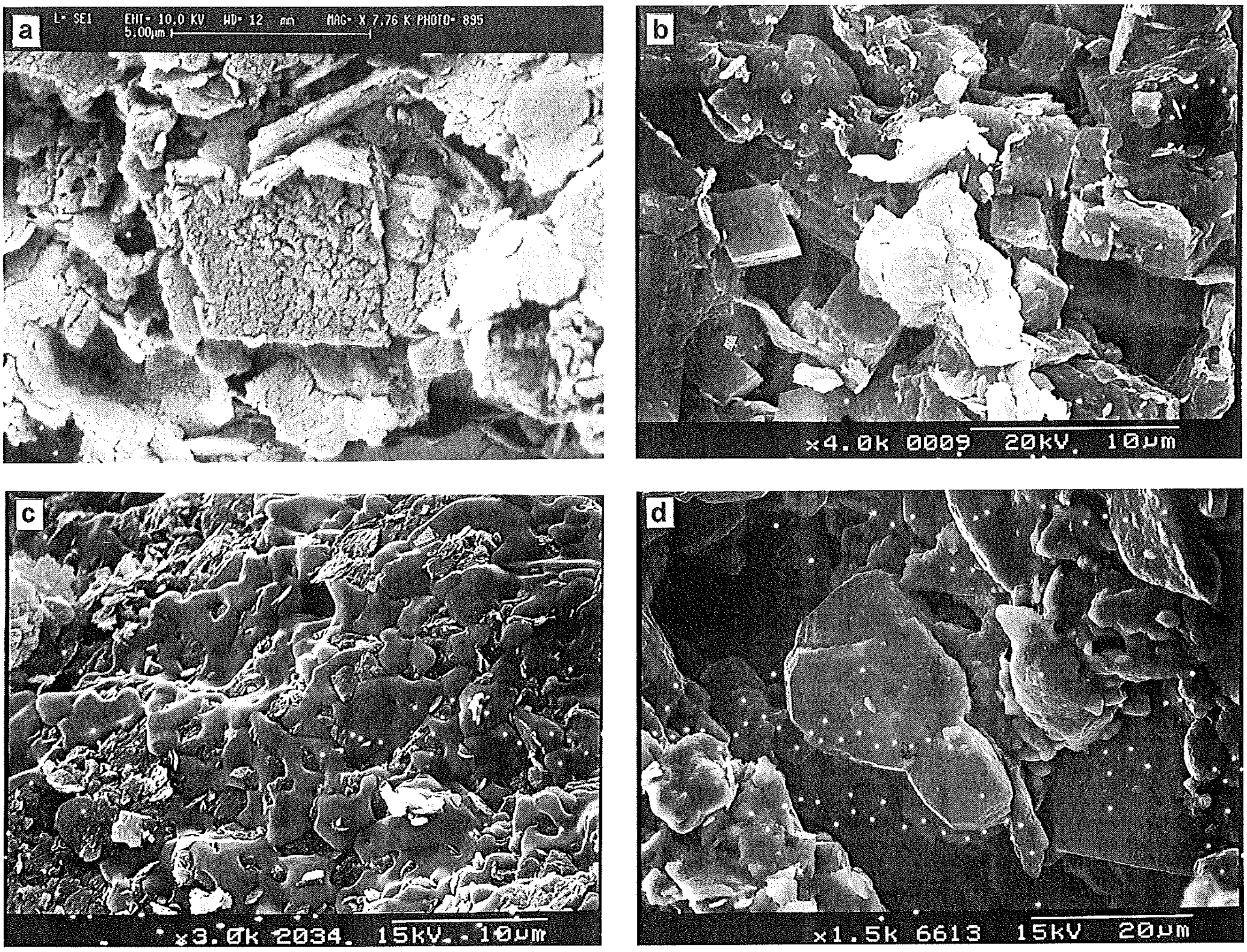


Fig. 7. Scanning electron micrographs of non-clay minerals from central saline lakes identified by EDX: (a) magnesite (LO section); (b) dolomite (PE section); (c) halite (PE section); and (d) analcime crystal in the centre of the picture (MA section).

ity of samples. Analcime (Fig. 7d) was detected only in the samples from the Puente La Reina Formation.

Carbonates. All the samples contain carbonates, either calcite or dolomite. Calcite is present in the majority of samples in concentrations ranging from 5% to 50% of rock weight. Dolomite is commonly predominant in central evaporitic deposits (1–45% of rock weight), where calcite is rare. SEM observations reveal dolomite rhombohedra of 1–2 μm in size (Fig. 7b). Dolomite also occurs in minor amounts in the carbonate deposits of the marginal lakes. Up to 15% of mudstones from the central saline lake contain small amounts of magnesite (Fig. 7a).

Evaporitic minerals. Small amounts of gypsum were detected by X-ray diffraction in mudstones interbedded in evaporitic formations. Celestite was identified by means of X-ray diffraction in the mudstones of the Puente La Reina Formation. In addition, small amounts of celestite were observed during SEM and EDX analyses in some samples from the Ablitas gypsum. Halite was identified in the mudstones from the central saline lakes (Fig. 7c).

4.3. Mineral distribution

Alluvial systems. Mineralogical composition changes with the age of the deposits and the evaporitic influence. Illite is present in all the samples. In addition, Eocene and Lower Oligocene samples contain kaolinite. In the Upper Oligocene–Miocene, there is no kaolinite, but chlorite and interstratified illite–smectite were recorded. Furthermore, in the Middle and Upper Miocene kaolinite is found occasionally and mixed-layers illite–chlorite were recorded in some samples of alluvial fan deposits. The presence of chlorite and mixed-layer illite–smectite increases from bottom to top and towards the centre of the basin, the inverse of the case of kaolinite. Minor amounts of palygorskite are present in the saline flood plain around marginal saline lakes.

In addition to clays, quartz and small amounts of plagioclase and K-feldspar were recorded. Calcite is commonly the predominant carbonate mineral; in the Upper Eocene–Lower Oligocene it does not exceed 15% of the rock weight but increases up to 45% in some samples from the Upper Miocene.

Marginal saline lakes. The main clay minerals are illite, chlorite and smectite. Kaolinite occasionally occurs in the Ribafrecha gypsum unit located close to the margin of the basin. The presence of palygorskite (Figs. 3 and 4) is noticeable, as is that of Mg-rich smectite (Fig. 5) in the Ablitas and Ribafrecha gypsum units. Quartz and calcite are the most abundant non-clay minerals and occur together with minor amounts of plagioclase and K-feldspar. Gypsum and celestite (in the Ablitas section) occasionally occur in small amounts.

Central saline lakes. Illite and chlorite are recorded in all the samples. Kaolinite is present only in samples from sections of the Lerín Formation close to the Iberian margin (EA and LO sections). In the Puente La Reina Formation small amounts of interstratified illite–smectite are recorded. Quartz and plagioclase are ubiquitous, as is dolomite. Magnesite is found in some samples spread throughout the evaporitic facies. Calcite occurs with dolomite in the Lerín Formation and with dolomite and analcime in the Puente La Reina Formation.

Carbonate lakes. The clay mineral assemblage is the same as that reported in the alluvial facies with which carbonate lakes are related. Calcite is the only carbonate recorded; it is very abundant (30–40% of the rock weight) and occurred with quartz and minor amounts of plagioclase.

5. Discussion

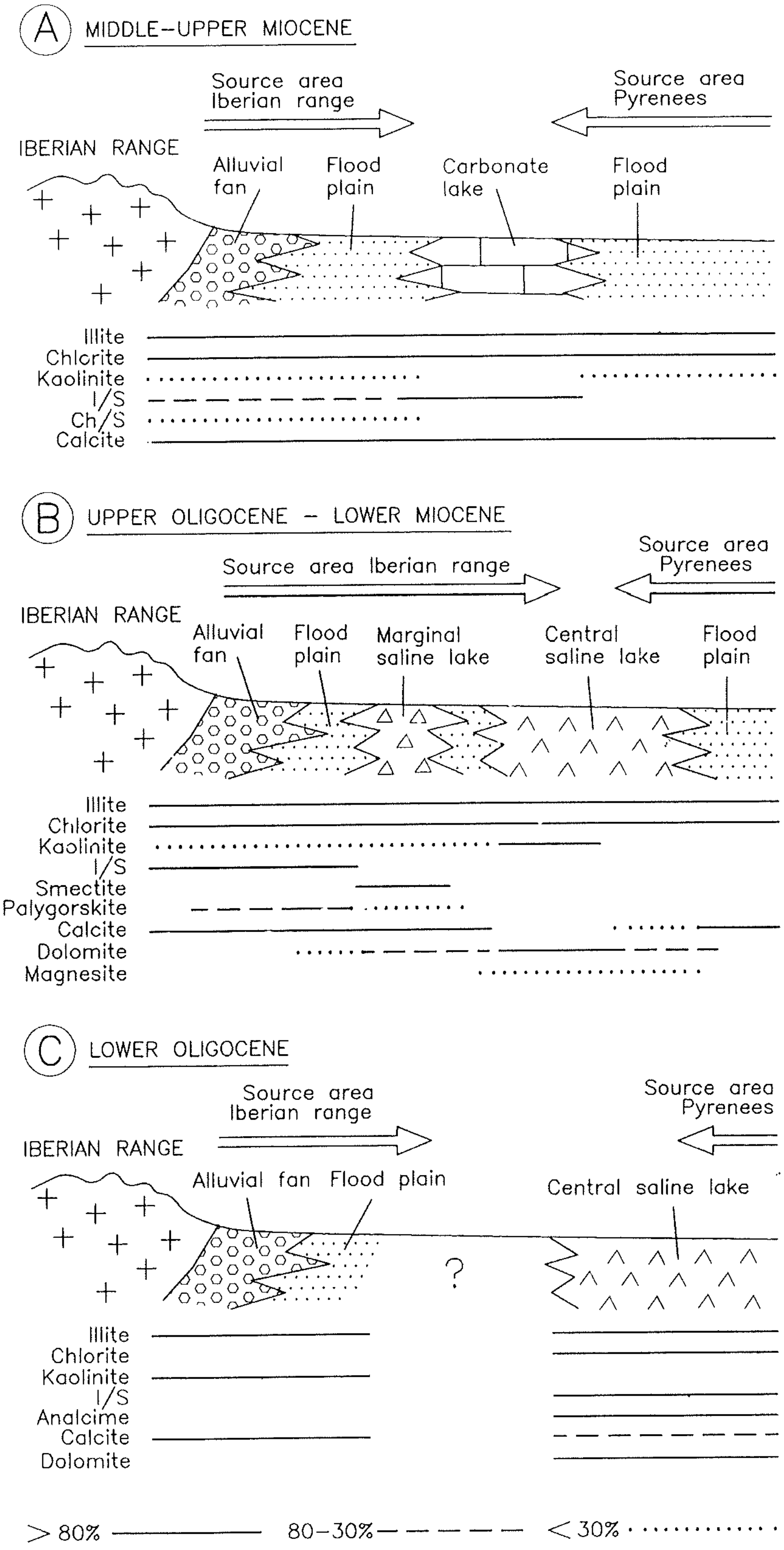
Illite, chlorite, kaolinite and mixed-layer illite–smectite and illite–chlorite are considered of detrital origin, as are quartz, plagioclase and K-feldspar. The distribution of the detrital minerals is related to the direction of detrital inputs and the compositional variations of the Iberian and Pyrenean source areas through time (Fig. 8).

The palaeoclimatic conditions of the Ebro Basin have been established on the basis of palynological data (Cavagnetto and Anadón, 1996) and the charophyte succession (Feist et al., 1994). Dry climate conditions characterized the Late Eocene–Early Oligocene with a slight decrease of temperature with respect to the warmer climate of the Bartonian. In the Late Oligocene the temperature rose again.

The sharp diffraction peaks of illite and chlorite agree with the palaeoclimatic conditions described above, in which weathering produced minor alterations in the structure of the mica, and only a decrease in grain size during transport occurred. These conditions also favoured the formation of interstratified illite–smectite.

Kaolinite proceeds from the erosion of the Utrillas Formation, made up of kaolinitic sands and mudstones, which outcrop in the Cameros chain, the distribution in the basin being determined by palaeocurrents. Kaolinite is very common in the alluvial fan facies of the Eocene–Early Oligocene, but is lacking in the contemporary mudstones from the Puente La Reina Formation because of its Pyrenean origin. Kaolinite is not recorded in the Upper Oligocene mudstones and appears again in significant amounts in the alluvial fan and central saline lake environments of the Lower Miocene. Occasionally it is recorded in the Upper Miocene samples.

The interstratified illite–smectite distribution is found to be due as much to the source area, either Iberian or Pyrenean, as to the age of the weathered material. In the Lower Oligocene these clays are lacking in the alluvial sediments close to the southern margin and are found in small quantities in the mudstones of the Puente La Reina Formation, which have a Pyrenean origin. In the Upper Oligocene and Miocene, interstratified clay minerals are found only in the alluvial and carbonate lake sediments of the southern margin profiles. A detrital and Iberian origin is attributed to this illite–smectite mixed-layer and also to the illite–chlorite mixed-layer, which is recorded only in some alluvial fan deposits from the Middle and Upper Miocene. The absence of illite–


A
MIDDLE–UPPER MIOCENE
Source area Iberian range
Source area Pyrenees
IBERIAN RANGE
Alluvial fan
Flood plain
Carbonate lake
Flood plain
Illite
Chlorite
Kaolinite
I/S
Ch/S
Calcite
B
UPPER OLIGOCENE – LOWER MIOCENE
Source area Iberian range
Source area Pyrenees
IBERIAN RANGE
Alluvial fan
Flood plain
Marginal saline lake
Central saline lake
Flood plain
Illite
Chlorite
Kaolinite
I/S
Smectite
Palygorskite
Calcite
Dolomite
Magnesite
C
LOWER OLIGOCENE
Source area Iberian range
Source area Pyrenees
IBERIAN RANGE
Alluvial fan
Flood plain
Central saline lake
?
Illite
Chlorite
Kaolinite
I/S
Analcime
Calcite
Dolomite
> 80%
80–30%
< 30%

smectite mixed-layer in the saline flood plain and marginal saline lake deposits contemporary with the alluvial sediments allows us to interpret that these mixed-layer minerals have been transformed in the saline environments.

The calcite identified in the alluvial mudstones is of detrital origin coming from the denudation of the carbonate Mesozoic formations of not only the Iberian Range and the Pyrenees but also the marine Palaeogene of the Pamplona Basin. The calcite in the lacustrine deposits is detrital and autochthonous, but usually it is not possible to distinguish between them because of its micritic texture and, in the central lakes, its subsequent dolomitisation.

Palygorskite, Mg-rich smectite, dolomite, magnesite, analcime and celestite are considered diagenetic minerals.

Palygorskite and Mg-rich smectite was found exclusively in the marginal saline deposits, palygorskite mainly in the saline flood plain and Mg-rich smectite in the mudstones interbedded in the gypsum units. According to Jones (1986), the conditions of these environments, with strong alkalinity, water stagnation and solute silica and magnesium, appear to be critical in the formation of these minerals, and the final product depends on the hydrologic environment and the proportion of water to sediment inflow.

Several authors have emphasized the formation of palygorskite in ephemeral saline lakes and saline flood plain either by the transformation of precursor clay minerals or by a dissolution–precipitation mechanism (Velde, 1985; Jones and Galan, 1988). In the Ebro Basin the formation of palygorskite from precursor detrital clays has been described by Inglès and Anadón (1991) and López Galindo et al. (1996). In the environments considered in our study, palygorskite is present, although in small amounts, in the saline flood plain and in the clay layers interbedded in the marginal saline lake deposits. The mats of palygorskite fibres coating detrital and evaporitic grains suggest a transformation from pre-existing detrital clay minerals. We interpret the scattered, short and apparently broken-ended palygorskite fibres (Fig. 3a) as reworked in the sedimentary environment.

Magnesium smectites have been documented in various modern and ancient saline lakes (Jones and Weird, 1983; Hay et al., 1986; Darragi and Tardy, 1987). Mg-rich smectite is exclusively found in the mudstones interbedded in the marginal saline lake deposits and in the carbonate deposits around the Autol gypsum. The presence of delicate fibres points to an in-situ formation. The qualitative composition of this mineral is shown in Fig. 5. The aluminium content excludes a precipitation origin and some kind of transformation mechanism is supposed. According to Jones (1986) pre-existing 2 : 1 sheet structures can play an important role in the formation of Mg-rich smectites by mechanisms of interstratification, starting with the fixation of cations in the interlayer positions. The precursor clay minerals were probably interstratified illite–smectite, the only detrital mineral which is almost absent in these saline environments.

There is a good relationship between the distribution of diagenetic clay minerals and the evaporitic precipitation in the saline lacustrine systems. The salinity of present-day subsurface drainage waters from the Cameros and Moncayo chains is between 1000 and 3000 mg/l of total dissolved solids. The waters are mainly of the calcium-sulphate type, with minor concentrations of HCO_3^-, Cl^-, Na^+, Mg^{2+}, K^+ and Si (with concentrations of up to 47 mg/l of $Si0_2$) (San Román, 1994; Coloma, 1997). According to Martínez-Gil et al. (1988) the present-day chemistry of the waters and the hydrogeological characteristics of this sector of the Ebro Basin are very similar to those of the basin during the Late Tertiary.

The marginal saline lakes formed on the alluvial plain where the subsurface waters of the Sierra de Cameros and Moncayo discharged. These lakes experienced cycles of expansion–dilution, with deposition of biogenic calcium carbonate, and contraction–concentration with precipitation of anhydrite–gypsum. The lack of halite and other sulphates indicates that the brines did not reach high

Fig. 8. Sedimentary schemes showing the distribution of clay and some non-clay minerals in the depositional environments in the southwestern Ebro Basin. Three main temporal stages were differentiated related to the Iberian source area evolution from the Early Oligocene to the Late Miocene. The percentages express the number of samples in which the various minerals are present.

salinities. Another characteristic feature of these marginal lakes is the formation of diagenetic chert nodules replacing both gypsum and carbonate.

As described above, minor amounts of palygorskite were formed in the saline flood plain and Mg-rich smectite formed in greater proportion in the lakes. The high silica and magnesium content of the waters favoured the diagenetic formation of both clay minerals from a detrital interstratified illite–smectite precursor which provided the necessary aluminium and iron. Palygorskite formed in conditions of lower salinity and higher detrital supply than smectite.

The water of the central saline lakes came from both the northern and southern margins of the basin and, in addition, incorporated the residual brines of the marginal saline lakes. The central lakes have a more varied evaporitic mineral assemblage than the marginal ones because the brines had a wide range of concentrations. During periods of lake expansion and moderate concentration of the water, carbonate sediment formed (although in a lesser proportion than in the marginal lakes) and precipitation of gypsum and diagenetic anhydrite occurred. During phases of lake contraction when the brine was highly saline, halite, glauberite and polyhalite formed. The first of these precipitated mainly as a free water sediment in the lake. Glauberite and polyhalite formed as diagenetic minerals, either as replacive secondary or displacive primary minerals (details in Salvany and Ortí, 1994). During stages of higher concentrations the calcium carbonate was dolomitised and occasionally transformed into magnesite.

In the central saline lakes of Falces and Lerín the clay mineral assemblage is made up of illite, chlorite, with subordinate kaolinite, but no diagenetic clay mineral formation is recorded. The high crystallinity indicates well-ordered structures and may indicate and uptake of cations in the sedimentary environment.

In these lakes no chert nodules are found, suggesting a much lower silica content than that of the marginal ones. Moreover, no mixed-layer clay minerals are recorded. The lack of these minerals, abundant in the contemporary alluvial deposits, and the low silica content, probably favoured the preservation of the detrital clay assemblage and the magnesium was only fixed in the carbonates as dolomite or magnesite.

The central saline lake of the Puente La Reina Formation deserves some attention. The lack of glauberite and polyhalite and the presence of celestine and analcime, identified by X-ray diffraction in the mudstones as well as in the gypsum deposits, allow us to interpret that the hydrochemistry of this lake was different from that of Falces and Lerín. This difference is probably related to the Pyrenean origin of the water and the detrital inputs. The clay minerals present are illite and chlorite with subordinate amounts of interstratified illite–smectite, all of them with a low crystallinity contrasting with the high crystallinities of the other central saline lakes. Analcime was reported in the basal anhydrite of the Navarra potash by Rosell and Ortí (1980). According to these authors it was formed by interaction of concentrated brines with detrital clays, because no volcaniclastic materials are recorded in the basin during the Late Eocene. Some analogies between the mineral paragenesis of the Puente La Reina Formation and the Navarra potash (of marine origin) together with the geographical and stratigraphical proximity of both evaporitic deposits do not exclude the possibility of some marine influence in the lacustrine deposits of the Puente La Reina Formation. Further studies must be carried out to verify this hypothesis.

6. Conclusions

(1) In the non-marine mudstones from the alluvial and lacustrine Tertiary deposits of the southwest Ebro Basin, the minerals identified are: (a) clay minerals: illite, chlorite, Mg-rich smectite, kaolinite, palygorskite and interstratified illite–smectite and illite–chlorite; (b) carbonates: calcite, dolomite and magnesite; (c) other silicates: quartz, feldspars and analcime; and (d) sulphates: gypsum and celestite. Palygorskite, Mg-rich smectite, dolomite, magnesite, celestite and analcime are of diagenetic origin. Calcite is in part detrital and in part biogenic. The other minerals are detrital, being derived from the erosion of the Iberian Range and to a lesser degree from the Pyrenees.

(2) The distribution of detrital minerals must be attributed to the source area composition and their evolution during the Tertiary. The following three main evolutionary stages can be differentiated (Fig. 8).

(a) *Eocene–Early Oligocene.* The alluvial deposits of the Iberian margin are characterised by high illite, kaolinite and calcite content. On the other hand, there is no kaolinite in the evaporitic deposits with Pyrenean influence, but they are rich in illite, chlorite and interstratified illite–smectite. The kaolinite derives from the erosion of kaoliniferous sands and clays from the Utrillas Formation (Early Cretaceous), which outcrops only in the Iberian Range.

(b) *Late Oligocene–Early Miocene.* The alluvial deposits from the Iberian margin are characterised by illite, chlorite and mixed-layer illite–smectite. Kaolinite has only been found locally. The Pyrenean input consisted exclusively of illite and chlorite. On the Iberian margin the change was due to the prevalent denudation of the carbonate formations of the Early Cretaceous over the detrital one (Utrillas Formation).

(c) *Middle and Late Miocene.* The clay mineral assemblage is similar to that from the Oligocene and Early Miocene, except for a higher proportion of mixed-layer clay minerals. The preservation of mixed-layer clays may have been influenced by the lack of evaporitic systems.

(3) According to the clay mineral distribution trends, the alluvial, flood plain (without saline influence), carbonate lacustrine and central saline lake environments preserve the detrital clay mineral associations. The distribution of diagenetic minerals is related to the saline environments and depends on the increase in salinity towards the centre of the basin and the silica concentration of interstitial and lake waters.

In the saline flood plain and marginal saline lakes the diagenetic transformations of detrital phyllosilicates led to the formation of palygorskite and Mg-rich smectite. Palygorskite is recorded in the saline flood plain and formed in conditions of lower salinity and higher detrital supply than the Mg-rich smectite which occurs exclusively in the mudstone layers interbedded in the gypsum. The high magnesium and silica content of the waters (the latter evidenced by chert nodules replacing the host sediment) favoured the diagenetic formation of both clay minerals from a detrital interstratified illite–smectite precursor which provided the necessary aluminium and iron.

In the central saline lakes of Falces and Lerín the magnesium-rich brines caused the transformation of the original calcite mud into dolomite and magnesite. On the other hand, no diagenetic clay minerals have been observed in these lakes. The lack of mixed-layer clay minerals and the low silica content, suggested by the absence of chert nodules, probably favoured the preservation of the detrital clay mineral assemblage.

Acknowledgements

We are grateful to W.M. Last and an anonymous reviewer, who both provided us with helpful comments and suggestions. X-ray diffraction analyses, TEM and SEM observations and analyses were carried out in the Serveis Científico-Tècnics at the Universitat de Barcelona. This study was partially financed by DGICYT PB93-0580.

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