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Geological factors controlling clay miner patterns across the Cretaceous-Tertiary boundary in Mediterranean and Atlantic sections

M. ORTEGA, I. PALOMO, F. MARTINEZ* AND I. GONZALEZ†

*Dpto. Mineralogía y Petrología. Fac. Ciencias. Univ. Granada. Avda. Fuentenueva, s/n. 18002 Granada, *Institut*
Andaluz de Ciencias de la Tierra. Fac. Ciencias. Univ. Granada. Avda. Fuentenueva, s/n. 18002 Granada, and
†Dpto. Cristalografía y Mineralogía. Fac. Química. Prof. García González, s/n. 41071 Sevilla, Spain

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ABSTRACT: The clay mineral associations in the Cretaceous-Tertiary Boundary (KTB) and in the Danian and Maastrichtian levels of sections from the Mediterranean and the Atlantic Domains have been studied. The Mediterranean sections have a single mineral association consisting of smectite-illite and kaolinite, whereas the Atlantic sections have several associations: illite-chlorite, illite-R1 I-S-kaolinite and illite-R1 I-S-chlorite. Data are presented relating to the influence of K-feldspars and Fe oxide spherules on the clay mineral associations. Study of rare-earth elements shows that regional geological factors affect the clay mineralogy of the KTB, examples showing significant authigenesis in the Mediterranean sections, and important detrital supply in all the Atlantic sections. We propose that the KTB studied in these marine sections is equivalent to the uppermost layer of the two-layered clay unit originating in a cloud of a vapourized bolide. Regional tectonic conditions have been responsible for differences in clay sedimentation in these geological domains and among the stratigraphic sections of the Atlantic Domain.

The palaeoceanographic changes leading to the mass extinction marking the Cretaceous-Tertiary boundary (KTB) are recorded in marine sections by a sharp fall in carbonate sedimentation resulting from a decrease in biological productivity, and the concomitant increase in clay mineral content. The clay layer is characterized by large Ir and other platinum group element (PGE) contents and the presence of spherules. Thus, a clayey layer occurs in the studied KTB sections that contain mineralogical and geochemical anomalies providing evidence of the Cretaceous-Tertiary event. Clay mineral assemblages are potentially sensitive to environmental modifications, including climatic change, erosion, tectonic activity, variations in oceanic circulation, diagenetic processes and volcanic activity (Chamley, 1989; Robert & Chamley, 1990) and can, therefore, reflect the environmental conditions prevailing during dep
tion of the KTB and surrounding layers.

Clay mineral associations have been use
support hypotheses of terrestrial or extraterres
causes for the changes at the KTB. For instanc
the Stevns Klint section (Denmark), Kastner e
(1984) found that the KTB was exclusively n
up of pure magnesian smectite, while illite, il
smectite mixed-layers and quartz are present i
sediments lying above and below the boundary
the basis of the high Ir and Au contents, the lac
a negative Ce anomaly and the high $\delta^{18}O$ va
these authors proposed that these authig
smectites originated from alteration of g
spherules in a marine environment and in a
water/rock ratio. The spherules are Fe-rich al
nous or aluminosilicate resulting from an im
An extraterrestrial impact was also suggeste

Bohor *et al.* (1984, 1987) from the study of a continental section with palaeosoil development in the Lance Formation at Doggie Creek (Wyoming, USA), where the KTB consists of kaolinite clay with goyacite spherules, and an overlying smectite layer in which the Ir content is 21 ppb. Pollastro & Pillmore (1987) considered that the clay minerals (well crystallized kaolinite and mixed-layer illite-smectite) associated with shocked quartz and the Ir anomaly found in the KTB of the New Mexico and the Raton Basin (Colorado) sections were formed by *in situ* alteration of impact-derived fallout material. The kaolinite is described as the stable diagenetic phase of pulverized radioactive material initially altered to halloysite or allophane microspherules. Pollastro & Bohor (1993) interpreted the clay mineral associations of Western Interior continental deposits (USA) as originating in the weathering and diagenesis of a two-layered clay unit. The lower claystone layer of this KTB unit represents melted siliciclastic target rocks altered mainly to kaolin minerals, while the upper layer mostly consists of mafic vitric dust altered to smectite.

Other authors, however, consider that the different clay mineral associations in the KTB are related to intense, widespread volcanic activity (e.g. Courtillot & Cisowski, 1987; Hallam, 1987). After studying the KTB in European and African sections (Nye Klov in Denmark, Gubbio in Italy, Caravaca in Spain, and El Kef in Tunisia). Rampino & Reynolds (1983) concluded that there were significant differences among the clay minerals in each section. The smectites in the Nye Klov and Stevns Klint sections, which are 300 km apart, resulted from alteration of volcanic material. In the Gubbio section, detrital illite and kaolinite are found in the KTB and as much as 1.73 m beneath it. Several authors (e.g. Wezel *et al.*, 1981; Johnsson & Reynolds, 1986; Jéhanno *et al.*, 1987) have interpreted this assemblage to be the result of an increase in erosion. This change is due to movements of the continental margin, or changes in depositional patterns, climatic variations, fall in sea-level, or the influence of new detrital source areas. Following the same line of argument and in opposition to Bohor *et al.* (1984, 1987), Fastovsky *et al.* (1989) considered that clay minerals in the KTB at the Doggie Creek section (Wyoming) are due to changes in soil conditions and not to an extraterrestrial event. According to Vannuci *et al.* (1990), the presence of a zeolite-rich interval in the
upper part of the Maastrichtian shows th
smectite in the KTB of the Caravaca section
result of the transformation of volcano
material. The wide variation in clay m
associations found in KTB sections loca
both the northern and southern hemisph
interpreted by Robert & Chamley (19
indicative of global changes in sea lev
tectonic activity. Ortega Huertas *et al.*
examined sequences in the Betic Cordille
the Basque-Cantabrian Basin, concluding th
minerals in the KTB are the products of a r
or local geodynamic event and diagenetic ev

This paper reviews the clay mineralogy
KTB and the associated Maastrichtian and
sediments in order to compare the qualitati
quantitative differences in stratigraphic s
These data are complemented by new microa
data on the clay minerals, consideration
effect on the clay minerals' characteristics,
occurrence of differently composed spherules
KTB and the comparative study of the rar
element (*REE*) content in the different strati
sections. This paper is intended to repre
synthesis of most of the Mediterranean and A
sequences, including new mineralogica
geochemical data from the Petriccio and
sections as well as data partially publish
Ortega Huertas *et al.* (1995). This study p
further evidence on the distribution of th
mineral associations in these sections and h
clarify the ongoing discussion concerning c
vs. similarities in clay mineral composition
the KTB.

MATERIALS AND METHOD

The clay mineral associations investiga
sections of the KTB in both the Medite
(Agost and Caravaca in the Betic Cord
Spain; Petriccio in Italy; El Kef in Tunisi
Atlantic Domains (Basque-Cantabrian Basin:
Urko, Sopelana and Zumaya in Spain, Henda
Biarritz in France, Fig. 1) are the focus
investigation. The clay minerals in the K
some of these sections have been partially
by Rampino & Reynolds (1983), Jéhanno
(1987), Lindinger (1988), Robert & C
(1990), Vannuci *et al.* (1990), Martínez
(1994), and Ortega Huertas *et al.* (1995).
Caravaca and El Kef provide three of th
continuous records across the KTB kno

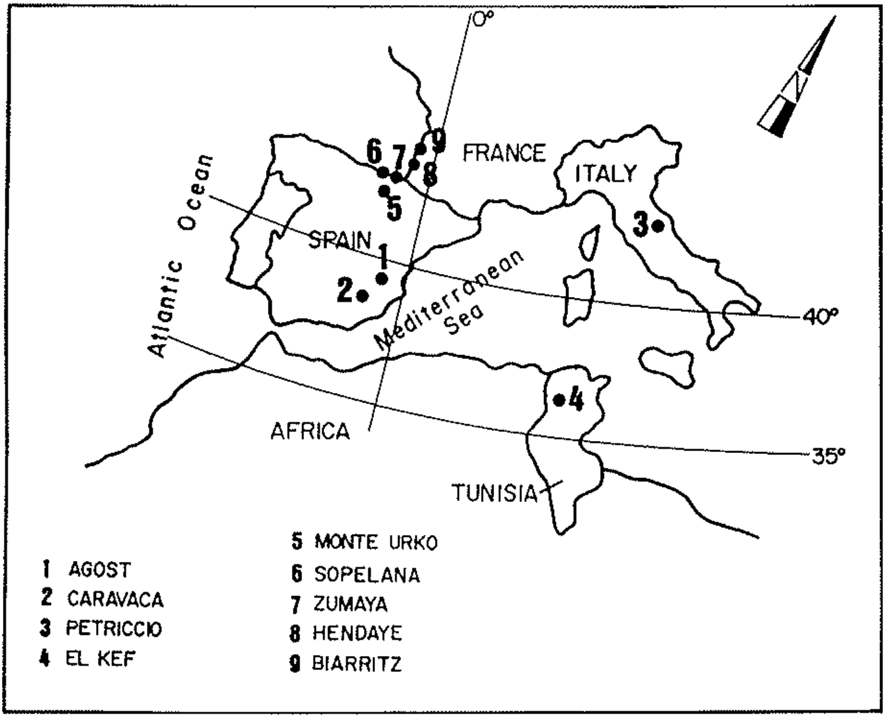

FIG. 1. Geographic location of the stratigraphic sections studied.

Europe and Africa, together with three sections in the Brazos River Valley, Texas (MacLeod & Keller, 1991).

The Betic Cordillera, which is part of the peri-Mediterranean Alpine orogenic belt, is divided on a palaeogeographic and structural basis into External and Internal Zones (Azema *et al.*, 1979). The sequences studied in this paper belong to the realm of the External Zones, which formed part of the continental margin of the Iberian plate. Although the structure of the External Zones is complex in detail, with lateral and local variations, there is a considerable difference in stratigraphic characteristics, particularly in the Jurassic and Cretaceous, between an autochthonous to parautochthonous set, known as the Prebetic Zone, and an allochthonous set, known as the Subbetic Zone. Between these two Zones the 'Intermediate Units' are distinguished, corresponding to realms of 'intermediate' palaeogeographic position. The Agost sequence belongs to the 'Intermediate Units', whereas the Caravaca sequence is located in the Subbetic Zone – the southernmost part of the External Zones – which is characterized by pelagic facies from the Middle Lias onwards. The sediments were de ited on a continental margin where troughs swells began to appear from the Jurassic onwa

The Petriccio sequence is located in the no eastern Apennines of Italy, where the KTB is fo in the middle part of the pelagic Scaglia R formation. The Scaglia Rossa represents Turonian through the Early Eocene interval can be divided into four members (R1 to (Luterbacher & Premoli Silva, 1964). The K defines the boundary between members R2 and and is represented by a thin layer of c sandwiched between the limestone of the Mayaroensis Zone and the *G. eugubina* Z (Luterbacher & Premoli Silva, 1964). The u member of the Scaglia Rossa (R4) is character by the renewed appearance of red, nodular c beds. The Scaglia Rossa shows a clear increas syndepositional tectonism; slump folding ca seen at several levels and in parts of the basin t are striking occurrences of white calcare turbidite layers mainly consisting of rewor intraformational planktonic foramini (Montanari *et al.*, 1989).

The El Kef sequence is located in northwestern Tunisia and belongs to the El Haria formation, which contains Maastrichtian to Eocene sediments, characterized by marly and clayey units with some limestone intercalations (Burollet, 1966). The uppermost Maastrichtian is characterized by white-grey marls and the lowermost Danian by 50 cm thick black clay. The KTB is marked by a 1–3 mm rust-coloured ferruginous layer. The uppermost Maastrichtian is characterized by the *P. deformis* planktonic foraminiferal Zone (Keller, 1988), but does not contain the index species *A. mayaroensis*. One explanation for this is that *A. mayaroensis* is a deep swimming species and its absence at El Kef would therefore indicate a shallow environment or a change in lithofacies (Lindinger, 1988).

The Basque-Cantabrian Basin contains Cretaceous sediments with thicknesses up to 10,000 m and environments ranging from fluvial to pelagic. From the palaeogeographic and tectonic points of view, two successive basins can in fact be distinguished: one dating from Triassic to Jurassic and another dating from Late Jurassic–Early Cretaceous to Eocene. The second of these can be considered the true Basque-Cantabrian Basin (Rat, 1988). In the Late Albian-Cenomanian, detrital supply increased and a transgression from the Atlantic increased carbonate deposits during the Late Cenomanian-Conicacian. Siliciclastic flyschs were again deposited during the Campanian–Early Maastrichtian, and the large Orio trough extended from Hendaye to the Vizcaya synclinorium (Mathey, 1988). During the Middle Maastrichtian, the Orio trough narrowed considerably and eventually disappeared in the Late Maastrichtian. A period of calmer sedimentation followed, in which a broad depression ~1500 m deep (Delacotte, 1982) connected with the adjacent platforms across the taluses (Mathey, 1988). Late Maastrichtian sedimentation was marly and during the Danian, pelagic sedimentation gave rise to the so-called 'pink limestones' or 'limestones of the Dane', which are well known from Hendaye to the Bilbao ria. In the area of the flysch trough, therefore, there is continuous sedimentation across the KTB. The stratigraphic record has been most completely preserved in the sequences studied in this paper: Monte Urko, Sopelana, Zumaya, Hendaye and Biarritz, where the KTB has an average thickness of 2 mm of clay.

Some 226 representative samples were used for mineralogical analyses (bulk mineralogy and <2 μm clay fraction) using X-ray powder diffr (Philips PW 1710 diffractometer with aut divergence slit at the Department of Mine and Petrology, University of Granada, Spain mineral intensity factors calculated for this ment and the instrumental conditions are deta Ortega Huertas *et al.* (1995). Clay minerals extracted by centrifugation after removing nates with acetic acid and successive washin have adopted the nomenclature of Reynolds for mixed-layer R1 illite-smectite.

The morphology of the clay minerals a morphology and composition of the spherule examined with a Zeiss DSM-950 scanning e microscope (SEM) equipped with a Link QX microanalysis system at the 'Centr Instrumentación Científica' of the Univers Granada (Spain) and a Cambridge S360 equipped with a Link AN10000 microa (University of Bari, Italy).

Quantitative elemental microanalyses of th minerals were obtained with a Philips CM20 and an X-ray energy dispersive spectro (Philips EDAX DX4 in the 'Centr Instrumentación Científica' of the Univers Granada). The proportionality factors used we (1.81), Mg (1.25), Al (1.12), K (1.45), Ca (1. (1.45), Mn (1.35) and Fe (1.43). The minera formulae were calculated as described in Huertas *et al.* (1995).

The *REE* were analysed by inductively c plasma (ICP) and neutron activation (NA) s scopy at the University of Pavia (Italy) and X-ray Assay Laboratories in Ontario, Canada. element microanalyses of the spherules were out with a Perkin Elmer 302 laser ablation coupled to a PE Scier ICP-MS Elan Spectr (Uberlingen, Germany). Calibration was external, using NBS-612 glass, and internal, silicon (previously determined by microprobe same section) as standards. The detection li Platinum Group Elements (PGE) ~0.1–0.15 ppm.

CLAY MINERAL ASSOCIATIC

Figure 2 summarizes the average clay r composition of the KTB sections and the and Maastrichtian. The stratigraphic seq belonging to the Mediterranean Domai characterized by the association smectite kaolinite, with smectite as the dominant m

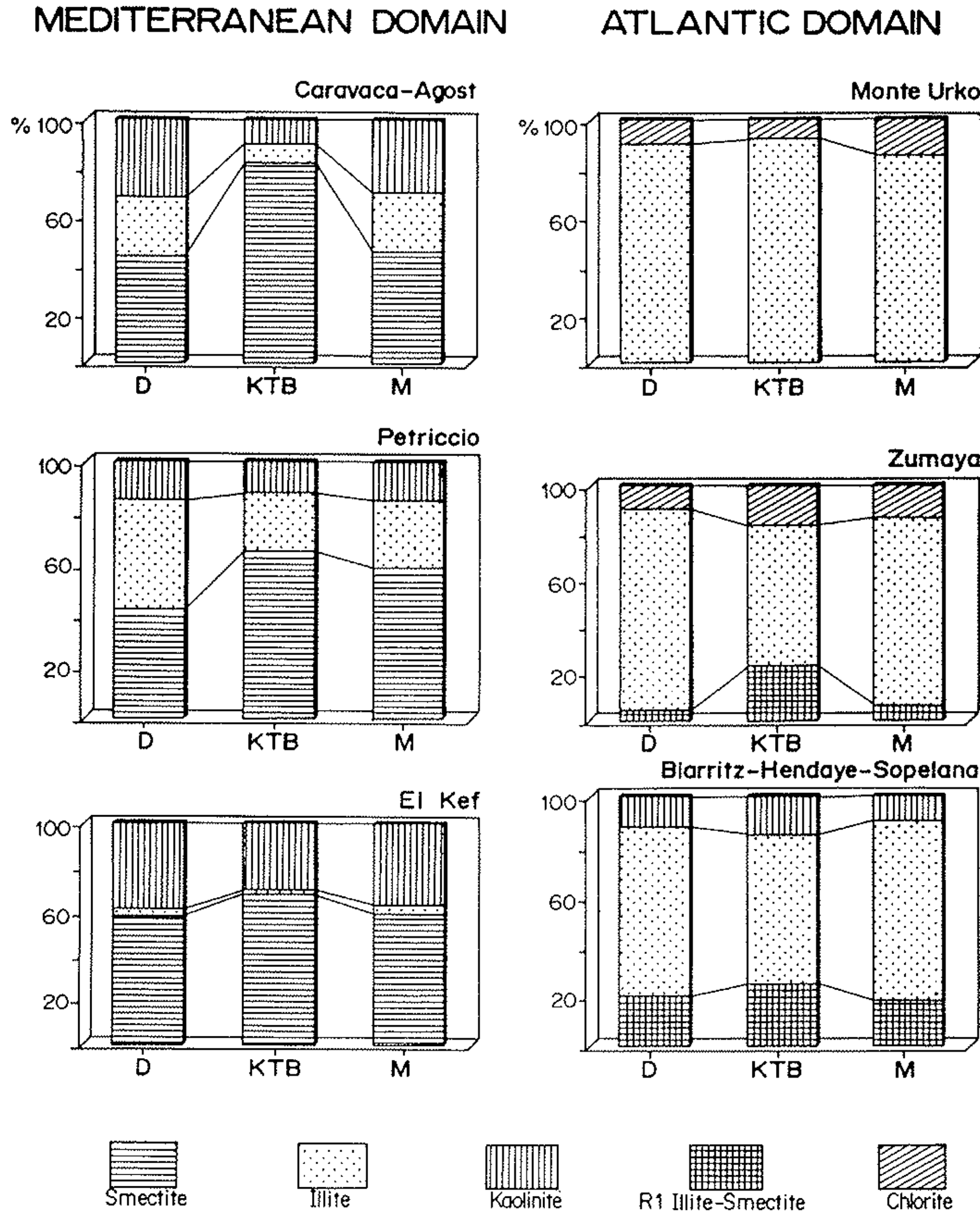

FIG. 2. Clay mineral contents (%) and distribution in the sections studied. D: Danian; KTB: Cretaceous-Ter boundary; M: Maastrichtian (Some data of the Betic Cordilleras and Basque-Cantabrian Basin from O Huertas *et al*., 1995).

In the KTB and Danian levels of the Agost and Caravaca sections (Ortega Huertas *et al*., 1995) and at El Kef, trace quantities of chlorite (chamosite end-member) and palygorskite were detected transmission electron microscopy. Sand-sized g conite grains were detected in the KTB at Ag

The mean chemical formulae of the smectites in the Mediterranean sections are given in Table 1. The (Al+Fe)/Mg ratio identifies these smectites as being dioctahedral (as shown by the diagram in Fig. 3A). They belong to the beidellite–nontronite series (following the chemical criterion of Caillère *et al.*, 1982: nontronite, Fe^{3+} >0.5; beidellite, Fe^{3+} <0.5). The compositions are homogeneous in the different sections studied, depending on the position they occupy in the AlAl-FeFe-Mg diagram of Güven (1988) (Fig. 3B). This chemical uniformity allows us to establish that there are no significant compositional differences among the smectites of the different stratigraphic sequences nor among the smectites from the KTB or from the Maastrichtian and Danian levels. In fact, 96% of the analysed particles have representative points within t of the Al smectites, corresponding to beidellites (field 1, Fig. 3B) and to montmorillonites (field 2, Fig. 3B). Th smectite analyses reach the Fe-smecti (field 3, Fig. 3B). Specifically, these several particles from the lowermost Dania Agost, Caravaca and El Kef sections, and tv the KTB in the Caravaca and El Kef s Smectites with similar composition were int by Brigatti (1983) as intermediate between nites and 'non-ideal' Fe-rich montmori following the nomenclature of Schultz They would, therefore, be equivalent to be type nontronites according to the chemical of Caillère *et al.* (1982). We can also sta

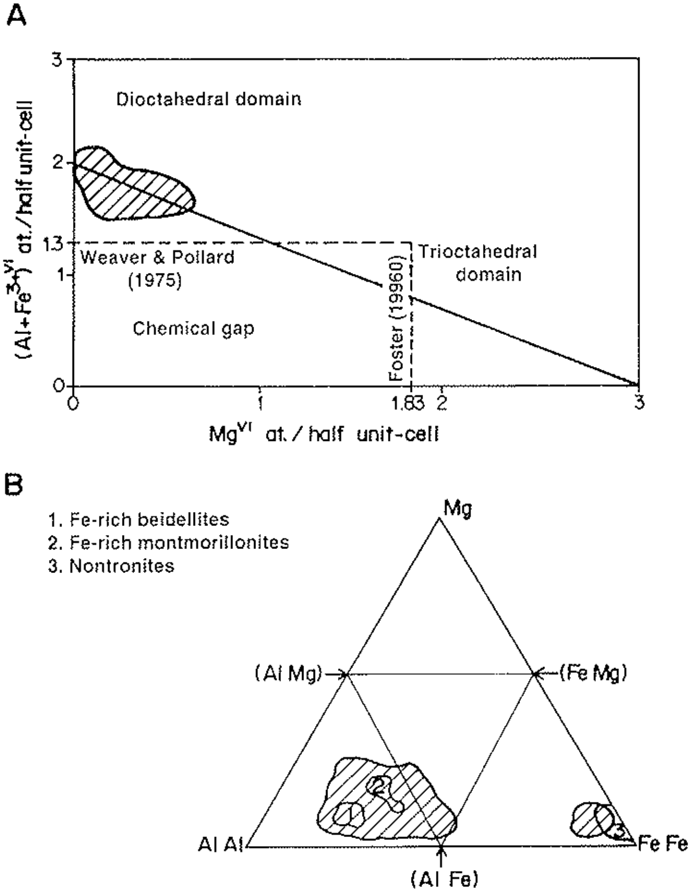

FIG. 3. Smectites in Mediterranean sections: (A) octahedral composition of the studied smectites (dashed the (Al+Fe^{3+})^{VI} *vs.* Mg^{VI} diagram of Grauby *et al.* (1993); (B) Ternary plot of dioctahedral aluminous a smectites (Güven, 1988) indicating the composition of smectites in Mediterranean sections (dashed

TABLE 1. AEM data for smectite formulae normalized to $O_{10}(OH)_2$; Mediterranean sections.

Section	Age	*n*	Si	Al^{IV}	Al^{VI}	Fe	Mg	Ti	Σoct	K	Ca	Σint
Agost	D	22	3.57(.01)	0.43(.02)	1.30(.04)	0.52(.02)	0.30(.10)	0.05(.09)	2.17	0.33(.01)	0.01(.02)	0.34
	KTB	43	3.60(.01)	0.40(.01)	1.40(.03)	0.48(.02)	0.20(.05)	-	2.08	0.35(.02)	0.05(.02)	0.40
	M	20	3.65(.03)	0.35(.02)	1.40(.03)	0.50(.02)	0.12(.05)	0.01(.09)	2.03	0.39(.01)	0.02(.02)	0.41
Caravaca	D	23	3.69(.06)	0.31(.03)	1.39(.03)	0.50(.02)	0.19(.09)	0.05(.09)	2.13	0.20(.01)	0.03(.02)	0.23
	KTB	49	3.66(.06)	0.34(.03)	1.50(.03)	0.38(.02)	0.21(.04)	0.03(.09)	2.12	0.23(.02)	—	0.23
	M	15	3.63(.06)	0.37(.02)	1.38(.03)	0.42(.03)	0.22(.09)	0.06(.09)	2.08	0.27(.02)	0.06(.02)	0.33
Petriccio	D	15	3.61(.03)	0.39(.01)	1.57(.03)	0.42(.02)	0.21(.04)	—	2.20	0.11(.01)	0.11(.02)	0.22
	KTB	29	3.64(.04)	0.36(.02)	1.38(.03)	0.54(.02)	0.31(.02)	0.03(.01)	2.26	0.27(.01)	0.12(.02)	0.39
	M	10	3.63(.03)	0.37(.02)	1.59(.04)	0.41(.02)	0.21(.02)	0.03(.02)	2.24	0.13(.01)	0.11(.01)	0.24
El Kef	D	17	3.66(.03)	0.34(.03)	1.54(.04)	0.44(.03)	0.19(.02)	—	2.17	0.10(.02)	0.09(.03)	0.19
	KTB	31	3.63(.06)	0.37(.02)	1.57(.03)	0.35(.03)	0.19(.03)	0.03(.02)	2.14	0.11(.01)	0.13(.02)	0.24
	M	16	3.63(.03)	0.37(.03)	1.59(.02)	0.36(.04)	0.21(.01)	0.02(.02)	2.18	0.11(.03)	0.10(.03)	0.21

n = number of analyses; D = Danian; KTB = Cretaceous-Tertiary boundary; M = Maastrichtian.
Standard deviation in parentheses.

generally speaking, the smectites belonging to the Maastrichtian and the Danian levels present a respective trend to smaller and larger Fe contents, whereas those of the KTB have an Fe content intermediate between these two.

The data from high-resolution transmission electron microscopy (HRTEM) of the fine fraction data (Ortega Huertas *et al.*, 1995) coincide with those obtained by XRD and show that these are smectites with a moderate proportion of illite layers (<30%), following the method of Reynolds & Hower (1970).

Table 2 summarizes the mean chemical composition of the illites, showing clear homogeneity in all the stratigraphic sections, irrespective of the age of the sediment. All micas show a phengitic trend according to the criteria of Velde (1985). The highest ranges of chemical variation correspond to the $3R^{2+}$ (Mg + Fe^{2+}) cations, whose variation coefficient V ranges from 29 to 45, depending on the stratigraphic section. In short, the micaceous minerals in uppermost Maastrichtian, KTB and lowermost Danian sediments in the Mediterranean sections correspond to phengite, illite or mica with a glauconite trend.

The clay minerals in the KTB in the Mediterranean Domain are accompanied in the bulk sample by quartz (5%) and calcite (10%), as well as the following minor (<5%) minerals, mainly detected using TEM: gypsum, baryte and celestite originated from diagenetic alteration; and apatite, monazite, ilmenite, rutile and zircon originated mainly as detrital phases.

In the Mediterranean sections, in bo sequences in the Caravaca-Agost and th Petriccio and El Kef, there are no drastic qua changes in the clay mineral associations KTB, Maastrichtian and Danian levels suggests non-changing sources and/or sedin and diagenetic processes, unlike the proposal by other authors for other stratigraphic s (e.g. Kastner *et al.*, 1984; Bohor *et al.*, 1984, The similarity also suggests the same pala graphical context for those sections and tha are no depositional changes in the clay assen across the KTB that can be related to the bo event. The lithological change from the upp Maastrichtian to the lowermost Danian is related to the decrease in the carbonate conte consequence of the fall in biological produ However, from a quantitative point of vie KTB layer with a much higher smectite cor these sections (Fig. 4A) clearly differs fr clay fraction of Danian and Maastrichtian le the case of Caravaca, the KTB level is al pure smectite.

Two hypotheses are proposed to expla abundance of smectite although we sha consider the possible influence of the sp found in the KTB. The first hypothe suggested by Ortega Huertas *et al.* (1995) Agost and Caravaca sections, is the altera volcanic rocks – probably calc-alkaline ar and Triassic ofites (Sebastián Pardo *et al.*, and basaltic rocks (López Galindo, 1986) the similarity of chemical compositio

TABLE 2. AEM data for dioctahedral micas in Mediterranean sections normalized to $O_{10}(OH)_2$.

Section	Age	*n*	Si	Al^{IV}	Al^{VI}	Mg	Fe	Ti	Σoct	
Agost	D	25	3.44(.05)	0.56(.06)	1.18(.04)	0.26(.06)	0.44(.09)	0.10(.09)	1.98	0.
	KTB	27	3.44(.05)	0.56(.06)	0.88(.04)	0.25(.05)	0.90(.09)	–	2.03	0.
	M	29	3.26(.06)	0.74(.06)	1.47(.02)	0.05(.05)	0.63(.04)	–	2.15	0.
Caravaca	D	20	3.50(.07)	0.50(.05)	1.56(.04)	0.17(.05)	0.17(.10)	0.13(.09)	2.03	0.
	KTB	29	3.47(.07)	0.53(.05)	1.35(.04)	0.10(.04)	0.10(.09)	–	1.55	0.
	M	25	3.26(.07)	0.74(.05)	1.68(.02)	0.09(.02)	0.18(.04)	–	1.95	0.
Petriccio	D	15	3.31(.08)	0.69(.05)	1.69(.01)	0.21(.02)	0.21(.06)	–	2.11	0.
	KTB	20	3.23(.08)	0.77(.04)	1.21(.02)	0.28(.04)	0.53(.03)	–	2.02	0.
	M	15	3.26(.04)	0.74(.04)	1.71(.04)	0.22(.02)	0.09(.07)	–	2.20	0.
El Kef	D	20	3.26(.06)	0.74(.03)	1.47(.03)	0.05(.02)	0.63(.04)	–	2.15	0.
	KTB	21	3.26(.07)	0.74(.07)	1.71(.03)	0.22(.04)	0.09(.04)	–	2.02	0.
	M	20	3.28(.06)	0.72(.04)	1.75(.03)	0.03(.04)	0.20(.04)	–	1.98	0.

n = number of analyses; D = Danian; KTB = Cretaceous-Tertiary boundary; M = Maastrichtian.
Standard deviation in parentheses.

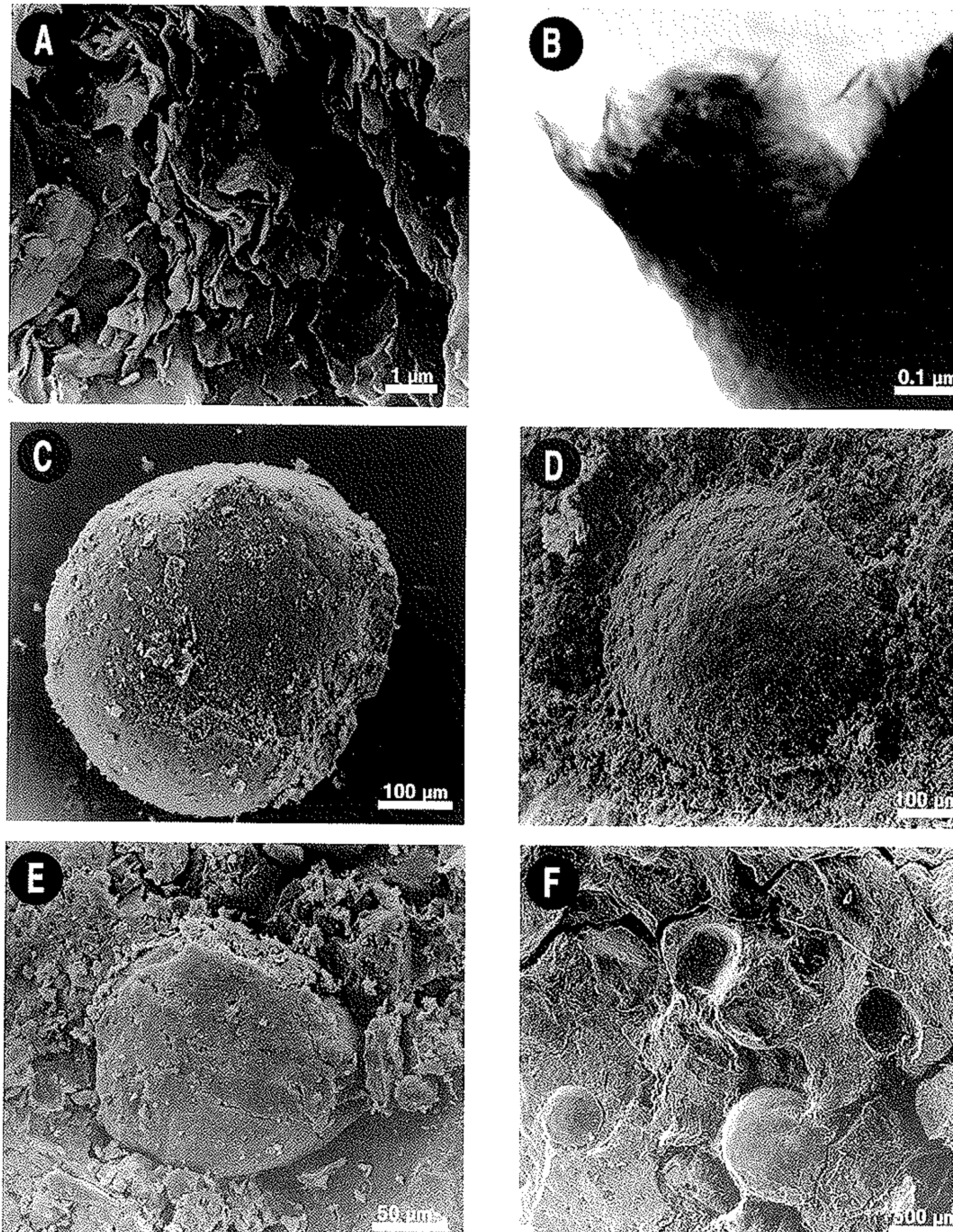

FIG. 4. SEM and TEM micrographs from the KTB. (A) Smectite, El Kef; (B) fleecy-type morphology of smec Caravaca; (C) K-feldspar spherule, Petriccio; (D) pyrite spherule, Zumaya; (E) nontronite spherule, Biar (F) relationship between K-feldspar and F oxide spherules and the clay matrix at Agost.

smectites of this origin from other locations (Kastner *et al.*, 1984; López Galindo, 1986; Münch *et al.*, 1996) and their lath-like micromorphology, which makes them compatible with this suggestion (Chamley *et al.*, 1985; Holtzappfel & Chamley, 1986). Two suggestions have been made for the origin of these rocks. The first is that they were deposited on a communication zone between the proto-Atlantic and Mesogea during a period of significant creation of oceanic crust in the North Atlantic (Thiry & Jacquin, 1993) whereas López Aguayo *et al.* (1985) suggested the influence of closer volcanic rocks during the extensive stage occurring on the southern margin of the Iberian plate in the Cretaceous. The second hypothesis is that these are detrital smectites inherited from the erosion of soils developed on surrounding areas in warm-humid conditions, as suggested by the presence of Al-rich beidellites (Table 1), their compositional similarity with smectites from recent soils (Paquet, 1970; Duplay, 1982) and their fleecy-type morphology (Fig. 4B). In the Agost and Caravaca sections, the Prebetic part of the External Zones of the Betic Cordillera could have acted as source area. In the Petriccio section, the significant proportion of illite suggests that, in addition to inheritance of soil smectite and kaolinite, there was also erosion involving the crystalline rocks of the source area. In the El Kef section, the large smectite and kaolinite contents and the extreme scarcity of illite can be interpreted as evidence that derivation from soil predominated over inheritance from crystalline rocks. The assemblage also records a tectonic stability on the continental margin of Tunisia from late Mesozoic to early Cenozoic. The smaller amount of kaolinite in the KTB compared with the Maastrichtian and Danian levels in all the Mediterranean sections (Fig. 2) is probably not due to climatic change, since this mineral basically originated in the soil, but rather to the increased supply of minerals eroded from rocky substrata (illite and, less extensively, chlorite in some stratigraphic sections).

As regards the presence of palygorskite in the KTB of the Betic Cordillera, we consider that it may be related to pH oscillations due to compartments in the basin where the sediments were deposited and/or to diagenetic transformation from dioctahedral smectites. In this process the biogenic opal widely found in Cretaceous sediments would have provided Si and Mg, as reported by López Galindo (1987) from the Betic Cretaceous bentonite deposits.

In the Atlantic Domain (Basque-Cant
Basin) there are several clay mineral associ
whose qualitative and quantitative compositi
summarized in Fig. 2: illite-chlorite in the
Urko section; illite-R1 illite-smectite-kaoli
the Sopelana, Biarritz and Hendaye sectior
illite-R1 illite-smectite-chlorite in the Z
section. The chemical composition of
minerals was studied in part by Ortega Huc
al. (1995) using TEM, and new resul
presented herein. Table 3 summarizes the
chemical composition of dioctahedral micas
sentative of the three clay mineral assoc
mentioned above.

Illite is the predominant mineral in
stratigraphic sections (Fig. 2). The followin
acteristics are common: (a) there is a predon
of compositions corresponding to detrital
close to or in some cases coinciding with mu
(Hendaye section); (b) the phengitic trend
clear in the Zumaya and Sopelana sections a
clear at Monte Urko and Biarritz; (c) the
character is a minor component, except fo
samples from the Hendaye section; (d) co
tional variability is not significant in th
(Na+K+2Ca) cation group, whose coeffic
variation (V) ranges from 3 to 15, but i
important in the $3R^2$ ($Mg+Fe^{2+}$) (V = 16–5
$2R^3$ ($Al+Fe^{3+} - MR^3$) (V = 17–57) cation

The chemical composition of the R1
smectite mixed-layers is relatively homog
as can be inferred from the graphic represe
of Si/Al^{total} *vs.* (K+Ca) (Fig. 5), in wh
compositional differences can be detected ac
to stratigraphic section or age. The conte
formula unit (pfu) in octahedral cations are
Al^{VI} from 1.95 to 1.65, Mg from 0.14 to 0.
Fe from 0.19 to 0.81. In the samples fr

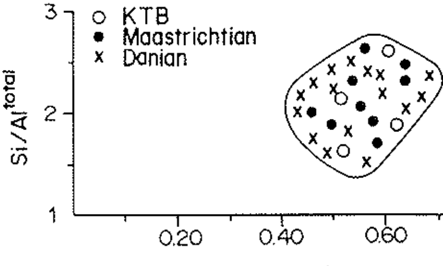

FIG. 5. AEM data for R1 illite-smectite mixe
normalized to $O_{10}(OH)_2$, Atlantic sectior

TABLE 3. AEM data for dioctahedral micas in Atlantic sections normalized to $O_{10}(OH)_2$.

Section	Age	n	Si	Al^{IV}	Al^{VI}	Mg	Fe	Ti	Σoct	K
Monte Urko	D	30	3.31(.05)	0.69(.04)	1.63(.04)	0.20(.09)	0.21(.06)	–	2.04	0.98
	KTB	29	3.12(.07)	0.88(.04)	1.24(.04)	0.20(.09)	0.33(.07)	0.21(.02)	1.98	0.84
	M	30	3.27(.05)	0.73(.04)	1.74(.04)	0.15(.04)	0.15(.07)	–	2.04	0.92
Zumaya	D	30	3.34(.05)	0.66(.03)	1.74(.04)	0.17(.09)	0.30(.07)	0.02(.01)	2.23	0.96
	KTB	30	3.19(.04)	0.81(.07)	1.56(.04)	0.04(.07)	0.33(.04)	0.02(.01)	1.95	0.98
	M	25	3.51(.04)	0.49(.04)	1.66(.05)	0.04(.09)	0.17(.07)	–	1.87	0.79
Biarritz	D	20	3.31(.05)	0.69(.04)	1.71(.03)	0.20(.09)	0.22(.03)	0.02(.01)	2.15	0.99
	KTB	29	3.19(.07)	0.81(.04)	1.63(.04)	0.20(.08)	0.30(.01)	0.10(.01)	2.23	0.96
	M	22	3.22(.04)	0.78(.03)	1.80(.04)	0.06(.08)	0.16(.01)	–	2.02	0.99
Hendaye	D	30	3.20(.03)	0.80(.04)	1.76(.05)	–	0.22(.02)	–	1.98	1.00
	KTB	30	3.15(.04)	0.85(.04)	1.79(.05)	–	0.20(.02)	–	1.99	0.99
	M	30	3.22(.05)	0.78(.04)	1.82(.04)	–	0.16(.04)	–	1.98	0.99
Sopelana	D	20	3.26(.04)	0.74(.03)	1.27(.05)	0.69(.07)	0.15(.02)	0.15(.01)	2.26	0.93
	KTB	25	3.33(.07)	0.67(.07)	1.62(.05)	0.22(.04)	0.06(.02)	0.02(.01)	1.92	0.90
	M	22	3.57(.04)	0.33(.04)	1.66(.03)	0.31(.04)	0.15(.04)	0.09(.01)	2.21	0.98

n = number of analyses; D = Danian; KTB = Cretaceous-Tertiary boundary; M = Maastrichtian.
Standard deviation in parentheses.

Sopelana section, the R1 I-S contains Ti (0.10–0.24 pfu) and Mn (0.01–0.02 pfu). These cations appear in similar proportions in the KTB samples from the Zumaya and Biarritz sections.

Chlorite is found in the clay mineral assemblages from Monte Urko and Zumaya. It has also been detected as a minor mineral in the Sopelana section. In any case, chlorite is not a very abundant mineral in the sediments of the Basque-Cantabrian Basin. With the exception of a sample from Monte Urko in which clinochlore was detected (Mg = 2.08, Fe = 1.04 pfu), the AEM data from all the other samples confirm that their composition corresponds to that of chamosite (Fe = 1.87–2.56 pfu; Mg = 0.95–1.57 pfu). Our opinion is that these are detrital chlorites showing the chemical characteristics described by Shau *et al.* (1991) as representative of contamination by corrensite or smectite interlayers, high Si content (2.50–3.05 pfu), an Al^{VI} content (1.73–2.42 pfu) much higher than Al^{IV} content (0.95–1.50 pfu), and total octahedral population much lower than 6 cations pfu (5.24–5.71). However, chlorites have been detected in the Monte Urko section whose chemical composition close to ideal chlorite formulae means that they may be authigenic chlorites ($\Sigma_{oct.}$ = 5.93 pfu; Fe/Fe+Mg = 0.67). These data agree with those of Nieto *et al.* (1996), who studied the Mesozoic-Cenozoic sediments of the Basque-Cantabrian Basin using HRTEM-AEM.

The clay minerals in the KTB of the Atl sections are qualitatively similar to those o Maastrichtian and Danian levels (Figs. 2 and 5 Table 3). This is the same general associ described for the Mediterranean sections. In Atlantic Domain, the micas and chlorite are de derived from the erosion of rock substrata, wh kaolinite is inherited from soils developed unde warm and humid climate that prevailed in Atlantic domains during the Cretaceous and mo the Tertiary (e.g. Miller *et al.*, 1987; Char 1989). The abundance of kaolinite in the Sope Biarritz and Hendaye sections (Fig. 2) consequence of the relative proximity of eme areas exposed to erosion which, accordin Mathey (1988), could have been located ne on the eastern and western platforms of Cantabrian Sea. In general, as proposed by C Huertas *et al.* (1995), clay sedimentation in Basque-Cantabrian Basin was controlled by tec processes occurring during the Maastrichtian Danian that were responsible for the supply of and chlorite and the absence of detrital smec The presence of significant amounts of R1 I the Sopelana and Zumaya sections and, to a extent, at Biarritz and Hendaye (Fig. 2) cou the result of burial diagenesis, which would ex the absence of smectite as an independent m phase in the sections of the Atlantic Domain. interpretation agrees with that of Aróstegui

(1991) and Nieto *et al.* (1996) for other sequences of the Basque-Cantabrian Basin, where the smectite developed in the surface Miocene levels disappears with depth before becoming R3 I-S in Lower Cretaceous deposits. These data are also consistent with the presence of some crystals attributed to authigenic chlorite, as mentioned above. In addition to the influence of diagenesis, other geological factors may have affected the distribution of the clay mineral assemblages. The abundance of kaolinite in the Biarritz, Hendaye and Sopelane sections suggests relative proximity to emerged areas. Indeed, in other sectors of the Basque-Cantabrian basin this is particularly evident during the Palaeocene, which is represented by continental facies deposited under a regressive regime (Ramirez del Pozo, 1973) when the kaolinite content was greatest.

INFLUENCE OF SPHERULES ON THE CLAY MINERAL COMPOSITION OF THE KTB LAYER

In the most of the known KTB sequences, spherules are completely or partially altered. One of the common results of diagenetic alteration is the formation of smectites (e.g. Smit *et al.*, 1992). We cannot dismiss, therefore, the fact that the smectites in the KTB layer may be partially related to the alteration of the precursor material of the spherules, which may also explain the significant increase in smectites in this layer.

Different types of spherules are found in the KTB of the Mediterranean sections. At Agost and Caravaca, K-feldspar and Fe oxide (goethite) spherule morphology, texture and chemical composition have been studied (e.g. Smit & Klaver, 1981; Martínez Ruiz *et al.*, 1992; Ortega Huertas *et al.*, 1992; Martínez Ruiz *et al.*, in press). In this paper we describe the K-feldspar spherules occurring in the Petriccio section (Italy) (Fig. 4C) and K-feldspar and Fe oxide spherules from the El Kef section (Tunisia), although Montanari (1991) first reported both types of spherules in these stratigraphic sections. The K-feldspar spherules consist of orthoclase (the triclinicity index was calculated following the formula of Goldsmith & Laves, 1954) (SiO_2 = 65.10–65.99%; Al_2O_3 = 17.94–18.75%; K_2O = 14.55–15.90%; Na_2O = 0.04–0.18%). The goethite spherules consist of a mixture of Fe-oxides and hydroxides (Fe_2O_3 = 83.88–94.19%).

In the KTB of the Atlantic domain, M
Ruiz (1994) reported K-feldspar spherules
Sopelana section, pyrite in the Zumaya
(Fig. 4D), and of Fe oxides and nontronite
Monte Urko and Biarritz sections (Fig. 4I
chemical compositions of the feldspar spheru
the Fe oxyhydroxide spherules are similar t
described for the KTB in the Mediter
domain. In all cases these are microkrys
the sense of Smit *et al.* (1992). The
chemical composition of the spherules is
differences in the diagenetic evolution
sediment (Martínez Ruiz *et al.*, 1992).

In the Mediterranean domain, the KTB
well preserved and the spherules are very al
(200 400/cm^3). They have a clear influence
KTB clay sedimentation, in particular the F
spherules (Fig. 4F). In our opinion, the incr
smectite in the KTB of these sections mu
have been influenced by the alteration pr
undergone by the spherules. In fact, the
proportion of spherules in the Caravaca
compared to the Agost section suggests th
have been almost totally altered, which
explain the greater proportion of smectites
KTB of the former stratigraphic section. T
also chemical evidence that could sugg-
relation between the spherules and the pres
smectites. The AEM microanalyses of
minerals show the existence of Ni as
cation (mean value of ~100 ppm). The core
K-feldspar spherules are rich in carbon and i
material, containing up to 3000 ppm Ni (M
Ruiz *et al.*, in press). Other authors have o
this type of alteration in other strati
sequences (e.g. Klaver *et al.*, 1986, in DS
93 Hole 603B in the northwestern Atlantic;
al., 1992, in Core 12 of DSDP Leg 86 Ho
in the northwestern Pacific and in the Beloc
Haiti). In the Agost and Caravaca section
ablation system analyses show that, apart f
the cores of these spherules also contain sig
amounts of PGE (Ir = 0.59 ppm, Pt = 2.89
= 15.70 ppm); these values could suggest th
microkrystites may have been derived f
expanding vapour plume with a significant
bution of extraterrestrial material.

In the Atlantic domain, spherules a
abundant (5–20/cm^3), since the KTB laye
as well preserved as in the Mediterranean
due to microtectonic deformations. Altera
these spherules must have followed th

general pattern described for the Mediterranean domain. However, the fact that smectite is not detected in the KTB of any of the Atlantic sections must be a consequence of the important diagenetic evolution undergone by these sequences, as shown in Fig. 2 by the presence of R1 I-S and even authigenic chlorite. In addition, the important contribution of detrital clay minerals (illite, chlorite, kaolinite) has masked the presence of authigenic smectite, although the presence of scarce nontronite spherules in the Monte Urko and Biarritz sections would be proof of the existence of authigenic smectites originating in the submarine alteration of spherules of mafic composition.

SIGNIFICANCE OF *REE* ELEMENTS

In the study of detrital sediments, the *REE* provide information concerning the source area of the sediments, as they are not fractionated during sedimentation processes and their secondary remobilization is not highly significant (Condi, 1991). In this case, the sedimentary particles conserve the chemical record of the source area (Condie, 1991). Most of the *REE* are concentrated in the clay fraction, while the silt and sand fractions present lower contents, mainly due to the dilution effect of quartz with a low *REE* content (Cullers *et al.*, 1988). For neoformed minerals in a marine sedimentary environment, the *REE* content depends on the behaviour of these elements in seawater where their concentration is very low (approximately $10-70\times10^{-12}$ mol.kg^{-1} for La-Nd, 0.5×10^{12} mol.kg^{-1} for Eu and $3-8\times10^{-12}$ mol.kg^{-1} for Sm-Yb, Elderfield & Greaves, 1982). In oxygenated marine environments, the oxidation of Ce^{3+} and its incorporation into Mn nodules causes a negative Ce anomaly, so that in oceanic accretion zones the sediments display this anomaly (Elderfield & Greaves, 1982), whereas in areas further from this influence, such as continental platforms, it is not displayed (Piper, 1974). Adsorption onto sedimentary particles is the main extraction mechanism of *REE* dissolved in seawater. Their total content in the sediment, as well as the development of Ce anomalies, depends on the environment and on the depositional conditions (Murray *et al.*, 1990).

Figure 6 shows the results of the normalization of *REE* contents to NASC (Haskin *et al.*, 1968) in the stratigraphic sections studied here. In the Atlantic sections (Fig. 6A) the pattern is the same for all the stratigraphic sequences. On the other hand, in the Mediterranean domain a pattern is observed tha common to the Agost, Caravaca (Fig. 6B) anc Kef (Fig. 6C) sections, but different from Petriccio section (Fig. 6D).

In the Atlantic sections, the KTB layer has average *REE* content (151 ppm) similar to tha the Maastrichtian (135 ppm) and Danian (142 p levels (Fig. 6A). The curves of normalization chondrites, with enrichment in light *REE* an basically flat pattern for heavy *REE*, agree those of sediments from the upper continental c (acid rocks), according to McLennan (1989). accumulation of sediments from emerged co nental areas on passive margins, which is the for the sections studied here, would consist ma of the recycling of sedimentary, plutonic an metamorphic rocks mixtures with small contr tions from contemporary volcanoes. The *REE* agree with an initially detrital origin of the minerals resulting from erosion of Palaeozoic r as well as the surrounding Mesozoic sedimen blankets. The fact that the boundary layer is impoverished in *REE* indicates that detrital supp predominated over possible neoformation of minerals in the KTB.

The *REE* content and distribution patterns similar in the Maastrichtian and Danian level Agost, Caravaca (Fig. 6B) and El Kef (Fig. where it is conditioned by the inherited minerals (illite, kaolinite and part of the smecti The normalization to NASC curves is also sim However, in these sections, the KTB is cle impoverished in *REE* compared with the underl and overlying layers (Fig. 6B,C). The deple suggests an authigenic origin for most of smectite and little influence from detrital minerals. This hypothesis is confirmed by the in Fig. 7, showing normalization to chondrite the *REE* contents in the clay fraction of the KT these sections, where it can be seen that the content correlates inversely with smectite co (more abundant smectites in Caravaca than A and in Agost than in El Kef, see Fig. 2) addition, the abundant K-feldspar and Fe c spherules in the KTB have not provided *REE* ei as they are authigenic phases derived from impact-related mafic precursor poor in *REE* (& Ten Kate, 1982; Martínez Ruíz *et al.*, Ortega Huertas *et al.*, 1994; Martínez Ruiz *e* 1997). The *REE* content in the Petriccio secti different from the other Mediterranean section does, however, show certain similarity with

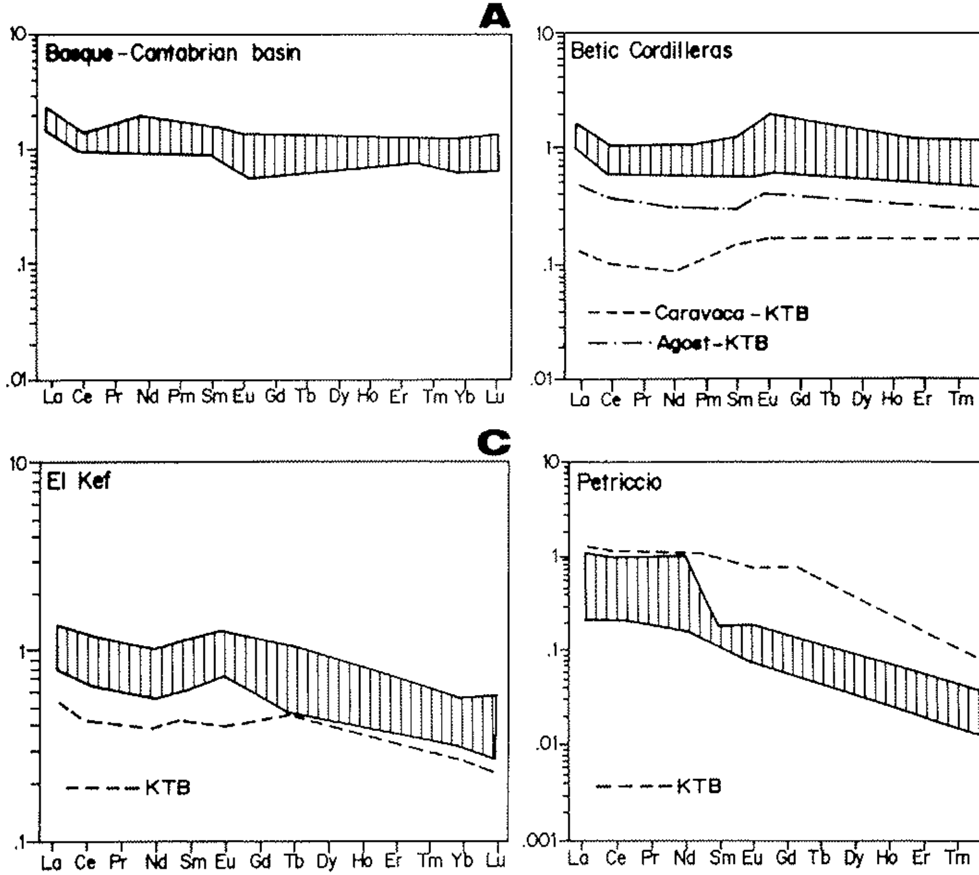

FIG. 6. *REE* content in studied sections normalized to NASC (Haskin *et al.*, 1968). The shaded zone cor to *REE* normalized values in Maastrichtian and Danian levels. (A) Atlantic sections. (B) Agost and C sections. (C) El Kef section. (D) Petriccio section. (Data of figures A and B from Ortega Huertas *et al*

Atlantic sequences, although the KTB layer is slightly enriched in *REE* compared with the Danian and Maastrichtian levels (Fig. 6D). This can be interpreted as being due to the fact that most of the smectites in the KTB are of detrital origin, while those of the underlying and overlying levels are derived, in part at least, from the alteration of volcanic rocks, thus indicating a change in the sedimentation of this stratigraphic section.

CONCLUSIONS

Source areas, sediment supply and diagenetic processes are the main factors controlling the clay mineral associations in Mediterranean and Atlantic domains at the KTB levels. The Mediterranean Domain is characterized by a simple clay
association (smectite-illite-kaolinite), with s
as the predominant mineral. In the Atlantic I
the KTB has several clay mineral asso
illite-chlorite, illite-R1 I-S mixed-layer-k
illite-R1 I-S mixed-layer-chlorite. In both
gical domains the qualitative composition
clays in the KTB layer is identical to tha
Danian and Maastrichtian levels. The TEM-
the clay minerals do not reveal any compo
differences between the KTB and the samp
the overlying and underlying levels which
similar sources and/or sedimentary and di
processes through the KTB.

The chemical composition and micromor
of the smectites in the Agost and Caravaca

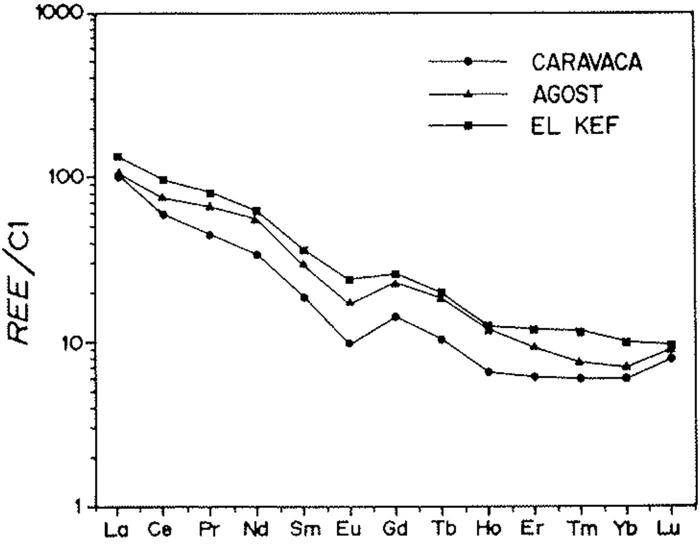

FIG. 7. *REE* content normalized to chondrites C1 (Anders & Ebihara, 1982) in the Agost, Caravaca and El sections.

confirm partial derivation from alteration of volcanic rocks and erosion of soils developed on emerged areas of the Prebetic of the External Zones of the Betic Cordilleras. In the El Kef section, soil processes also affected the erosion products derived from a stable continental margin, whereas in the Petriccio section the mineralogical composition of the KTB basically reflects the erosion of crystalline rocks in the source area. In the Mediterranean domain an additional factor to take into account is the role of the KTB spherules. The abundant K-feldspar and Fe oxide spherules in the Agost, Caravaca and El Kef sections can be related to the drastic increase of smectite in the KTB.

In the Atlantic Domain, clay sedimentation was controlled by the degree of burial diagenesis (responsible for the lack of smectite and the presence of R1 mixed-layer I-S and part of the chlorite), by Maastrichtian and Danian tectonic processes and by the erosion of emergent areas on the eastern and western platforms of the Cantabrian Sea, according to Mathey (1988).

The *REE* data provide evidence for the important influence of authigenic phenomena in the KTB of the Agost, Caravaca and El Kef sections; the strong detrital character and change of clay sedimentation in the KTB compared with the Danian and Maastrichtian levels in the Petriccio section; masking of authigenic phases caused by detrital ones in the Atlantic sequences, which w explain the existence of a single *REE* pat However, the presence of minor nontronite sp ules in the Monte Urko and Biarritz sections w be evidence for authigenic smectites originatin submarine alteration of mafic spherules.

The condensed mafic dust produced a consequence of the extraterrestrial impact c have been altered to smectite. However, diage conditions and local detrital supplies conditi the composition of the KTB layer, cau differences in the clay sedimentation of geological Domains studied and in the stratigra sections of the Atlantic Domain.

In the studied sections, all of which are ma the KTB layer is equivalent to the uppermost of the two-layered clay unit described in Western Interior Basin of North America Pollastro & Bohor (1993). This layer origi from a cloud of a vapourized bolide and entra target rock materials ejected above the atmosp

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