Lacustrine chalky carbonates: origin, physical properties and diagenesis (Palaeogene of the Madrid Basin, Spain)

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Abstract

The Palaeogene lacustrine chalky carbonates of the Madrid Basin are a peculiar type of very soft and friable carbonate facies with high porosity despite being covered by more than 800 m of sediment. Similar physical properties to those described in marine chalk reservoirs emphasize the interest in analysing and characterizing these carbonate facies within a lacustrine depositional system. Lithologically, they are calcitic and/or dolomitic poorly cemented carbonate muds with no significant amounts of skeletal debris. Clay minerals such as illite, smectite and palygorskite are present between the carbonate crystals. Palygorskite is the most common, covering the carbonate crystals and forming sheets between them. These lacustrine chalky carbonates were formed in the basinal areas of the lake as the result of inorganic carbonate precipitation and/or detrital sedimentation related to episodic reactivation of the adjacent fan systems. Their petrological, geochemical and physical properties indicate that few textural and compositional modifications occurred during diagenesis. Their main physical properties are a very low dry bulk and grain density (1.6–2.2 and 2.62 g/cm^3, respectively) and medium to high porosity (10–40%) due to micropores (<2 μm, 70%) and macropores (>2 μm, 30%). The convergence of lacustrine sedimentation dynamics (rapid sedimentation), the original mineralogy of these calcareous lacustrine muds (relatively stable low-magnesian calcite and dolomite), the early formation of the palygorskite cement of these muds, and the retention of Mg-enriched fluids in the pore system, were decisive in the partial inhibition of calcite cementation, compaction and recrystallization. The chalky carbonates are also intercalated between impermeable littoral carbonate facies that impeded fluid flow through their pore systems.

Keywords: Chalky carbonates; Lacustrine deposits; Physical properties; Overpressure; Palygorskite; Palaeogene

1. Introduction

Traditionally, chalk is defined as a light-coloured, fine-grained, porous, friable carbonate rock of marine origin (Ziljstra, 1995). Chalks are pelagic carbonate muds composed mainly of calcareous tests of the floating microorganisms and of remains of calcareous algae (Schlanger and Douglas, 1974; Ziljstra, 1995).

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Due to the preservation of interparticle primary porosity that chalks often present these deposits may constitute important carbonate reservoirs. For this reason, the petrological and physical characterizations of marine chalks have been of special interest in the research into carbonate reservoirs (Schölle, 1974; Schölle, 1977; Feazel and Schatzinger, 1985; Maliva and Dickson, 1992; Holail and Lohmann, 1994). Moreover, limestone petroleum reservoirs showing a high porosity, common in Mesozoic and Tertiary carbonate platform deposits (Moshier, 1989), had been characterized as chalky textured carbonates, due to their similarity to chalks.

Analogous facies in continental environments were described by Kelts and Hsü (1978). These authors use the term chalk to describe lacustrine sediments typically fine grained and porous, either rhythmically laminated or massive, white to dull-yellowish grey. In this case, the bulk carbonate content boundary is around 60% and the dominant mineral is calcite. Lacustrine chalks have been described only rarely in the geological record (Kelts and Hsü, 1978; Gierlowski-Kordesch and Kelts, 1994; Krenmayr, 1997; Manikowska, 1997), some of them occurring in glacial lakes. Kelts and Hsü (1978) pointed out that, in contrast to the oceans, the main source of these lacustrine carbonates is inorganic precipitation.

Fine-grained, light-coloured carbonate deposits with high porosity (10–40%) and friability occur in the Palaeogene lacustrine deposits of the Madrid basin (Arribas and Bustillo, 1985; Bustillo et al., 1998; Bustillo et al., 2002). There is a similarity in physical properties with chalks described in the literature (both marine and lacustrine in origin), but the carbonate particles are crystals and non-skeletal debris. As a result we proposed using the term chalky carbonates for these facies, because they are not true chalks in the sense that Zijlstra (1995) considered.

Bustillo et al. (1998, 2002) described these carbonates and linked their origin to the early formation of an inorganic carbonate sediment. However, they still pose several interesting and unanswered questions, which are examined in this study: Why do these facies, interlaid with limestones and dolostones, preserve high porosity? Why are they the purest carbonates of the Palaeogene lacustrine sequences? What is the sedimentological significance of these facies? Why is there a drastic change in the mineralogical composition (calcitic and dolomitic) between the different beds? The petrology of chalky carbonates with the characterization of their physical properties will help to understand the origin of these facies, retention of porosity and diagenetic evolution.

2. Geological setting

Palaeogene deposits are scattered along the northeast border of the Madrid Basin and are synchronous with the Alpine orogeny. The Palaeogene outcrops are nearest to the area of convergence between the Iberian Range and the Central System (Fig. 1A). The greater part of the Palaeogene deposits in this area are carbonate and detrital rocks ordered in a succession formed by two lithological units: the Carbonate and Detrital Units (Arribas, 1986a, b, 1994). These units are apparently conformable over an evaporitic unit that is possibly Palaeogene. Neogene sediments are more than 2000 m thick, and unconformably overlie Palaeogene and/or Cretaceous formations in the marginal parts of the basin (Vicente et al., 1996).

The Palaeogene deposits reflect a change from a lacustrine environment (Carbonate Unit) to prograding alluvial fans (Detrital Unit) originating in the Central System and Iberian Range (Arribas and Arribas, 1991). This Palaeogene carbonate-detrital succession shows changes in its lateral facies between the stratigraphic sections, although development over time was similar in each. These changes in the facies allowed three sectors to be identified by Arribas (1986b): Beleña de Sorbe, Huérmeces del Cerro and Torremocha de Jadraque sectors (Fig. 1B and C). The detailed petrographic analysis of the nature of rock fragments in the Palaeogene sandstones permits two source areas to be characterized (Arribas and Arribas, 1991): (i) Mesozoic sedimentary rocks (essentially limestones and dolostones) of the Iberian Range, in the east (Torremocha de Jadraque and Huermeces sectors) and (ii) Palaeozoic metamorphic basement (schists and slates) and Cretaceous cover of the Central System (limestones and dolostones) in the west (Beleña de Sorbe sector).

The Carbonate Unit reaches a maximum thickness of 500 m in the Torremocha de Jadraque sector, and a minimum of 200 m in the Huérmeces del Cerro sector. In the Beleña de Sorbe sector, the Carbonate Unit

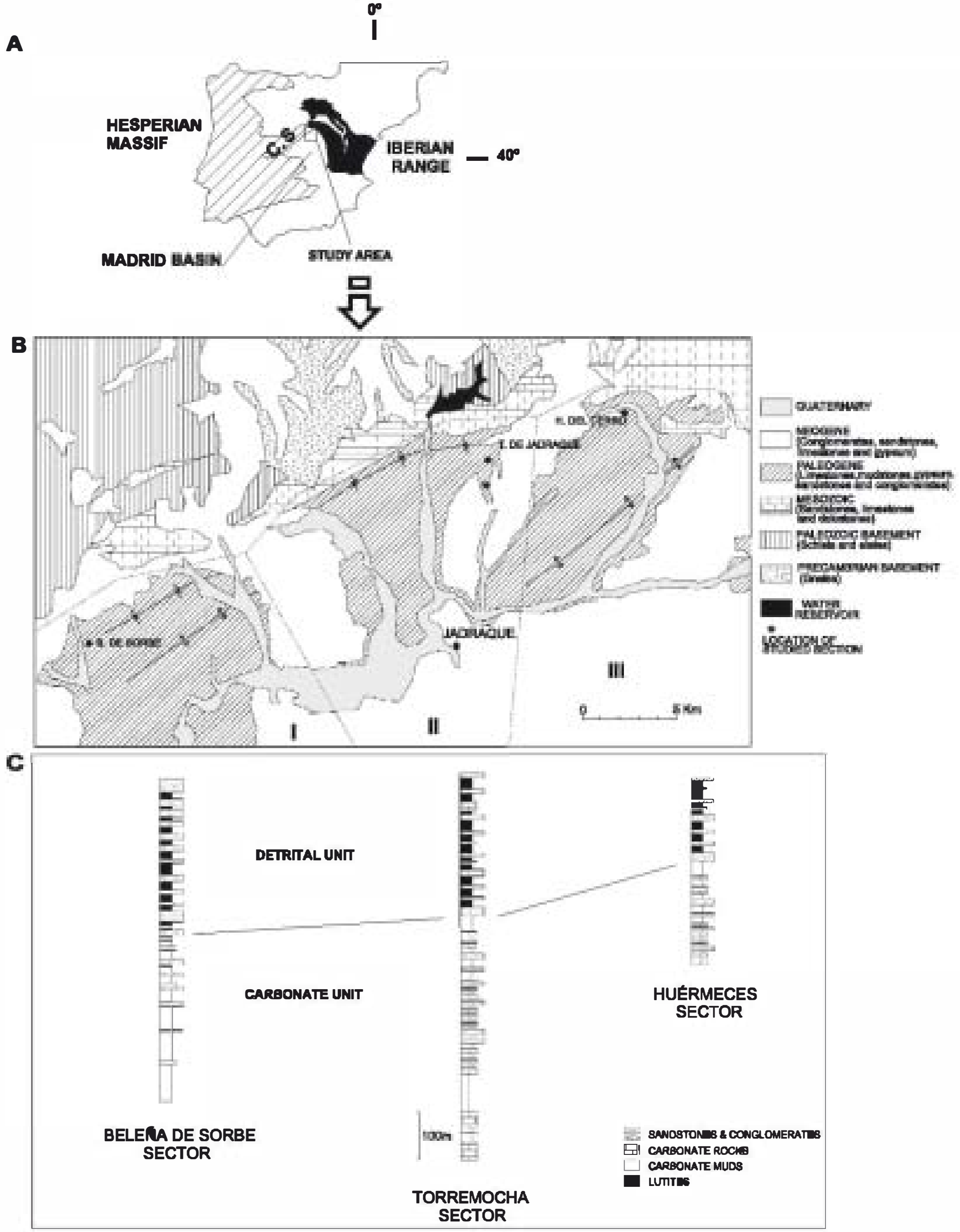

Fig. 1. Geological setting of the study area. (A) Distribution of the Hesperian Massif, Iberian Range and Madrid Basin in the Iberian Peninsula. C.S., Central system. (B) Geological map of Palaeogene deposits and distribution of sectors: I—Beleña de Sorbe sector, II—Torremocha de Jadraque sector and III—Huérmeces del Cerro sector. *Location of the studied stratigraphic section. (C) Cross-section of the three sectors.

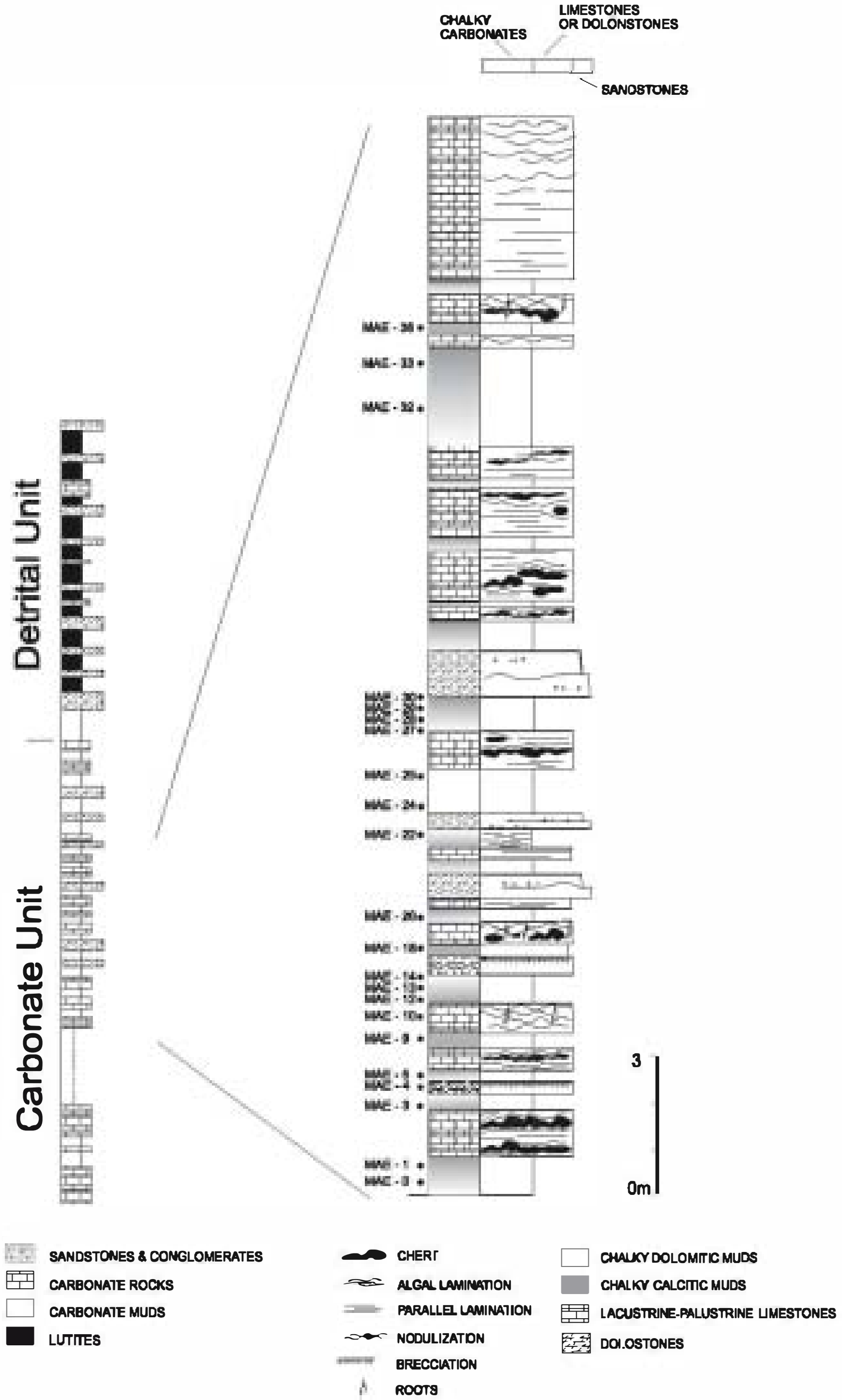

Fig. 2. General Palaeogene section and the local, studied section around Torremocha de Jadraque (from Bustillo et al., 2002).

consists of lacustrine carbonate sediments (marls, laminated marls with terrigenous and marly limestones) with intercalated, upward-thickening sandstone sequences that are interpreted as lacustrine delta deposits (Arribas et al., 1983). Towards the eastern sectors (Huérmeces del Cerro and Torremocha de Jadraque), the Carbonate Unit shows highly developed palustrine and lacustrine facies. Several palustrine facies have been described in the Huérmeces del Cerro sector where this unit is not as thick and pedogenesis was extensive. The Torremocha de Jadraque sector has more developed lacustrine sedimentation, reflected in its carbonate sediments over 500 m thick and the predominance of littoral and basinal facies (Arribas, 1986a,b). It is in this sector where several layers of chalky carbonates (very pure calcitic and dolomitic carbonates) appear forming the lower part of regressive lacustrine sequences (Fig. 2). Indurated lacustrine and palustrine limestones are interlaid with chalky carbonates, showing evidence of early diagenetic processes developed under arid-semiarid climate (Arribas, 1986a; Bustillo et al., 2002). Contemporaneous carbonate deposits in other sectors do not have this peculiar carbonate facies (Arribas, 1986a, b).

In the Palaeogene succession the burial depth could be estimated as 800 m maximum, considering the total thickness of Palaeogene deposits. Also, assuming a geothermal gradient between 25 and 30 °C for the intracratonic Madrid Basin (Tejero and Ruiz, 2002), temperature values could be estimated as 30–40 °C during burial.

3. Analytical methods

The lacustrine chalky carbonates were sampled in the Torremocha de Jadraque sector. Twenty-two samples were taken in order to collect a diversity of types. The stratigraphic positions of the samples are shown in Fig. 2.

The mineralogy of the samples was determined using a Philips X-ray diffraction (XRD) system operating at 40 kV and 30 mA with monochromated CuK$_\alpha$ radiation. The carbonate content of the samples was determined as the difference between the total sample and HCl-insoluble residues. The relative amounts of calcite and dolomite were realized by XRD using calibration curves with known mixtures of both minerals and introducing halite as internal standard (Hardy and Tucker, 1988). The type of calcite, the proportion of $CaCO_3$ in dolomite, and the degree of ordering of the dolomite, were also determined by XRD (Hardy and Tucker, 1988).

Polarized light and scanning electron microscopy (SEM) were used to determine the petrological properties of the samples, including textures and mineralogy. SEM was performed using a Philips KL-20 scanning electron microscope equipped with an energy dispersive X-ray analyser (EDAX-DX-4i). Fresh fracture surfaces of the samples were gold covered.

Major and trace-element contents were calculated in individual calcite and dolomite crystals (1 μm in size) from the two mineralogically purest samples of each chalky carbonate type using electron microprobe analysis. Working on polished and carbon-coated surfaces, these analyses were performed with a JEOL electron microprobe (JXA 8.900 M) equipped with four spectrometers at the *Universidad Complutense de Madrid*. Backscattered electron analysis was also performed. The standards used are described by Jarosewich et al. (1980) and were provided by the Department of Mineral Sciences of the Smithsonian Institution (Washington).

Petrophysical testing included grain density, dry bulk density, free water absorption and porosity, following the recommendations of the International Society of Rock Mechanics (ISRM, 1979). It was not possible to determine the saturated density nor water absorption due to the slaking of the samples in the presence of water. A durability test was performed to see whether there was any lack of crystal bonding due to chemical cementation. The one cycle slaking in water test (Lutton, 1977; Seedsman, 1986) followed methods used to assess the durability of shales. This involved immersing dry samples in distilled water to observe their disintegration mechanisms, and to estimate the extent of slaking. Slaking is the process through which a material (compacted but not cemented) disintegrates or crumbles into small particles or flakes when exposed to moisture. The extent of slaking in the presence of water, and the mechanisms by which it occurs, depends on the mineral and chemical composition of the sample, the nature of the inter-crystal bonds, and the size of pores and permeability. After immersion in water, the rocks were observed continuously for 24 h and their disintegration monitored. Samples were recorded as having undergone complete breakdown, partial breakdown or no change. The durability of the rock was estimated using the “jar slake index” (Ij), proposed by Lutton (1977). This gives a simple descriptive index for slaking behaviour. A six point classification scale is used to describe the observed behaviour, ranging from 1, in which the material degrades to a pile of flakes or mud, to 6, in which no change is observed.

4. Composition of the chalky carbonates

4.1. *Mineralogy and petrology*

The most characteristic features of the chalky carbonates are their white colour and massive and disaggregated appearance. They form beds 0.5–1 m thick and comprise the lower layers of lacustrine regressive sequences (Fig. 2). These facies have been interpreted as basinal lacustrine deposits formed in the areas farthest from the shore (Bustillo et al., 2002).

Table 1 shows the bulk mineralogical composition of the chalky carbonates. The carbonate fraction consists of calcite and dolomite of variable proportions. Non-carbonate particles (clays and very fine quartz) form less than 15% of the rock volume. Two mineralogical types of chalky carbonates can be defined on the basis of their mineralogical composition: *chalky calcitic* and *chalky dolomitic muds*.

The *chalky calcitic muds* contain more than 80% calcite (low Mg-calcite with 2–4 mol% MgCO$_3$, according to XRD data). These have a low clay mineral content (< 10%), mainly Al-smectite, illite and palygorskite. Thin sections show a homogeneous microcrystalline texture. Charophyte and ostracod fragments may be present in small quantities (< 2%). Under SEM

Table 1
Mineralogical composition and main physical properties of sampled Paleogene chalky carbonates

Samples	Mineralogical composition					Physical properties			Stable isotopes	
	MT	C (%)	D (%)	C-M (%)	Q (%)	DRY-D	GD	P (%)	$\delta^{13}C$	$\delta^{18}O$
Mae-0	CD	29	59	9	3		2.55	40		
Mae-1	C	90	6	4	0	1.95	2.60	23		
Mae-3	C	100	0	0	0	2.00	2.54	22	−6.41	−5.58
Mae-4	D	5	89	6	0	1.70	2.61	33	−4.1	−0.65
Mae-5	CD	65	29	6	0	1.60	2.64	39	(−3.40, −5.30)	(−0.82, −4.25)
Mae-9	C	87	5	7	1					
Mae-10	C	90	6	4	0	2.00	2.40	17		
Mae-10	C	90	6	4	0	2.00	2.40	17		
Mae-12	C	93	4	3	0	1.90		17		
Mae-13	CD	74	13	12	1	1.85	2.56	38		
Mae-14	D	0	91	9	0	2.15	2.64	19	−3.75	0.7
Mae-18	C	94	3	2	1	2.10	2.58	21	−7.01	−5.38
Mae-20	CD	71	20	6	3	2.20	2.45	10	(−2.80, −6.05)	(−1.44, −4.63)
Mae-22	CD	31	39	9	21	2.10	2.63	20		
Mae-24	D	3	84	12	1	1.95	2.62	25		
Mae-25	D	3	84	12	1	1.95	2.61	25		
Mae-27	D	1	80	17	2	2.00	2.63	24		
Mae-28	C	82	6	12	0		2.49	21		
Mae-29	C	88	6	6	0	1.95	2.59	24		
Mae-30	D	2	84	12	2				−4.37	1.24
Mae-32	CD	50	31	13	6		2.60	25		
Mae-33	C	89	0	11	0		2.56	24		
Mae-36	C	96	0	4	0		2.59	24	−5.8	−4.98

MT, mineralogical types (C = chalky calcitic mud, D = chalky dolomitic mud), C = calcite, D = dolomite, C-M = clay minerals, Q = quartz, Dry-D = dry bulk density (g/cm^3), GD = grain density (g/cm^3), P = porosity (%). Stable isotopes data from Bustillo et al. (2002).

examination, the size and shape of the calcite crystals is very variable, but most are less than 10 μm in diameter (commonly 0.3–7 μm) (Fig. 3A). The crystals are euhedral (rhombic) and subeuhedral (Fig. 3A), sometimes with a spherical or rounded appearance (Fig. 3B). The mosaic has a high intercrystalline porosity (Fig. 3A), but some locally show intracrystalline porosity. In some places, the largest crystals (up to 25 μm) locally occur as calcitic cement (Fig. 3D). The surfaces of the crystals are covered by fibrous clay minerals such as phyllosilicate cement (Fig. 3C), which locally appears as intercrystalline sheets (Fig. 3B). EDAX semi-quantitative analysis showed these fibrous clay minerals to have amounts (% weight) of major oxides: $SiO_2 = 46.85$, $Al_2O_3 = 12.75$ and $MgO = 12.21$, that agree with the chemical composition of palygorskite (Weaver and Pollard, 1973) and with their presence found by XRD.

The *chalky dolomitic muds* contain more than 80% dolomite. According to XRD data, this is almost stoichiometric (with 49.00–50.65 mol% $CaCO_3$) and poorly ordered, considering the values (0.37–0.54) obtained by the relative intensities of the 015 peak and 110 peak (Hardy and Tucker, 1988). The highest ordering values correspond to samples with a significant quantity of extrabasinal dolomitic grains, which show spheroidal shapes and corroded surfaces (Fig. 4D). Their clay mineral content includes illite, Al-smectite and palygorskite (10–15%). Thin sections show a homogeneous microcrystalline texture. Skeletal grains are not present. Under SEM examination, the pure dolomitic muds appear to be made of small euhedral dolomite rhombohedra <7 μm in size (Fig. 4A). The large calcite crystals can enclose small euhedral dolomite crystals as a consequence of local calcitic cementation, but this is not a volumetrically important process. Palygorskite occurs on the crystal edges and the faces of euhedral dolomite rhombohedra (Fig. 4A and B) and locally as dense aggregates associated with the edges of illite and smectite laminae (Bustillo et al., 1998). Chalky dolomitic

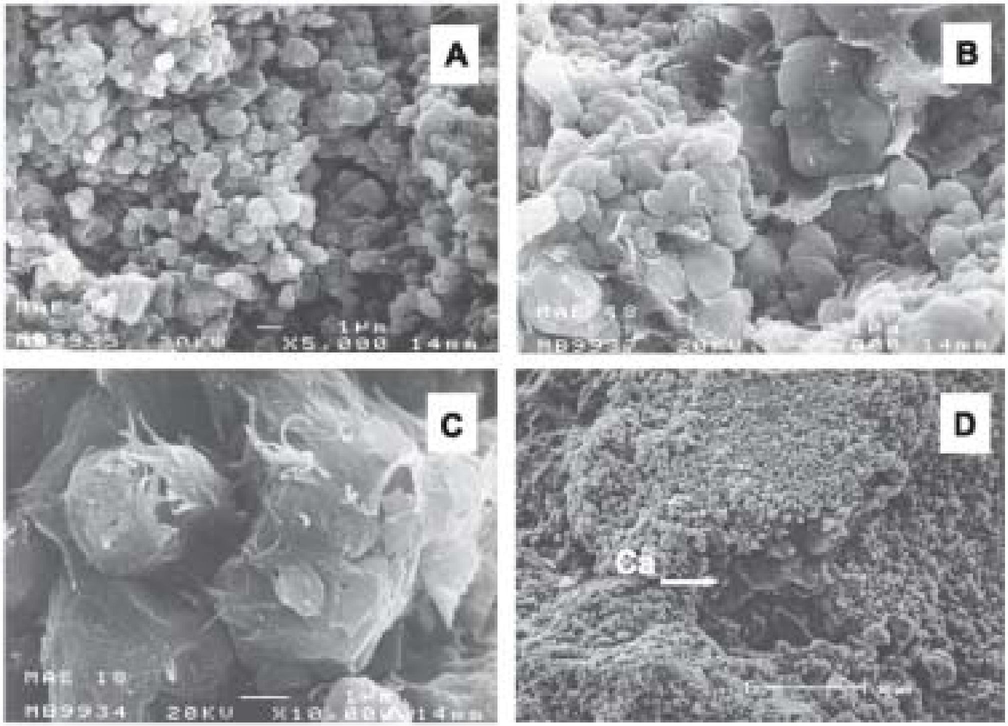

Fig. 3. SEM pictures of chalky calcitic muds. (A) Mosaic of calcite crystals with high porosity due to macro- and micropores. The size and shape of the calcite crystals are variable. (B) Some of the crystals are rounded; fibrous
crystals entirely covered by palygorskite. (D) General view of the chalky calcitic mud with large calcite crystals as local cement.

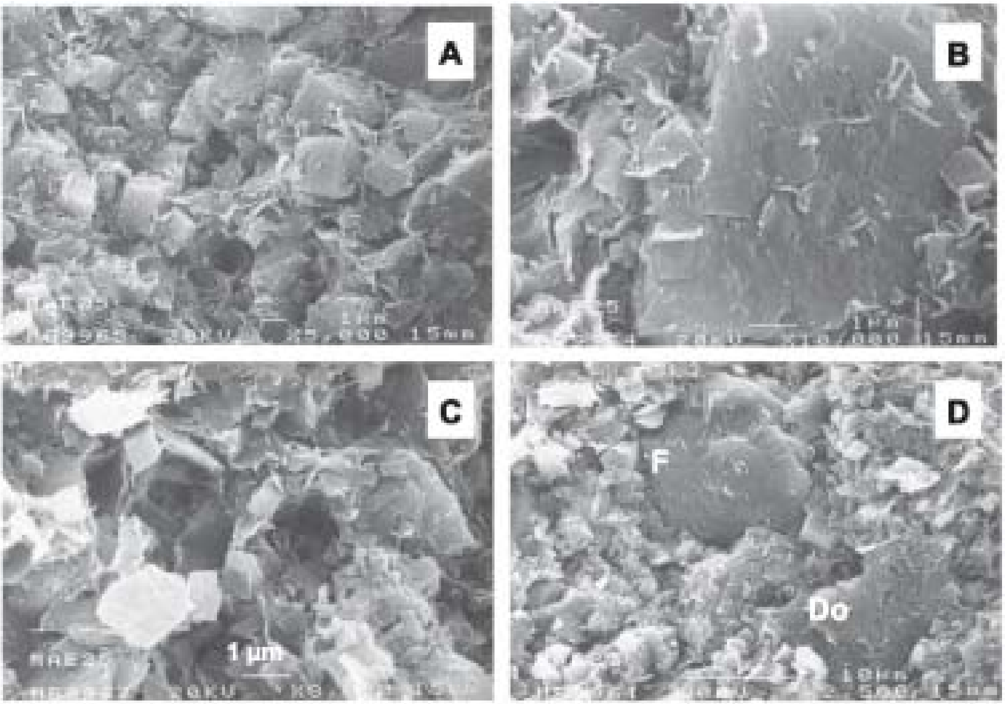

Fig. 4. SEM pictures of chalky dolomitic muds. (A) Mosaic of euhedral dolomite crystals with intercrystalline porosity and palygorskite cement. (B) Close-up of the dolomite crystals showing palygorskite fibres on their faces. (C) Dissolution of the dolomite crystals gave rise to moulds between the palygorskite sheets. (D) Dolomitic grain (Do) showing corrosion on the surface. (F) A feldspar grain appears as extrabasinal grain.

muds show great intercrystalline porosity (Fig. 4A); less frequently they also show intracrystalline porosity. The total dissolution of the carbonate crystals covered with palygorskite sheets caused a secondary moldic porosity (Fig. 4C). Where chalky dolomitic muds are overlain by lacustrine sandstones, high percentages of extrabasinal dolomite and other grains are seen, all of which show signs of corrosion and dissolution (Fig. 4D).

Some samples show intermediate mixtures of calcite and dolomite, but generally there is more of the former than the latter (Table 1). Under SEM examination, anhedral and rounded calcite crystals appear mixed with dolomite crystals in a random distribution and with intercrystalline porosity (Figs. 5A–D). The rounded calcite crystals are probably relics of the primary calcitic muds, affected by dissolution. The dolomite crystals appear as euhedral rhombohedra similar to those described in the chalky dolomitic muds. Some show intracrystalline and moldic porosity (Fig. 5A and B). Palygorskite is very common, covering the carbonate crystals or forming sheets between them (Fig. 5D). Locally, palygorskite also appears in sheets associated with smectites and as isolated aggregates that sometimes include small, rhombic dolomite crystals.

4.2. Geochemistry

The electron microprobe data of isolated crystals of calcite and dolomite from the mineralogically purest samples (Mae-18, calcite; Mae-4, dolomite) together with the percentages in the different types of carbonates are summarized in Table 2. The chalky carbonates showed small quantities of alumina and silica due to the presence of clay minerals between carbonate crystals. The impossibility of separating the clays from the carbonate crystals led to small readings for alumina and silica in the microprobe analysis of isolated carbonate crystals. Isotopic data of these

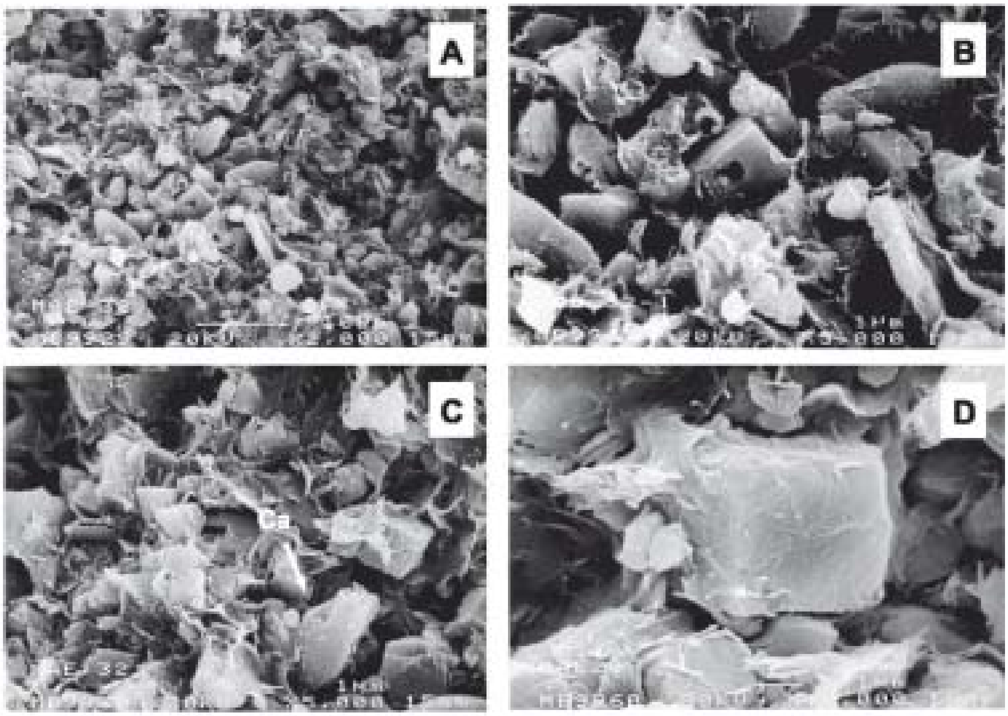

Fig. 5. SEM pictures of chalky calcitic-dolomitic muds. (A) General view of a chalky calcitic-dolomitic mud with intercrystalline, moldic (arrow) and intracrystalline porosity. (B) Close-up of the intracrystalline microporosity. (C) The calcite crystals are distinguished from the dolomite crystals by their rounded and anhedral shapes. (D) Palygorskite cementing and covering the carbonate crystals.

samples come from Bustillo et al. (2002) and are shown in Table 1.

The chemical composition of the chalky calcitic muds is very homogeneous and corresponds to low Mg-calcite with $<2\%$ mole $MgCO_3$ (Table 2). Contents in Sr (mean = 411 ppm), Mn (mean = 178 ppm) and Fe (mean = 235 ppm) are low but variable (Table 2). These values are similar to other lacustrine carbonates (Tlig, 1987; Wright et al., 1997), indicating oxygenated and non-saline continental water. For the other hand, Mn and Fe contents are low compared with those proposed by Veizer (1983) for a theoretical average composition of a meteoric diagenetic low-Magnesian calcite.

In the chalky dolomitic muds, the mol% $CaCO_3$ values estimated from the microprobe analysis data vary between 48.9% and 50.5% (Table 2), indicating that the dolomite is nearly stoichiometric. Mn (<217 when Mn was detected) and Fe (mean = 595 ppm) contents are low and very variable as occur in chalky-calcitic muds (Table 2). Sr contents (<262 ppm when Sr was detected) are very low, but similar to those estimated by Tlig (1987) in dolomites formed in lacustrine environments under meteoric water influence. García del Cura et al. (2001) give values slightly higher in Sr (mean = 655 ppm) in lacustrine dolomites.

5. Physical properties

5.1. Microfabric

The studied samples are relatively soft, friable and easily eroded but show cohesion. Most of the chalky carbonate porosity is intercrystalline in origin (Figs. 3–5); therefore, water transmission is through the body of the chalky carbonates rather than along solution channels. SEM analysis shows that the shape and size of the intercrystalline pores in the samples are not homogeneous. Porosity varies between 10–40% (Table 1) and corresponds to micro and macro-

Table 2
Chemical composition of chalky carbonates

Calcitic mud	Mae18-1	Mae18-2	Mae18-3	Mae18-4	Mae18-5	Mae18-6	Mae18-7	Mae18-8	Mae18-9	Mean
CaO (%)	51,267	51,735	50,941	50,934	50,894	51,745	51,243	51,079	52,106	51,327
MgO (%)	0.483	0.458	0.469	0.579	0.717	0.380	0.416	0.449	0.479	0.492
SiO_2 (%)	0.151	0.032	0.344	0.252	0.140	0.131	0.161	0.091	0.061	0.151
Al_2O_3 (%)	0.013	0.001	0.113	0.009	–	0.03	0.037	0.019	0.011	0.029
Fe (ppm)	194	319	218	194	70	606	–	47	–	235
Mn (ppm)	–	–	457	–	–	–	54	–	23	178
Sr (ppm)	178	279	144	617	744	812	550	524	414	411
% Carbonates										
$CaCO_3$	98,646	98,690	98,589	98,333	97,975	98,775	98,804	98,716	98,684	98,579
$MgCO_3$	1295	1215	1262	1554	1920	1011	1117	1209	1261	0.013
$MnCO_3$	0.000	0.000	0.089	0.000	0.000	0.000	0.010	0.000	0.005	0.012
$SrCO_3$	0.021	0.035	0.017	0.076	0.092	0.099	0.069	0.065	0.050	0.058
$FeCO_3$	0.037	0.060	0.042	0.037	0.013	0.116	0.000	0.010	0.000	0.035

Dolomitic mud	Mae4-1	Mae4-2	Mae4-3	Mae4-4	Mae4-5	Mae4-6	Mae4-7	Mae4-8	Mae4-9	Mae4-10	Mean
CaO (%)	28,579	28,647	28,052	28,407	30,478	29,065	29,477	29,333	28,951	28,902	28,989
MgO (%)	20,037	20,252	20,807	20,633	21,403	20,951	21,008	21,365	20,698	21,610	20,876
SiO_2 (%)	0.147	0.384	0.318	0.306	0.058	0.662	0.257	0.314	1,048	0.676	0.417
Al_2O3 (%)	0.101	0.191	0.104	0.118	0.028	0.310	0.123	0.095	0.397	0.251	0.171
Fe (ppm)	1213	233	295	653	319	948	199	902	801	389	595
Mn (ppm)	–	–	–	186	217	132	23	–	–	108	111
Sr (ppm)	178	–	237	211	51	–	–	262	–	–	188
% Carbonates											
$CaCO_3$	50,503	50,391	49,177	49,653	50,536	49,836	50,041	49,580	50,065	48,972	49,875
$MgCO_3$	49,261	49,561	50,745	50,175	49,370	49,977	49,615	50,239	49,796	50,942	49,968
$MnCO_3$	–	–	–	0.034	0.037	0.024	0.005	–	–	0.019	0.012
$SrCO_3$	0.020	–	0.027	0.024	0.005	–	–	0.029	–	–	0.010
$FeCO_3$	0.215	0.048	0.051	0.115	0.052	0.163	0.339	0.152	0.139	0.067	0.134

Values below the detection limit (–).

porosity. Micropores, with an average size of around 2 μm, are rounded except where they result from the total dissolution of the crystals. Microporosity is around 70% of the total porosity. Macropores (2–20 μm) represent around 20% of the total porosity and are more irregular in size and shape. Locally, larger pores >20 μm are also encountered between the larger calcite and dolomite crystals (>80 μm). Clay minerals partially fill the original porosity of the chalky carbonates and play an important role in controlling the final porosity of these sediments. Clays also give a medium-to-high cohesion to the chalky carbonates due to clay bonding. However, the lack of a significant carbonate cementation renders these rocks friable.

5.2. Grain density, dry bulk density and porosity

Dominant physical properties of the studied chalky carbonates are their very low dry bulk density (1.6–2.2) g/cm^3 and medium to relatively high porosity (10–40%; Table 1). These values are typical of low to medium compacted materials. The absolute values of the dry bulk density obtained here are very low compared to materials with similar percentage porosities (Table 1). The relationship between dry bulk density and percentage total porosity is shown in Fig. 6A. The expected negative linear correlation between dry bulk density and porosity is seen, except in the case of the medium dense samples (2.0 g/cm^3) where there is a large variation in porosity.

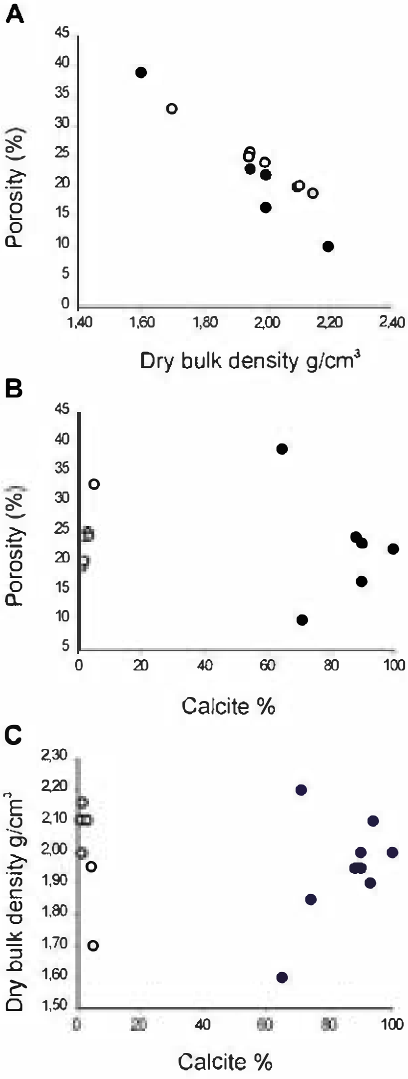

Fig. 6. Relationship between porosity and the bulk grain density (A) and their relationship with calcite content (B and C). Black circles = chalky calcitic muds and white circles = chalky dolomitic muds.

The grain density is almost constant, the mean of 2.62 g/cm^3 being independent of the mineralogical composition of the carbonates in the sample (Table 1). These values are very low compared to those of typical limestones or dolomites, which normally have an average grain density of 2.70–2.80 and over 2.9 g/cm^3, respectively.

To detect any relationship between mineralogical composition and variation in these physical properties, the percentage of calcite in the samples was plotted against porosity and dry bulk density (Fig. 6B and C, respectively). The graphs show no clear evidence of any systematic relationship between calcite content and these properties. However, it can be seen that the chalky dolomitic muds generally have a somewhat higher dry bulk density than the chalky calcitic muds.

The chalky calcitic muds (>60% calcite content) show the largest variation values in dry bulk density and porosity (minimum: 1.6 g/cm^3 and 10%; maximum: 2.2 g/cm^3 and 40%, respectively). This, plus the weak correlation between the calcite content and physical properties, shows the influence of other factors such as: (i) the variable content of fibrous

Table 3
Results of the slaking test in water

Sample	CC/CM	Slaking time	Lutton Index	Remarks
Mae-0	88/9	4–6 h	0	Completely breaks down
Mae-1	96/4	10–15 min	0	Completely breaks down
Mae-4	94/6	Partial slaking in 24 h	1	About one third of the material is reduced to very small pieces
Mae-5	94/6	15–20 min	0	Completely breaks down
Mae-10	96/4	Partial slaking in 24 h	1	About one third of the material is reduced to very small pieces
Mae-20	81/6	20–30 min	0	Completely breaks down
Mae-22	70/9	4–6 h	0	Completely breaks down
Mae-24	87/12	10–15 min	0	Completely breaks down
Mae-29	94/6	24 h	2	About three fourths of the material is reduced to very small pieces
Me-30	86/12	4–6 h	0	Completely breaks down to small pieces
Me-36	96/4	24 h	2	About three fourths of the material is reduced to very small pieces

CC/CM: relation between carbonate content (%) and clay minerals content (%); Lutton Index (0-1-2).

clay minerals (which have a lower grain density) binding the carbonate crystals and (ii) the presence of an important quantity of irregularly distributed intracrystalline porosity (as observed under the scanning electron microscope). The presence of the latter affects the absolute density (both the dry bulk density and grain density) but not the percentage porosity defined as the relationship between mass and volume. This is because the grain density of hollow crystals cannot be determined by common laboratory tests, and it is less than that of non-dissolved crystals.

The slaking of the samples was also studied (Table 3). The chalky carbonates showed high levels of slaking and dispersion, with “jar slake index” (Ij, Lutton, 1977) values of between 0 and 2 (Table 3). After 1 h of immersion in the distilled water, the majority of the samples (except two) crumbled to form coarse-grained heaps and some dispersed, finer material at the bottom of the beaker. Complete breakdown occurred within 2 h. This is typical of most non-cemented sediments such as muds, marls or clay shales (Wood and Deo, 1975; Seedsman, 1986; Dick and Shakoor, 1992).

On the basis of the results, the chalky carbonates can be classified as non- durable “soil-like” materials (Lutton, 1977), when they degrade rapidly with complete disruption of the original structure of the rock. One reason for this may be related to the failure in tension between the particles due to the compression of trapped air inside the small pores between the crystals. As indicated by Terzaghi and Peck (1967), this is one of the main reasons for the slaking (disaggregation) of most sediments with small pores. In the studied samples, the micropores made up almost 70% of the total porosity. However, it may also be related to the loss of clay bonds by clay-water reactions, during the wetting and drying process. As observed with SEM, clay minerals are the main connectors between the calcite and dolomite crystals (Figs. 3–5). Once these bonds are broken, the calcite and dolomite crystals and the clays are free to disperse. The quantity of clay minerals detected by XRD may not seem important, but many of them are fibrous and, though scarce, are uniformly distributed. They occur at all contacts between calcite and dolomite crystals, with *crystal–clay–crystal* being the main interaction.

6. Discussion

These Palaeogene chalky carbonates have withstood a cover of more than 800 m of sediments without significant diagenetic processes occurring. They also show high porosity (Table 1). The origin and the sedimentary processes involved in the accumulation of carbonate muds, their original mineralogical composition and their diagenetic history can help explain their particular physical properties.

6.1. Origin of the carbonate muds

Bustillo et al. (2002) interpreted these deposits as being an inorganic carbonate sediment due to the absence of skeletal debris. But other possibilities exist such as the accumulation of fine detrital particles or bio-induced precipitation. Kelts and Hsü (1978) indicated the importance of detrital carbonates in the bulk of lacustrine marls and chalks, and the difficulty in distinguishing between primary and detrital lacustrine carbonate. Carbonates precipitated in freshwater lakes commonly have very negative $\delta^{13}C$ and $\delta^{18}O$ values, which may permit the detrital component to be estimated (Kelts and Hsü, 1978). Isotopic analyses of the studied chalky carbonates suggests that these carbonates precipitated in equilibrium with isotopically light meteoric waters (Bustillo et al., 2002; Table 1). Locally the high $\delta^{18}O$ values in some chalky dolomitic muds (Table 1, Mae-4 and Mae-14) may be explained by the early formation of dolomite from water more enriched in heavy isotopes and increased evaporation in the sedimentation area (Bustillo et al., 2002). Thus, most of chalky carbonate muds probably formed in situ in the basinal areas of the lake as the result of inorganic calcite precipitation from supersaturated lake water. The origin would be similar to the abiotic whitings of calcite triggered by bio-mediated coccoid algal blooms or evaporative concentration described by Wet et al. (2002) in lacustrine chalks. Seasonal whitings in lakes have been documented in ancient and modern lakes (Müller and Wagner, 1978; Platt and Wright, 1991). In some modern lacustrine dolomite sediments, bacterial morphologies in carbonate crystals have been described providing evidence that dolomite growth was influenced by microbial activity (Vasconcelos and McKenzie, 1997; García del Cura et al., 2001; Sánz-Montero et al., 2003). In the studied muds, scanning electron micrographs show mosaics of euhedral (rhombic) to subhedral crystals (both calcite or dolomite) with no direct evidence of organic features (Figs. 3–5).

Moreover, some chalky carbonates below sheets of lacustrine sandstones had high $\delta^{18}O$ values (Table 1, Mae-20 and Mae-30), which may possibly be due to detrital input from the Mesozoic carbonates of the Iberian Range. There is evidence of alluvial reactivation of the adjacent fan systems, as demonstrated by the presence of sheet-flood and debris-flow deposits in both the Beleña de Sorbe and Torremocha de Jadraque sectors (Arribas, 1986a). As a consequence, extrabasinal carbonate components, together with littoral calcareous mud (composed of very finely charophyte debris, <10 μm), would have been deposited in the most distal areas of the shore lake. As occurs in some marine chalks a rapid sedimentation and resedimentation by turbidity currents may have developed a porous calcareous sediment with little early cementation, whereas slow sedimentation rates together with much bioturbation and bottom current activity may facilitate early cementation and loss of porosity (Tucker and Wright, 1990).

The accumulation of calcareous muds in the basinal areas of the lake would be very rapid and would have preserved the high porosity of the original sediment. The sedimentation of these muds contrasts with the lacustrine dynamics in the littoral and supralittoral areas where active biogenic carbonate production, together with the development of an early meteoric diagenesis (cementation and recrystallization), contributed to consolidated lacustrine limestones (Arribas, 1986a).

6.2. *Original mineralogy and pore fluid composition*

The chalky carbonate muds formed under distinct geochemical conditions. The textural, chemical and mineralogical characteristics suggest that the chalky calcitic muds probably precipitated as low Mg-calcite (<2 mol% $MgCO_3$) from low salinity fresh water, as occurs in Lake Constanza (Müller, 1971). The dolomite appears to have originated by early diagenetic replacement as suggested by the presence of microrhombic crystals, near stoichiometry and poor order according to X-ray values (Gunatilaka, 1990; Last, 1990). This replacement may have occurred via a high Mg-calcite precursor mud since this is dolomitized in preference to low Mg-calcite mud, as occurs in the recent lacustrine sediments of Central Spain described by Yébenes et al. (1973). In the present case, high intercrystalline and intracrystalline porosity could be associated with a possible replacement process, as occurs in the lacustrine micrites described by Wright et al. (1997). The formation of high Mg-calcite lacustrine muds can be a consequence of chemical changes in lake water due to increased evaporation and raised salinity, or an increase in the Mg/Ca ratio (Müller et al., 1972; Kelts and Hsü, 1978). Müller et al. (1972) proposed a “dynamic “ model to explain the formation of calcite and dolomite in the same sequence, in which extreme fluctuations of the Mg/Ca ratio are the most important factor. In the present case, the cyclic increase in the Mg/Ca ratio of the lake waters would be associated with the input of Mg^{2+} derived from the weathering of Mesozoic carbonates in the source area, and with an important development of palaeosols in the supralittoral areas (Huérmeces del Cerro sector, Arribas, 1986a) and the subsequent loss of Ca ions. In this sedimentological model, the composition of lacustrine water changed periodically from slightly magnesian ($Mg/Ca<2$) to magnesian (Mg/Ca between 2 and 12, Müller et al., 1972), resulting in calcitic or dolomitic muds formation respectively.

The original stable mineralogy (low Mg-calcite and dolomite) of these chalky carbonates would have induced a very low diagenetic potential (Schölle, 1977). According to Moore (2001), the stable mineralogy at the time of burial is one of the most important factors that retards chemical compaction.

6.3. *The importance of clay minerals*

The chalky carbonates contain clay minerals such as illite, smectite, and palygorskite (Bustillo et al., 1998). According to SEM observations, the most volumetrically important is palygorskite. The XRD results probably reveal smaller amounts of palygorskite than actually exist, because the quantitative analysis is based on peak area. Ouhadi and Yong (2003) worked in several artificial mixtures of palygorskite and calcite and found that this quantitative analysis underestimates the presence of palygorskite and overestimates the presence of calcite.

According to SEM observations, palygorskite appears widely dispersed through the chalky carbonates (Figs. 3–5). Palygorskite fibres coat the carbonate crystals, cement pores and build aggregates locally with Al-smectite or illite.

Two main origins for palygorskite have been proposed in the literature: inheritance or by authigenesis. In hot, arid regions palygorskite can be transported by alluvial or aeolian process from the sources areas and be incorporated into sediment as a detrital component (Verrechia and Le Coustumer, 1996). The detrital origin is rejected because in the lutites that occur in floodplains related laterally to the lacustrine carbonates only smectite and illite appear, not palygorskite (Arribas, 1985). On the other hand, palygorskite authigenesis can be explained by two process (Verrechia and Le Coustumer, 1996; Worden and Morad, 2003): (1) alteration of pre-existing phyllosilicate minerals (such as mica and smectites) and then transformation into palygorskite and (2) precipitation from hypersaline pore waters.

The aggregates of palygorskite with Al-smectite or illite, observed under SEM, indicate that the original clay assemblage was mildly to strongly transformed into palygorskite. But palygorskite fibres also coat the carbonate crystals and it is probably formed during early diagenesis because they form the network of the secondary porosity (Fig. 4C). Microporosity and the texture of silt-size carbonate provided additional appropriate conditions for early palygorskite precipitation (Verrechia and Le Coustumer, 1996). The high silica content of the waters, evidenced by chert and opaline nodules of the interlayered limestones (Fig. 2; Bustillo et al., 2002), favoured the early diagenetic formation of the palygorskite from a detrital clay minerals precursor which provided the necessary aluminium. The high content in Mg in the pore waters is linked to the composition of the source areas (dolostones), the formation of calcimorphic paleosols in close by supralittoral areas and also to the partial dissolution of the dolomite extrabasinal grains.

The formation of the palygorskite cement at an early diagenetic stage would strongly influence the physical properties of these chalky carbonates. The strong slaking of the chalks (Table 3) is partly explained in that palygorskite is found at all the contacts between the carbonate crystals. The presence of palygorskite caused two important connected phenomena: the retention of pore water in the original carbonate muds and, as a consequence, a decrease in permeability. On the other hand, Tucker and Wright (1990) suggest that clay content in marine chalks would be important because generally it inhibits early cementation. The fibrous clay coating on the crystals, formed during early diagenesis, inhibits from the outset any chemical bonding of calcite or dolomite.

6.4. Porosity and diagenesis

Both chalky textured carbonates and chalks present a high porosity, which can be secondary or primary in origin (Moshier, 1989). Chalky texture in shallow marine carbonates is determined by a secondary porosity (intercrystalline, vug, moldic, etc., Choquette and Pray, 1970), which is formed during diagenesis (Harris and Frost, 1984; Kaldi, 1989; Moshier, 1989) and must be distinguished from the depositional porosity (interparticle and intraparticle porosity, Choquette and Pray, 1970), which characterizes marine pelagic chalks (Moshier, 1989). Dissolution and aragonite-to-calcite conversion are the main processes involved in the secondary porosity development (Kaldi, 1989; Moshier, 1989; Saller and Moore, 1989; Holail and Lohmann, 1994), in most cases as a consequence of the early stabilization of the original metastable muds (composed of aragonite and high-Magnesium calcite). Some workers relate this porosity to dissolution associated with unconformity exposure (Harris and Frost, 1984; Holail and Lohmann, 1994). The diagenetic origin of this porosity contrasts with the preservation of original depositional porosity (intraparticle and interparticle porosity) in overpressured chalks during burial diagenesis (Neugebauer, 1974; Schölle, 1977; Feazel and Schatzinger, 1985; Tucker and Wright, 1990; Maliva and Dickson, 1992).

In carbonate muds the dominant, prevailing trend during burial is towards complete or nearly complete occlusion of porosity (Choquette and James, 1990). The Palaeogene chalky carbonates had undergone a maximum burial depth of 800 m with temperature values between 30 and 40 °C, and consequently dewatering, drastic loss of porosity and compaction could be expected during burial. But this does not occur. The formation of very fine, mineralogically stable carbonate sediments (calcitic and dolomitic carbonate muds), held together by palygorskite, influenced the diagenesis path of these facies.

The neoformation of palygorskite around the carbonate crystals as a phyllosilicate cement during eodiagenesis (early diagenesis, according to Worden and Burley, 2003) helped trap the original lacustrine water in the pore system of the original carbonate muds. This would be of great importance during mesodiagenesis (burial diagenesis, according Worden and Burley, 2003) because it would maintain the fluid pressure between the crystals. Under these conditions, compaction (physical and chemical) and cementation would be retarded (Neugebauer, 1974; Schölle, 1974; Feazel and Schatzinger, 1985; Choquette and James, 1990; Tucker and Wright, 1990; Maliva and Dickson, 1992). Again, the composition of the lacustrine waters (lightly magnesian to magnesian) trapped in the pore system could have helped to preserve the original porosity during burial (Moore, 2001). The overpressured chalky carbonates could theoretically be isolated from the surrounding diagenetic waters. The very low Mn and Fe contents in chalky carbonates (Table 2) might indicate original contents in the carbonate muds formed from continental highly oxygenated waters (Veizer, 1983). According to this author, calcites precipitated by continental waters should be depleted in Na, Sr, Mn and Fe. The possible preservation of low original contents in these elements suggests a non-modification of the original chemical composition.

The original mineralogy of the chalky carbonates would influence burial diagenesis. Syndepositional or early assemblages of stable minerals (low-Mg calcite and dolomite) typically suffer less burial alteration than sediments with metastable mineral components (Schölle, 1977; Schölle et al., 1983; Feazel and Schatzinger, 1985; Moore, 2001). If there was no aragonite in the original sediment for an early dissolution to supply $CaCO_3$, calcite cementation and lithification would be retarded. The chalky lacustrine carbonates, formed only from low-Mg calcite and dolomite, would have a low susceptibility to chemical compaction on burial.

Facies analysis of Palaeogene carbonates (Arribas, 1986a; Bustillo et al., 2002), has shown that these chalky carbonates are intercalated between impermeable lacustrine-palustrine limestones and carbonate sandstones (Fig. 2), which tend to act as physical barriers, impeding fluid flow and keeping the chalky carbonates compartmentalized. According to Feazel and Schatzinger (1985), permeability barriers due to sedimentary processes would contribute towards preserving the original porosity of the chalky carbonates, and would facilitate the retention of overpressured pore fluids during burial. Active biogenic carbonate production, together with the early meteoric diagenesis in the littoral and eulittoral areas, were responsible for the configuration of natural permeability barriers.

7. Conclusions

1. The petrological, chemical, isotopic and physical properties of Palaeogene chalky carbonates of the Madrid Basin indicate a lack of any diagenetic processes during burial. An important volume of primary porosity is preserved (between 10% and 40%) in these lacustrine carbonate muds in spite of undergoing 800 m on burial, characteristic of the chalky texture development.
2. The retention of porosity could be related to the convergence of several positive factors: (i) the origin and the sedimentary processes involved in the formation of the carbonate muds (rapid accumulation in basinal lacustrine areas); (ii) the original stable mineralogy (low-Magnesian calcite and dolomite) of the primary carbonate sediments; (iii) the occurrence of palygorskite cement that filled part of the original porosity (intercrystalline); (iv) the chemical composition of the pore water (lightly enriched in Mg); (v) the isolation of chalky muds due to the development of permeability barriers; and in consequence (vi) possible overpressure during burial.
3. Most of the factors retarding diagenetic processes during burial are coincident with those analysed and estimated in pelagic marine chalks. The early palygorskite formation together with carbonate mud in lacustrine systems can be considered as a new factor, which would retard compaction during burial diagenesis, preserving depositional primary porosity.
4. The identification of chalky carbonates as well as freshwater-chalks—such as basinal and deep carbonate facies—within the continental lacustrine systems would be very interesting in the explora-

tion and characterization of possible reservoirs in continental carbonate sequences.

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