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Comparative mineralogical and geochemical clay sedimentation in the Betic Cordilleras and Basque-Cantabrian Basin areas at the Cretaceous–Tertiary boundary

M. Ortega Huertas [a], F. Martínez Ruíz [a,1], I. Palomo [a], H. Chamley [b]

[a] *Departamento de Mineralogía y Petrología, Facultad de Ciencias, Universidad de Granada, 18002 Granada, Spain*
[b] *Laboratoire de Sédimentologie et Géodynamique, URA 719 CNRS, Université de Lille I, 59655 Villeneuve d'Ascq cedex, France*

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Abstract

The mineralogy and geochemistry of the bulk rock and clay fraction of sediments deposited at the Cretaceous–Tertiary transition and in the KTB layer have been investigated by various methods in two sections from the Betic Cordilleras (Agost, Caravaca) and five sections from the Basque-Cantabrian Basin (Monte Urko, Sopelana, Zumaya, Hendaye, Biarritz). Active terrigenous supply prevailed in both regions during the latest Maastrichtian and earliest Paleocene. Very different clay associations occur in the regions, smectite being dominant to the south and illite to the north. The Betic Cordilleras series mainly reflects climate and weathering conditions, as well as volcanic activity, with the KTB layer displaying a specific source and diagenesis control expressed as increased amounts of smectite. The sequences cropping out in the Basque-Cantabrian Basin mainly reflect tectonic activity and burial diagenesis, the effects of which differ according to the palaeogeographical location. The clay sedimentation patterns in the North and South Iberian sections across the Cretaceous–Tertiary passage are controlled overwhelmingly by regional or local geodynamic and diagenetic phenomena. Thus any global, namely extraterrestrial, influence cannot be identified.

1. Introduction

The biological extinctions marking the end of the Cretaceous belong to one of the most controversial problems in Earth Sciences (e.g., Alvarez et al., 1980; Officer and Drake, 1983, 1985; Courtillot et al., 1986; Raup, 1987, 1988). The marine sedimentary record shows a strong decrease of biological production, leading to a dramatic decrease in carbonate sedimentation. Thus, a clayey layer occurs in most of the studied KTB sections that contain mineralogical and geochemical anomalies providing evidence for a catastrophic event. The high contents of Ir and other platinoids, as well as the presence of spherules (e.g., Smit and Klaver, 1981; Montanari, 1991; Martínez Ruíz, 1994), shocked quartz (e.g., Bohor, 1990) and Ni-rich spinels (Kyte and Smit, 1986; Robin et al., 1991, 1992; Rocchia et al., 1992) in the

[1] Present address: Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093-0212, USA.

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K/T boundary (KTB) layer, which are considered as cosmic signatures, support the proposal by Alvarez et al. (1980) of an impact phenomenon as responsible for the mass extinction. However, this hypothesis has not been accepted by all (e.g., Officer and Drake, 1983, 1985; Courtillot et al., 1986) and many other studies have examined the KTB anomalies in a search for distinguishing "impact markers" relative to non-impact sedimentary components.

The clay mineral associations may potentially reflect the environmental conditions prevailing during the KTB and surrounding layers deposition. Different authors have used these associations to support hypotheses of terrestrial or extraterrestrial causes for the KTB event. For instance, Kastner et al. (1984) suggested that the pure smectite identified in the KTB at Stevns Klint (Denmark) formed authigenically by alteration of glass. In their opinion, the major element chemistry of the smectite, as well as the high content of iridium, suggest formation from impact glass rather than from volcanic glass. Pollastro and Pillmore (1987) also considered the clay minerals of the KTB in Raton Basin (USA) as being formed by alteration of the fallout material produced by an impact. Pollastro and Bohor (1993) have recently interpreted the KTB clay mineral associations of Western Interior continental deposits (USA) as derived from weathering and subsequent diagenesis of a two-phase meteorite impact ejection comprising successive melted silicic rock and mafic vitric dust.

Other authors such as Elliot et al. (1989), considered that the Mg-smectite at Stevns Klint was related to volcanism rather than impact. Although Johnsson and Reynolds (1986) did not exclude the possibility of a small proportion of the KTB in the Gubbio section being made up of impact-derived materials, they considered that the clay minerals in the KTB do not differ from those in the Cretaceous and Tertiary sediments above and below the KTB. Rampino and Reynolds (1983) failed to detect ejecta-derived components in the KTB of the same section.

Vannuci et al. (1990) considered that the predominance of smectite in the Caravaca section (southwestern Spain) was the result of the transformation of volcaniclastic material, which in their opinion is supported by the presence of a zeolite-rich interval in the upper part of the underlying Cretaceous sequence. Robert and Chamley (1990) suggested that the clay mineral associations across the KTB, studied at various locations from northern and southern hemispheres, express a global instability at the surface of the Earth and, therefore, cannot be used to document the existence of a unique catastrophic event at the end of the Cretaceous. The wide variations recorded in the nature and proportions of clay minerals at different sections indicate global changes in sea level and tectonic activity at that time.

In the present paper, we present and discuss the clay mineral associations in different outcrops of the KTB in both the Betic Cordilleras (Agost and Caravaca sections, Fig. 1A) and the Basque-Cantabrian Basin (Monte Urko, Sopelana and Zumaya in Spain, Hendaye and Biarritz in France, Fig. 1B). Caravaca and Agost sections are two of the most continuous records known across the KTB, together with El Kef in Tunisia and three sections in Brazos River, Texas (MacLeod and Keller, 1991). The purpose of this paper is to provide further evidence on the origin of the clay mineral associations in the studied sections and their possible relationship to the catastrophic event at the end of the Cretaceous, as well as to compare sedimentation in both regions from a palaeogeographic and diagenetic point-of-view.

2. Methods

2.1. X-ray diffraction

A homogeneous and representative fraction of the samples was used for mineralogical study of the bulk rock, another was used for the extraction and study of the clay fraction. The equipment used was a Philips PW 1710 diffractometer with automatic slit. The reflecting factors calculated for this equipment and its instrumental conditions were (1) for powder diffractograms—phyllosilicates, 0.09; quartz, 1.43; calcite, 1.05; feldspars, 1.03; (2) for oriented aggregate diffrac-

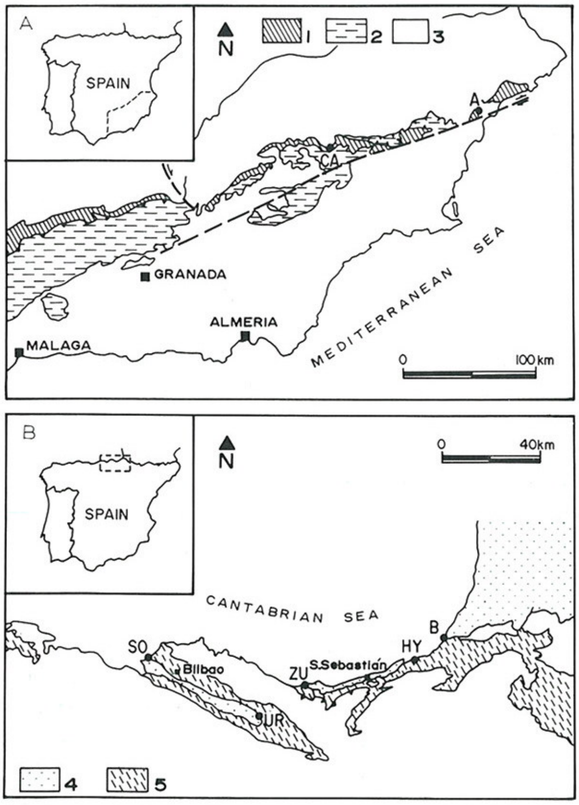

Fig. 1. Geological setting of the sections studied. (A) Betic Cordilleras: *A* = Agost; *CA* = Caravaca; *1* = Intermediate Units; *2* = Subbetic Zone; *3* = Prebetic Zone. (B) Basque-Cantabrian Basin: *UR* = Monte Urko; *SO* = Sopelana; *ZU* = Zumaya; *HY* = Hendaye; *B* = Biarritz; *4* = Tertiary; *5* = uppermost Cretaceous.

tograms—illite, 0.36; chlorite, kaolinite, 0.98; smectite, 0.93; mixed-layer R1 illite/smectite, 0.65. The estimated error for the quantitative analyses is $\pm 5\%$. We have adopted the nomenclature of Reynolds (1980) for the mixed-layers R1 illite/smectite, in which the proportion of expandable layers may vary from 40 to 15%, as quantified by the methods of Reynolds and Hower (1970) and Srodon (1984). Separation of the clay fraction and preparation of the samples for diffractometric study were carried out following the international recommendations compiled by Kisch (1991) from investigations performed by the international community.

2.2. Electron microscopy

The morphological study of the clay minerals was carried out using Scanning Electron Microscopy (Zeiss DSM-950, Centro de Instrumentación Científica of the University of Granada, Spain). The quantitative geochemical microanalyses of the clay minerals were obtained by means of Transmission Electron Microscopy using a Jeol JEM 2000 FX fitted with Link AN 10,000 microanalysis (Complutense University of Madrid, Spain) and a Jeol JEM 1200 FX also equipped with the same microanalysis (University of Cádiz, Spain).

The mineralogical formulae were calculated assuming that all the chemical charges were compensated, using the procedure of López Galindo et al. (1989). The formulae of micas, smectites and mixed-layers illite/smectite R1 were normalized to eleven oxygens and the chlorite formulae to fourteen oxygens. We took the total Fe as FeO for the illites and phengites and Fe_2O_3 for the smectites, whereas for the chlorites we considered 10% of the total Fe as Fe_2O_3 following Whittle (1986). The terms phengite and illite are used in the sense of Bailey et al. (1984), and glauconitic mica in a sense intermediate between those of Bailey et al. (1984), and of Chamley (1989). Beidellite and nontronite of the smectite group were differentiated following Caillère et al. (1982). The internationally accepted mineral abbreviations of Kretz (1983) were adopted. Notice that the initials CM refer to clay minerals.

2.3. Geochemistry

Analyses of Al, Fe, Mn and rare-earth elements (REE) were carried out using X-ray fluorescence, inductively coupled plasma and neutron activation at the X-Ray Assay Laboratories in Ontario, Canada.

3. Betic Cordilleras sections

3.1. Geological setting

The Betic Cordilleras, which are part of the peri-Mediterranean Alpine orogenic belt, have been divided into External and Internal Zones on the basis of palaeogeographical and structural data. The Internal Zones are characterized by the existence of large nappes often intensely affected by Alpine metamorphism. The External Zones formed part of the continental margin of the Iberian plate (e.g., Vera et al., 1982; Vera, 1983, 1988). The evolution of this passive Mesozoic margin was similar to that of other Alpine margins (Vera, 1988). From a stratigraphic point of view, the External Zones are subdivided into the Prebetic Zone located to the north, close to the Spanish Meseta, the Subbetic Zone to the south, and Intermediate units (Fig. 1A).

During the Jurassic and Cretaceous in the Prebetic Zone, rather shallow marine sedimentation occurred on the inner part of the Iberian margin (García Hernández et al., 1981; Vera et al., 1982). In the Subbetic Zone, deeper facies were deposited from the middle Lias. Various rates of subsidence occurred depending on the location, especially during the Jurassic, leading to different stratigraphic features. According to these differences, External, Median and Internal domains can be distinguished in the Subbetic Zone. Throughout the Late Jurassic and Cretaceous, the Subbetic basin became progressively less variable, and more uniform topographic and depositional conditions existed during the Late Cretaceous. The end of the Maastrichtian and early Danian are characterized by the deposition of marls and marly limestones with abundant planktic fauna.

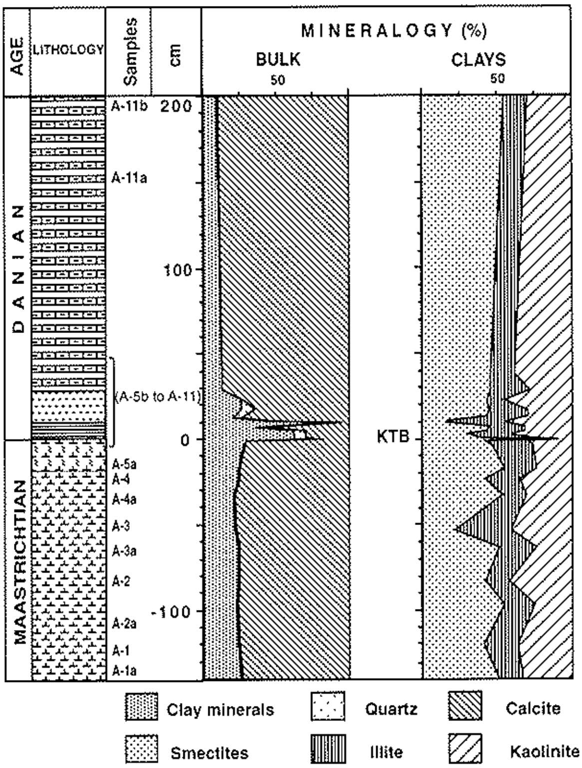

Fig. 2. Mineralogy at the Cretaceous–Tertiary transition in the Agost section.

The series investigated in Agost (A) and Caravaca (CA) belong to the Intermediate Units and Subbetic Zone, respectively (Fig. 1A). The uppermost Cretaceous deposits consist of light-green marly limestones which are lithologically very uniform. A 2–3 mm thick dark clayey layer occurs with a sharp contact on the top of these limestones. This layer marks the KTB and is partially altered, thus explaining its usual reddish appearance. The lowermost Danian deposits consist of 8–10 cm thick dark-green marly clays, the carbonate content of which gradually increases up section, giving way to marls and marly limestones.

3.2. Results

The bulk mineralogy of Agost and Caravaca sediments is essentially characterized by calcite, phyllosilicates and quartz. The KTB layer also contains K-feldspar and Fe-oxide spherules (Martínez Ruíz et al., 1992a; Ortega Huertas et al., 1992), as well as small amounts of celestite, barite, gypsum, apatite, monazite, ilmenite, rutile and zircon, some of which also occur in the lowermost Danian levels. The clay associations are dominated by smectite (Figs. 2 and 3), associated with minor amounts of illite and kaolinite. In the KTB and Danian levels, the systematic presence of chlorite and palygorskite traces have been detected by transmission electron microscopy. In the Agost section chlorite is present up to 12 cm above the KTB, and palygorskite up to 1080 cm. In the Caravaca section, both minerals have been found in samples located up to 12

Table 1
Betic Cordilleras; chlorite formulae

Sample	Si	Al^{IV}	Al^{VI}	Fe	Mg	Ti	Σ(Oct.)	K
A-9 (11 cm +)	2.97	1.03	1.35	3.23	1.26	–	5.84	–
A-6 (0.5 cm +)	2.72	1.28	1.87	2.38	1.45	–	5.70	–
	2.88	1.12	1.90	2.37	1.27	–	5.54	–
CA-12 [a]	2.80	1.20	1.35	2.44	0.81	0.02	4.62	0.18
CA-5 [a]	2.92	1.08	2.06	2.33	0.97	0.03	5.39	0.23
CA-K/T [b]	2.97	1.04	1.42	2.21	0.98	1.17	5.78	0.05

[a] Contamination of smectite as indicates the K content.
[b] Contamination of rutile as indicates the Ti content.

cm above the KTB. The chlorite invariably corresponds to the chamosite end-member (Table 1).

The micaceous minerals in sediments of the uppermost Maastrichtian, KTB and lowermost Danian correspond to phengite, illite or mica with a glauconitic trend, as shown by their chemical composition summarized in Table 2.

High-resolution transmission electron microscopy investigations of smectite show that this mineral occasionally appears as anastomosed packages with a development of illite packages of 270–300 Å and some deformation due to compaction phenomena causing interlayer slip. These data are consistent with the moderate proportion of illite layers (< 30%) obtained by applying the method of Reynolds and Hower (1970). The chemical compositions of smectites are summarized in Table 3. This mineral group comprises dioctahedral types of the nontronite–beidellite series, which contain traces of V, Ni, Cr, Zn, Co and Cu. Their location in the Mg–FeFe–AlAl diagram of Güven (1988) shows that smectites of the Betic Cordilleras sections display a good compositional homogeneity.

From a qualitative point of view the clay mineral association in both sections is the same for uppermost Maastrichtian, KTB and lowermost Danian deposits (Fig. 4). Similarly, the characterization of the micas and smectites shows that their chemical composition is identical in the KTB and layers immediately above and below. This similarity in composition of the smectites differs from the data of Kastner et al. (1984), who identified in the KTB at Stevns Klint a Mg-smectite clearly different from those of the uppermost Cretaceous and lowermost Paleocene.

3.3. Discussion

The presence of very similar bulk and clay mineral associations at Agost and Caravaca sections (Figs. 2–4), which are presently located at about 100 km from each other, indicates that sources and/or sedimentary and diagenetic pro-

Table 2
Betic Cordilleras; dioctahedral micas formulae

Sample	Si	Al^{IV}	Al^{VI}	Mg	Fe	Ti	Mn	Σ(Oct.)	K
A-K/T (0 cm)	3.23	0.77	1.21	0.28	0.53	–	–	2.02	0.98
	3.65	0.35	0.45	0.22	1.26	–	–	1.93	0.79
A-5 (1 cm –)	3.28	0.72	1.75	0.03	0.20	–	–	1.98	0.96
A-4 (23 cm –)	3.21	0.79	1.35	0.10	0.76	–	–	2.21	0.99
	3.26	0.74	1.47	0.05	0.63	–	–	2.15	0.97
CA-11 (14 cm +)	3.47	0.53	0.67	0.33	0.99	–	–	1.99	0.90
CA-5 (1 cm +)	3.50	0.50	1.56	0.17	0.17	0.13	–	1.99	0.88
CA-K/T (0 cm)	3.26	0.74	1.71	0.22	0.09	–	–	2.02	0.98
	3.47	0.53	1.35	0.10	0.62	0.04	0.05	2.16	0.83
CA-2 (8 cm –)	3.26	0.74	1.68	0.09	0.18	–	–	1.95	0.97

cesses were comparable in both geographical sectors.

The presence of smectite as the predominant mineral at the Cretaceous–Tertiary transition can be interpreted in different ways. The first explanation could be that the smectite is an alteration product of volcanic rocks, which is indicated by the fact that the chemical composition of some studied smectites is very similar to that of smectites associated with marine volcanic rocks (Fig. 5A). Such an explanation was proposed by López-Galindo (1986) for the Middle Cretaceous

Table 3
Betic Cordilleras; smectite formulae

Sample	Si	Al^{IV}	Al^{VI}	Mg	Fe	Ti	Mn	Σ(Oct.)	K	Ca	ΣInt.
A-11 (38 cm +)	3.64	0.36	0.88	0.03	1.05	0.05	–	2.01	0.29	0.06	0.35
	3.66	0.34	0.74	0.08	1.21	0.01	–	2.04	0.31	–	0.31
	3.62	0.38	1.50	–	0.44	0.03	–	1.97	0.38	0.06	0.44
	3.64	0.36	0.96	0.26	0.90	0.01	–	2.13	0.25	–	0.25
A-9 (11 cm +)	3.62	0.38	0.97	0.18	0.93	–	–	2.08	0.27	0.03	0.30
	3.61	0.39	0.70	0.22	1.17	–	–	2.09	0.33	–	0.33
A-7 (1.5 cm +)	3.57	0.43	0.82	0.24	1.01	–	–	2.07	0.33	0.06	0.39
	3.49	0.51	0.93	0.15	1.02	–	–	2.10	0.30	0.03	0.33
	3.67	0.33	0.97	0.23	0.86	–	–	2.06	0.25	0.07	0.32
A-6 (0.5 cm +)	3.56	0.44	1.30	0.14	0.69	–	–	2.13	0.19	–	0.19
	3.63	0.37	1.03	0.16	0.93	–	–	2.12	0.16	–	0.16
	3.62	0.38	1.20	0.15	0.70	–	–	2.05	0.18	0.02	0.20
A-K/T (0 cm)	3.60	0.40	1.42	0.02	0.60	0.05	0.03	2.12	0.15	–	0.15
	3.59	0.41	1.00	0.52	0.82	0.31	0.01	2.66	0.36	0.05	0.41
	3.62	0.38	0.79	0.24	0.79	–	0.40	2.22	0.35	–	0.35
	3.62	0.38	1.18	0.08	0.53	0.14	–	1.93	0.19	0.10	0.29
A-5 (1 cm −)	3.67	0.33	0.39	0.10	0.53	–	–	2.02	0.37	–	0.37
A-4 (23 cm −)	3.64	0.36	1.41	0.09	0.52	–	–	2.02	0.39	–	0.39
CA-12 (18 cm +)	3.65	0.35	1.05	0.18	0.79	0.04	–	2.06	0.39	–	0.39
	3.69	0.31	0.54	0.16	1.36	–	–	2.06	0.13	0.07	0.20
	3.60	0.40	1.10	0.21	0.81	–	–	2.12	0.21	0.02	0.23
CA-11 (14 cm +)	3.50	0.50	0.76	0.28	1.09	–	–	1.93	0.24	0.07	0.31
	3.64	0.36	0.75	0.14	1.17	–	–	2.06	0.28	0.02	0.30
	3.62	0.38	0.95	0.13	0.84	0.03	–	1.95	0.39	–	0.39
CA-5 (1 cm +)	3.69	0.31	1.10	–	0.86	0.08	–	2.04	0.26	–	0.26
	3.62	0.38	1.08	0.26	0.76	–	–	2.10	0.33	0.01	0.34
	3.65	0.35	0.88	0.53	0.81	–	–	2.22	0.21	–	0.21
	3.52	0.48	1.17	0.30	0.68	–	–	2.15	0.39	–	0.39
	3.65	0.35	1.23	0.09	0.74	–	–	2.06	0.21	0.03	0.24
	3.55	0.45	1.63	0.08	0.32	–	–	2.03	0.16	0.10	0.26
CA-K/T (0 cm)	3.61	0.39	1.13	0.05	0.77	0.10	0.03	2.08	0.34	–	0.34
	3.66	0.34	1.53	–	0.47	0.03	–	2.03	0.25	0.02	0.27
	3.63	0.37	1.30	0.34	0.46	0.04	–	2.14	0.23	–	0.23
	3.62	0.38	0.83	0.55	0.82	–	–	2.20	0.26	0.03	0.29
	3.67	0.33	1.23	0.22	0.67	–	–	2.12	0.20	–	0.20
CA-2 (8 cm −)	3.69	0.31	1.45	0.23	0.35	–	–	2.03	0.28	0.09	0.37
	3.68	0.32	1.10	0.15	0.69	0.06	–	2.00	0.46	–	0.46
	3.64	0.36	1.26	0.56	0.32	0.05	–	2.19	0.27	0.06	0.33
	3.63	0.37	1.50	0.12	0.42	–	–	2.04	0.37	–	0.37

black-shales in the External Zones of the Betic Cordilleras. TEM microanalyses reveal that the order of abundance of the octahedral cations is Al > Fe > Mg. Similar analytical data were interpreted by Kastner (1976) as being characteristic of smectites genetically related to the alteration of basaltic rocks. In addition, smectites from the Betic Cordilleras sometimes display a lathed shape. Such a shape can be of a volcanogenic origin (e.g. Chamley et al., 1985), although this is by far not systematic, especially in the Atlantic range (Holtzapffel and Chamley, 1986).

A second explanation is that smectites from the Betic Cordilleras result from the erosion of continental soils developed under warm-humid conditions, as shown by the frequent presence of Al-beidellites and fleecy-type morphologies (Paquet, 1970). Considering the location of the studied smectites in the Fe_2O_3–MgO–Al_2O_3 diagram of McMurtry et al. (1983), a great compositional variability is observed (Fig. 5B). Some of the smectites analyzed belong to the compositional field of soil-derived detrital beidellites. When comparing our smectite compositions (Table 3) to those of smectites from recent soils (Paquet, 1970; Duplay, 1982), we often found similar data. In the geological context of latest Cretaceous times, the Prebetic part of the External Zones, which was exposed, could have acted as a source area.

It is difficult to distinguish between these two explanations. A mixed volcanogenic and pedogenic origin of sedimentary smectites in the Betic Cordilleras basin is likely, and would have been facilitated by the exposure of local rocks comprising volcanic components to Late Cretaceous–Early Paleocene hydrolyzing climates and soil formation. An additional question is the particular abundance of smectite in the KTB level from the Betic Cordilleras sections (Figs. 2–4). In the Stevns Klint section, Kastner et al. (1984) found that the sediments above and below the KTB layer contained illite, mixed-layer illite/smectite

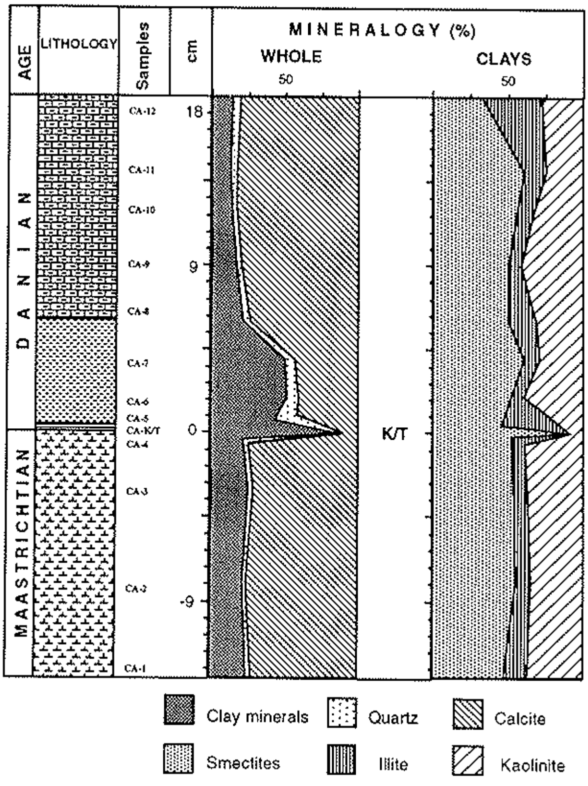

Fig. 3. Mineralogy at the Cretaceous–Tertiary transition in the Caravaca section.

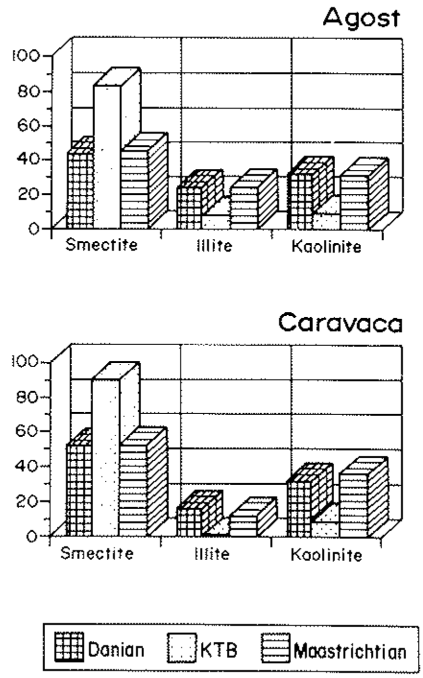

Fig. 4. Mean values of the mineral contents in the Betic Cordilleras expressed in percentages.

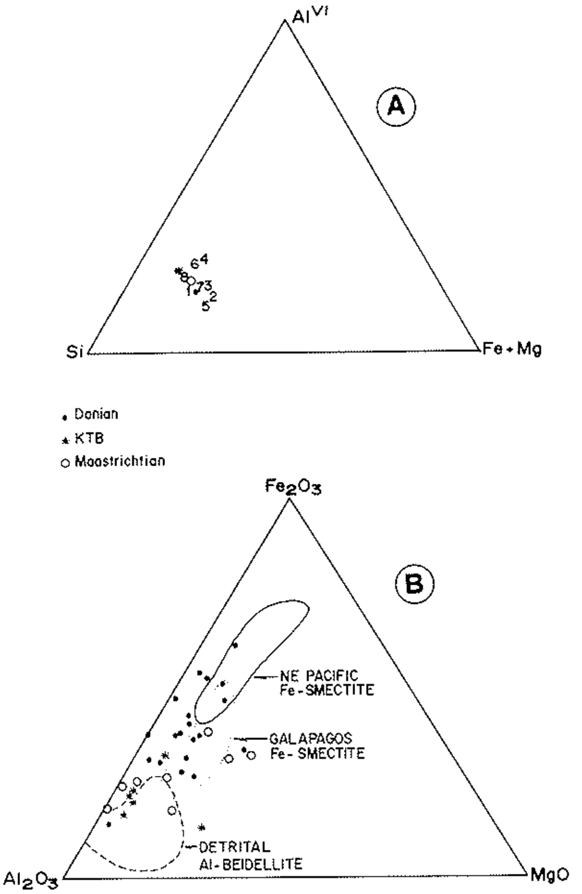

Fig. 5. (A) Plot showing the composition of the smectites from Agost and Caravaca sections compared to other oceanic smectites. Atlantic altered basalts: points *1* and *2* from Melson and Thompson (1973); points *3* and *4* from Mevel (1980); points *6* and *7* from Rusinov et al. (1980). Indian altered basalts: point *5* from Papavassiliou and Cosgrove (1981). Subbetic Cretaceous black-shale: point *8* from López Galindo (1986). (B) Location of Betic Cordilleras smectites in diagram of McMurtry et al. (1983).

and quartz, all minerals of detrital origin, in contrast to the KTB layer, which exclusively consists of smectite. In view of this characteristic, the high values of its $\delta^{18}O$ content, the high content of iridium and gold and the absence of a negative anomaly in cerium, these authors interpreted the smectite as originating in a submarine diagenetic environment and deriving from aluminium- and iron-rich aluminosilicate impact spherules. In other KTB sections, such as Core 12 of DSDP Leg 86 Hole 577 A in the Northwestern Pacific (Smit, 1990; Smit et al., 1992) or the Beloc site in Haiti (Smit et al., 1992), smectite is observed as an alteration product of the spherules. Moreover, Klaver et al. (1986) reported in DSDP Leg 93 Hole 603 B (Northwestern Atlantic) massive glass spherules, which had been completely altered to Fe-rich dioctahedral smectites and are indicative of the KTB. Following this line of thought, we could also consider that a portion of the smectite in the KTB layers of the Betic Cordilleras sections could derive from the alteration of the very abundant Fe-oxide and K-feldspar spherules. The higher percentage of smectites in the KTB layer of the Caravaca section in comparison to the Agost section (Figs. 2–4) could therefore be explained by the higher degree of alteration presented by the spherules of the KTB layer in that section (Martínez Ruíz et al., 1992b; Martínez Ruíz, 1994). Thus, the presence of spinels of cosmic origin in the Caravaca sequence (Jéhanno et al., 1987) and the enrichment in platinum-group elements in the KTB layer at Agost and Caravaca (Martínez Ruíz et al., 1992a; Martínez Ruíz, 1994) suggest the presence of cosmic material in both sequences. However, the compositional similarity of the KTB smectites in both sections with the overlying and underlying levels (Table 3) and their similarity to smectites derived from the alteration of marine volcanic rocks (Fig. 5A) or to smectites derived from soil erosion (Fig. 5B) lead us to think that the sudden increase in smectite at the KTB layer can not be used as a conclusive argument to support an extraterrestrial origin.

The sudden decrease of kaolinite abundance in the KTB layer of the Betic Cordilleras sections relative to Cretaceous and Tertiary layers (Figs. 2 and 3) probably does not result from a climatic change, since kaolinite which mostly formed in soils is mixed with minerals eroded from rocky substrates (illite, chlorite). The decrease of kaolinite, together with that of illite and the increase of smectite, appears to be essentially related to an increasing supply of smectite favoured by weathering under conditions of decreased tectonic activity. The highest proportions of kaolinite occur in uppermost Cretaceous and lowermost Paleocene deposits and remain perceptible up to level A-10 (45%) at Agost and CA-9 (42%) at Caravaca (Figs. 2 and 3). This increase in the detrital character is consistent with the systematic presence of chlorite in the Tertiary levels, although in unquantifiable proportions (Martínez Ruíz et al., 1992a), as well as an increase in quartz contents in the lower Danian of Agost (Fig. 2) and Caravaca (Fig. 3). Geochemical data, especially high values of the D index, $D = Al/(Al + Fe + Mn)$ (Boström et al., 1969), during the latest Cretaceous ($D = 0.70$–0.72) and earliest Paleocene ($D = 0.71$) indicate that the detrital input was important (see Chamley et al., 1985; Chamley, 1989). On the other hand, the low values found in the KTB level (0.47 at Agost and 0.46 at Caravaca) would concur with the existence of some volcanic activity. These data are also consistent with those provided by the Ce/Ce* ratios as a parameter indicative of the degree of detrital influence in a basin (Ce* corresponds to the concentration obtained by extrapolation between La and Nd, as described by Courtois and Hoffert, 1977). The values reach 0.81 in the uppermost Cretaceous levels and 0.71–0.90 in the lowermost Paleocene levels, implying increase in the detrital contribution.

Another question to be considered is the rare-earth element (REE) composition, which can provide information about the sedimentary evolution of the studied series. In the case of essentially detrital sediments, the information given by the clay fraction is relevant to the source area of the sediments, since this fraction concentrates most of the REE, whereas the silt and sand fractions present lower REE contents (e.g., McLennan, 1989). The REE content in marine sediments marked by abundant authigenic phases basically depends on the REE content in seawater (e.g. Murray et al., 1990). In both Agost and Caravaca sections, the high REE content in uppermost Cretaceous and lowermost Danian levels could reflect the importance of the detrital input. The samples of the KTB layers in both sections present a significant decrease in the total REE content: KTB layer at Agost 44.35 ppm, 90.37 ppm at level +0.5 cm, 56.76 ppm at level −1 cm; KTB layer at Caravaca 14.85 ppm, 50.75 ppm at level +1 cm and 54.25 ppm at level −1 cm. This

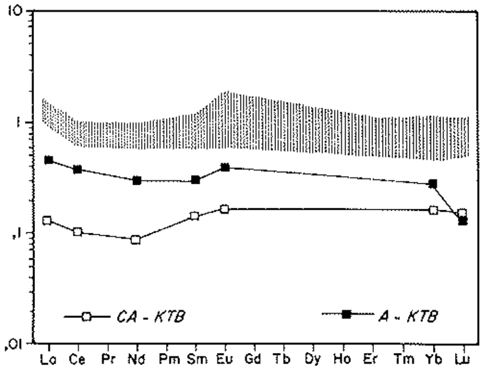

Fig. 6. REE content in the KTB samples from the Betic Cordilleras sections normalized to NASC (Haskin et al., 1968). The dotted zone corresponds to the REE-normalized values in Cretaceous and Tertiary levels.

is also indicated by the normalization to chondrites (Martínez Ruíz, 1994) and NASC patterns (Fig. 6). Smit and Ten Kate (1982) interpreted the low REE content in the KTB layer at Caravaca as a consequence of the low concentration of these elements in extraterrestrial material. Assuming the presence of such material, its contribution would have been very much diluted by the contribution of terrestrial material. However, in our opinion, the lower amounts of REE in the KTB layer would express the greater abundance of authigenic minerals (Fig. 6). The low REE content in seawater must also be taken into consideration since the smectites—the main components of the KTB layer in these series—are mostly formed authigenically in a marine environment (Fig. 5A). In this sense, the lower REE content in the Caravaca section (Fig. 6) could also correlate with the higher smectite content. In general in these sections, the REE content represents that inherited from the original minerals (illite, kaolinite, smectite), except in the KTB layer, where the presence of neoformed smectite could explain a lower amount of REE. In addition, the considerable development in the KTB layer of sulphides as framboids replacing the spherules during early diagenesis could also contribute to the low REE content.

4. Basque-Cantabrian Basin sections

4.1. Geological setting

The Basque-Cantabrian Basin is part of the Pyrenean system (Fig. 1B), its evolution continued from the Early Triassic to the end of the Eocene. From the latest Jurassic, the basin developed on a passive continental margin controlled by the displacements of the European and Iberian plates. Three major tectonic phases can be recognized (Rat, 1988): (1) a rifting phase during which the Iberian plate began to separate from the European plate, Late Jurassic–Barremian; (2) continental crust extension and development of the North Iberian margin, Aptian–middle Albian; and (3) formation of a marked continental slope separating the Iberian platform from bathyal floors, late Albian–Eocene. A calcareous flysch unit accumulated from the late Cenomanian to the Santonian in the St-Jean-de-Luz and Plencia troughs, and from the Campanian to the Maastrichtian in the large Orio trough extending from Hendaye to Biscay. The end of the Maastrichtian and the earliest Tertiary correspond to a period of quiet sedimentation (Rat, 1988). The sediments of the deep marine area were fine hemipelagites consisting of a mixture of calcareous and siliciclastic particles. The studied sections are located at Monte Urko (UR), Sopelana (SO) and Zumaya (ZU) in Spain, and at Hendaye (HY) and Biarritz (B) in France (Fig. 1B).

The lithology of the studied sections is dominated by marls and marly limestones. Except at

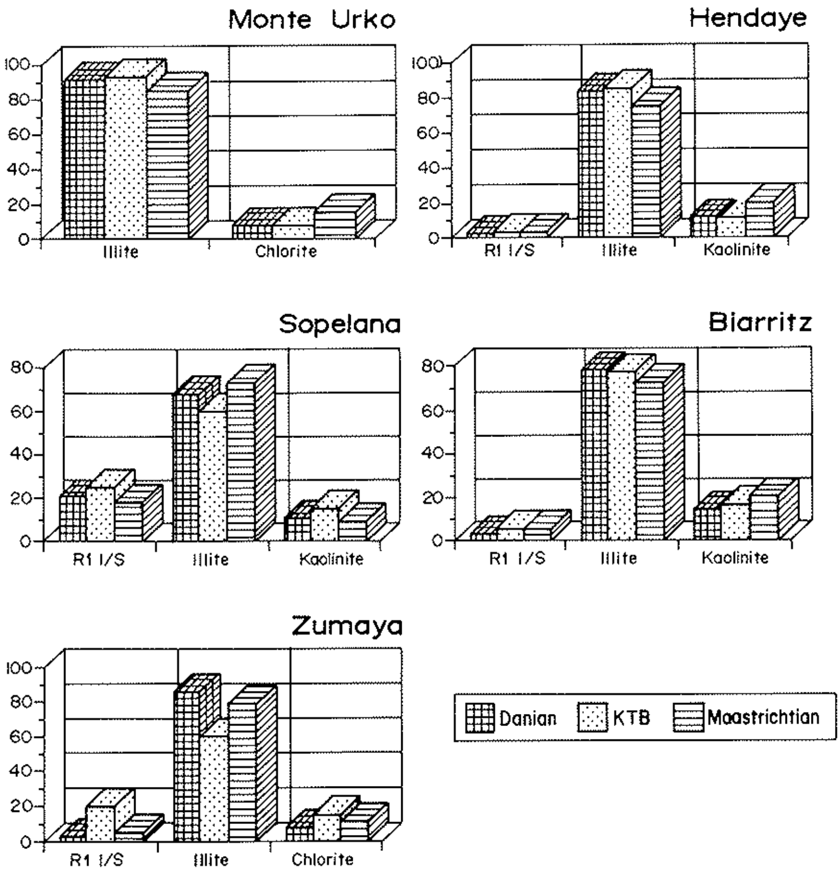

Fig. 7. Mean values (%) of the mineral contents in the sections investigated in the Basque-Cantabrian Basin.

Zumaya, the KTB layer is not as well preserved as in the Betic Cordilleras, and fewer spherules were found. The few spherules identified consist of pyrite at Zumaya and of Fe-oxides or nontronite in the other sections. At Monte Urko, the lithology of the uppermost Maastrichtian sediments consists of pink-red marls and marly limestones and the lowermost Paleocene comprises grey marls; a 2 mm thick, very clayey, brown, poorly preserved layer marks the KTB. At Sopelana, the uppermost Maastrichtian consists of alternating grey limestones and marly limestones, and the beginning of the Paleocene comprises a 30 cm thick layer of greyish-brown clayey marls; the KTB layer is 3 mm thick and consists of reddish-brown clay. At Zumaya, the KTB (3 mm) is composed of greyish-red clay, the uppermost Maastrichtian and lowermost Paleocene consist of marls. At Hendaye, the passage of the Maastrichtian light green marly limestones into the Paleocene is marked by a bright red clayey layer that gradually changes to pink marls and marly limestones; there is no boundary layer, in contrast to other sections. At Biarritz, the uppermost Maastrichtian comprises brown marly limestones, and the KTB is marked by a 2 cm thick layer of dark clay covered by Paleocene reddish-brown marly limestones.

4.2. Results

The clay mineral association of the KTB layer is characterized by dioctahedral detrital micas (phengite, illite) associated with illite/smectite mixed-layers R1, kaolinite and chlorite. There is no smectite. The nature of clay minerals in the KTB layer is similar to that of uppermost Cretaceous and lowermost Paleocene deposits (Fig. 7). Non-clayey accessory minerals detected by TEM in the KTB layer include rutile, Fe-oxides, pyrite, K-feldspar, gypsum and zircon. A relatively similar mineralogical composition is mentioned by Jéhanno et al. (1987) for the KTB layer in the Biarritz sequence, where these authors found illite, as the most abundant mineral, kaolinite, chlorite, quartz and feldspars, with absence of smectite.

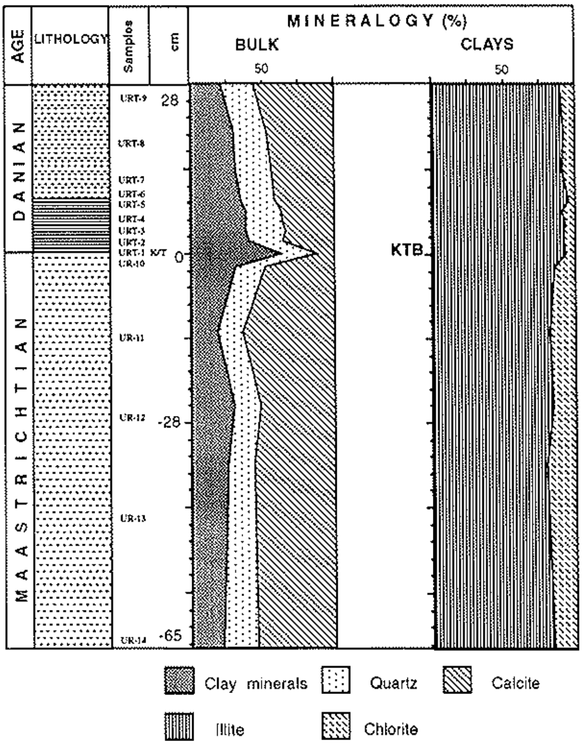

Fig. 8. Mineralogy at the Cretaceous–Tertiary transition in the Monte Urko section.

The quantitative mineralogical evolution of the series examined is shown in Figs. 8–12. The chemical characterization by TEM of detrital dioctahedral micas is given in Fig. 13. The chlorites correspond to the chamosite end-member, except for that analysed in the KTB layer at Monte Urko, which is clinochlore (Table 4). The illite/smectite mixed-layers R1 have the chemical composition shown in Table 5. The characteristic association of dioctahedral mica–R1 illite/smectite–kaolinite–chlorite indicates an important detrital contribution to the clay sedimentation (see Chamley, 1989). As in the Betic Cordilleras, the mineralogy at the Cretaceous–Tertiary transition in all the sections of the Basque-Cantabrian Basin is qualitatively very similar in the different levels investigated. In these sections, however, the clay mineral composition is quantitatively more varied according to the location than in the Betic Cordilleras (Fig. 7), although some general trends can be detected (Fig.

13). There is a predominance of compositions corresponding to detrital micas close to, or in some cases coincident with muscovite. There is a clear phengitic trend, with the illite character being minor and no relation existing between the chemical composition and the age of the samples. Chlorite is scarce or absent in the Biarritz, Hendaye and Sopelana sections, where it invariably appears as a trace mineral. By contrast, chlorite is very well defined in the Monte Urko and Zumaya sections (Figs. 8 and 10). The kaolinite contents vary from one section to another in the KTB layer, and from uppermost Maastrichtian to lowermost Danian deposits (Figs. 8–12).

4.3. Discussion

Micas and chlorite are considered as often derived from the erosion of rocky substrates, whereas kaolinite is dominantly inherited from soils developed under the warm and humid climate which prevailed in peri-Atlantic domains during the Cretaceous and most of the Tertiary (see Chamley, 1979, 1989; Miller et al., 1987). The greater abundance of kaolinite in some sections or at some levels can hardly be interpreted as the result of climatic change, as it is closely associated to minerals eroded from the rocky substrates, but rather indicates relative proximity to exposed areas. This is especially the case for the Biarritz, Hendaye and Sopelana sections (Fig. 1B), which are located in proximal positions on the eastern and western platforms of the Cantabria Sea (Mathey, 1988). In general in the Basque-Cantabrian Basin, the sedimentation was largely under the control of Late Cretaceous–early Cenozoic tectonic processes, which were responsible for the reworking of abundant detrital clay minerals, particularly illite and chlorite. The denudation of the Palaeozoic massifs, as well

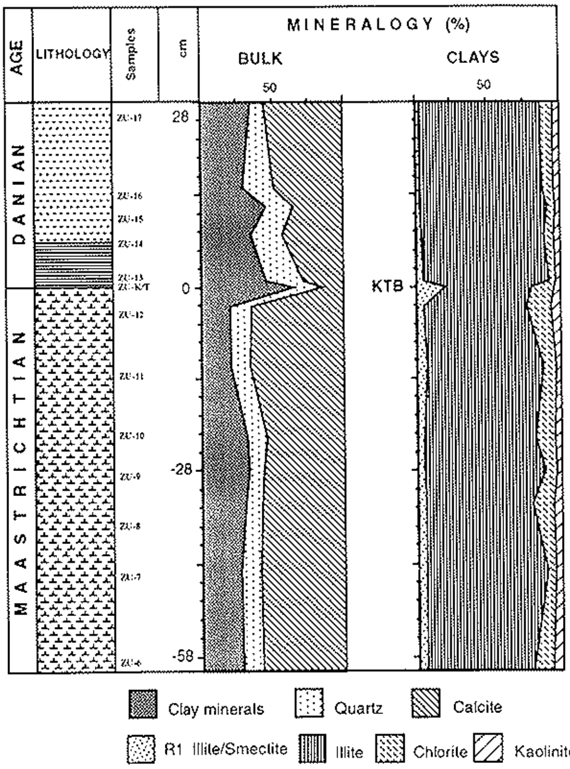

Fig. 10. Mineralogy at the Cretaceous–Tertiary transition in the Zumaya section.

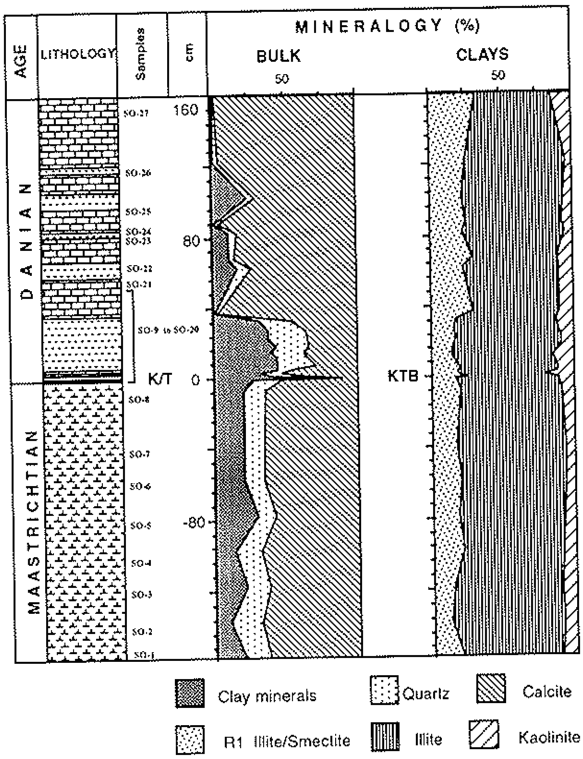

Fig. 9. Mineralogy at the Cretaceous–Tertiary transition in the Sopelana section.

as of the successive Mesozoic sedimentary blankets, favoured the direct supply to the basin of rock-derived minerals and prevented the formation of pedogenic smectite. The source areas underwent a continuous uplift and therefore a continuous and active erosion, which led to an active coarse siliciclastic, illite- and chlorite-bearing sedimentation in the basin. The siliciclastic supply became finer and enriched in clay in the Orio trough at the end of the Cretaceous and at the beginning of the Paleocene, suggesting the source areas had already been strongly eroded and partly flattened (Mathey, 1988).

The existence in noticeable amounts of illite/smectite mixed-layers R1 (up to 20% of the clay fraction) is attributed to the degree of burial diagenesis, which also explains the absence of smectite as an independent mineral phase in the sections of the Basque-Cantabrian Basin. This interpretation agrees with the data of Aróstegui

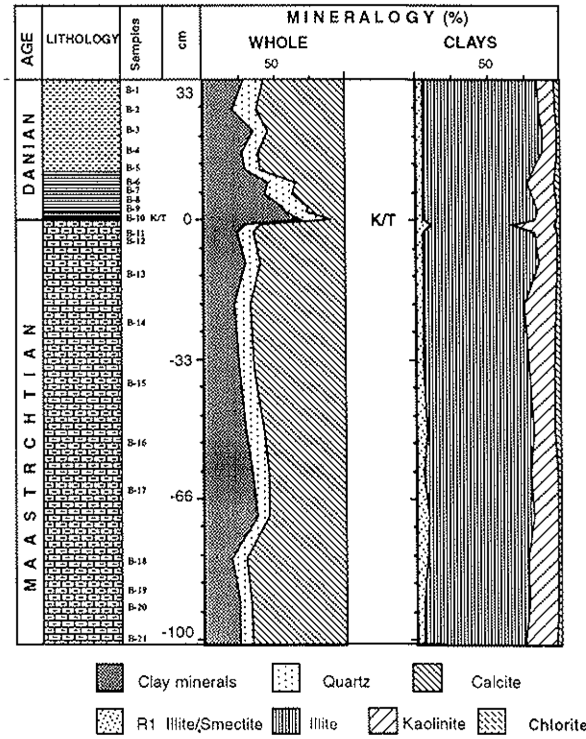

Fig. 12. Mineralogy at the Cretaceous–Tertiary transition in the Biarritz section.

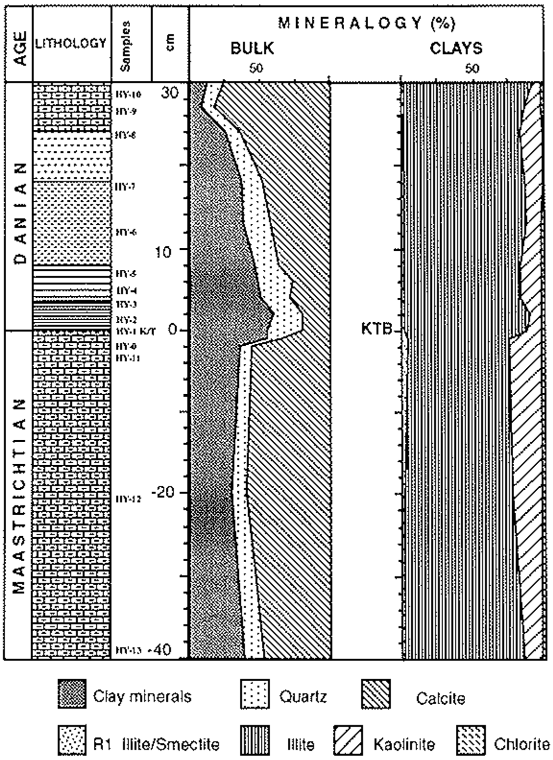

Fig. 11. Mineralogy at the Cretaceous–Tertiary transition in the Hendaye section.

et al. (1991) in other sections of the northern part of this basin, where diagenesis developed until the smectite surficial domains completely disappeared (formation of R = 3) in Lower Cretaceous deposits. The clay mineral association found in the sections studied here is compatible with moderate conditions of clay diagenesis attained in the basin in which kaolinite, illite/smectite mixed-layers R1, and of course detrital illite and chlorite, are stable. It should be stressed that the absence of smectite, due to its diagenetic conversion to R1 mixed-layers, prevents identification of the contribution of any exotic material (glass, meteorites), the alteration of which could have given way potentially to the formation of smectite before the clay diagenesis started.

The Monte Urko and Zumaya sections display especially high proportions of illite (average of 80%) and significant amounts of chlorite (up to 15%), and no or only very little kaolinite and/or R1 mixed-layers (Fig. 7). Both sections, and particularly the Monte Urko section where illite largely exceeds 80%, were situated during the Late Cretaceous and early Palaeogene in the Plencia trough (Mathey, 1988) where active deposition and overburden were favoured. These series may have experienced stronger burial diagenesis constraints than the series cropping out in the three other sections (Fig. 1B), which were located on lesser buried South Aquitaine or Navarro–Cantabrian platforms. The palaeogeo-

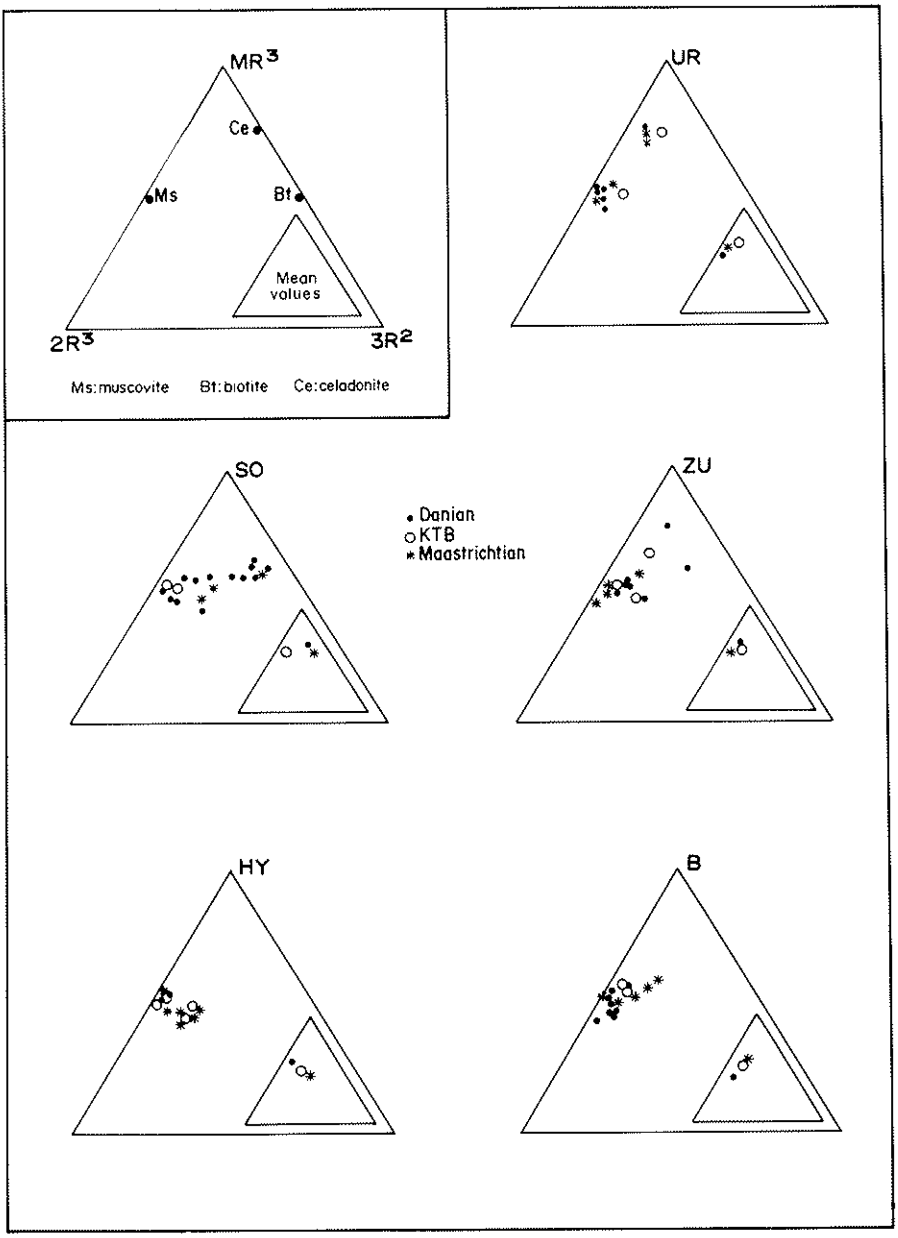

Fig. 13. Composition of the dioctahedral micas of the Basque-Cantabrian Basin in Velde's (1985) diagram. $MR^3 = \text{Na} + \text{K} + 2\text{Ca}$, $2R^3 = (\text{Al} + \text{Fe}^{3+} - MR^3)/2$, $3R^2 = (\text{Mg} + \text{Fe}^{2+})/3$.

Table 4
Basque-Cantabrian Basin; chlorite formulae

Sample	Si	Al^{IV}	Al^{VI}	Mg	Fe	Ti	Mn	Cr	Σ(Oct.)	K	Ca
URT-8 (20 cm +)	2.74	1.26	2.29	1.39	2.20	–	–	0.05	5.93	–	–
URT-2 (2 cm +)	2.96	1.04	1.75	1.26	2.56	–	–	–	5.57	0.15	–
URT-1K/T (0 cm)	2.83	1.17	2.31	2.08	1.04	–	–	–	5.43	–	–
URT-10 (2 cm –)	3.05	0.95	2.42	0.95	1.87	–	–	–	5.24	0.03	0.01
SO-K/T (0 cm)	2.70	1.30	2.00	1.21	2.24	–	–	–	5.45	0.03	0.03
ZU-13 (1 cm +)	2.92	1.08	1.73	1.57	1.97	0.27	0.01	–	5.55	0.16	0.03
ZU-K/T (0 cm)	2.50	1.50	1.90	1.47	1.87	0.47	–	–	5.71	0.14	0.02

Table 5
Basque-Cantabrian Basin; illite/smectite mixed-layer R1 formulae

Sample	Si	Al^{IV}	Al^{VI}	Mg	Fe	Ti	Mn	Σ(Oct.)	K	Ca
SO-10 (1 cm +)	3.80	0.20	1.30	0.21	0.37	0.10	0.01	1.99	0.48	0.08
SO-K/T (0 cm)	3.43	0.57	1.50	0.26	0.26	0.10	0.02	2.14	0.49	0.03
	3.41	0.54	0.91	0.22	0.64	0.24	0.02	2.03	0.65	0.04
	3.40	0.60	1.04	0.21	0.74	0.05	–	2.04	0.55	–
ZU-10 (23 cm –)	3.50	0.50	1.85	–	0.19	–	–	2.04	0.51	0.03
ZU-K/T (0 cm)	3.87	0.13	1.05	0.08	1.00	0.18	–	2.31	0.42	0.05
HY-O [a] (1 cm –)	3.68	0.32	1.40	0.14	0.34	–	–	1.88	0.51	–
HY-K/T (0 cm)	3.63	0.37	1.55	0.20	0.35	–	–	2.10	0.63	–
B-8 (3 cm +)	3.61	0.39	1.59	0.16	0.39	–	–	2.14	0.53	–
B-9 (2 cm +)	3.48	0.52	1.65	0.22	0.29	–	–	2.16	0.42	0.06
B-10K/T (0 cm)	3.85	0.15	1.31	0.08	0.70	0.02	–	2.11	0.61	–
	3.53	0.47	1.51	0.12	0.56	0.05	–	2.24	0.43	0.03
	3.54	0.46	1.31	0.17	0.57	–	0.01	2.06	0.39	0.04
	3.46	0.54	1.20	0.20	0.57	0.04	–	2.01	0.57	0.07
B-11 (1 cm –)	3.56	0.44	1.00	0.21	0.97	–	0.01	2.19	0.43	0.07
B-16 (50 cm –)	3.54	0.46	1.10	0.49	0.81	–	–	2.40	0.39	0.08

[a] Mean values of three points.

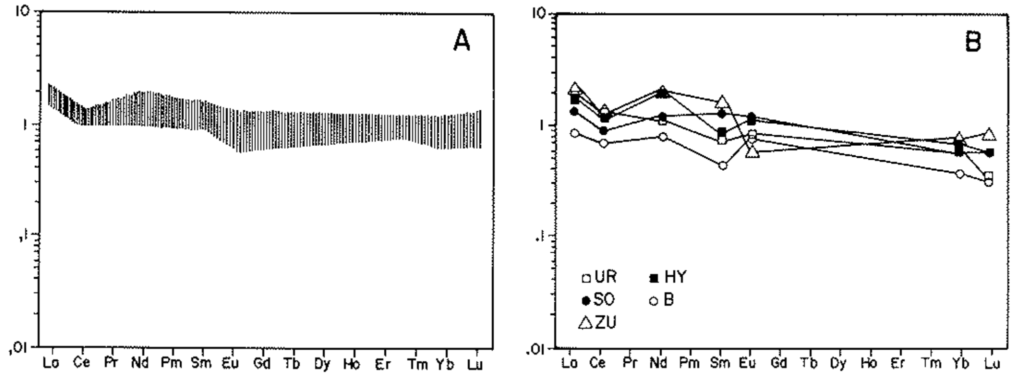

Fig. 14. REE content in Basque-Cantabrian Basin sections normalized to NASC (Haskin et al., 1968). (A) The shaded zone corresponds to REE-normalized values in Cretaceous and Tertiary levels. (B) REE-normalized values in the KTB layers.

graphic location of the deposits would therefore have determined: (1) a slight diagenetic evolution at Biarritz, Hendaye and Sopelana sections, which comprise less illite and chlorite and systematically contain kaolinite and mixed-layers; and (2) a relatively stronger diagenetic evolution at Monte Urko and Zumaya sections, which are richer in illite and chlorite and almost devoid of kaolinite.

Mineralogical and geochemical data from the Basque-Cantabrian Basin suggest that the detrital input was especially intense at the Cretaceous–Tertiary transition, probably because of tectonic uplift linked to the first formation stages of the Pyrenean chain: (1) the abundance of illite and chlorite is associated with significant amounts of detrital quartz (Figs. 8–12) and feldspars, all species which are much more abundant than in Betic Cordilleras sections; (2) the detrital *D* index, Al/(Al + Fe + Mn) (Boström et al., 1969) tends to be higher than in southeastern Spain—the values vary from 0.65 to 0.75 in the uppermost Maastrichtian, 0.64 to 0.78 in the lowermost Danian, and 0.64 to 0.71 in the KTB layer; (3) the rare-earth elements (REE) analysis reveals high values (Fig. 14) suggesting active detrital input. The samples of the KTB layer present patterns of REE normalization to NASC (Fig. 14B; Haskin et al., 1968) similar to those of Cretaceous and Tertiary levels (Fig. 14A); there is no decrease of REE contents in the KTB layer, which suggests an important detrital input to the basin obliterating the presence of possible authigenic minerals. The REE curves, which show an enrichment in light REE and a basically flat pattern for heavy REE, agree with an origin of sediments in the upper continental crust (acid rocks), according to Taylor and McLennan (1985) and McLennan (1989). The sediments issuing from exposed continental areas probably consist of reworked products from old sedimentary rocks and metamorphic rocks.

5. Comparison of both areas and conclusion

The Cretaceous–Tertiary transition in southeastern and central northern Spain is characterized by two different clay mineral associations: smectite, kaolinite and illite dominate in the Betic Cordilleras, whereas illite, R1 illite/smectite, and/or kaolinite and chlorite prevail in the Basque-Cantabrian Basin. Trace amounts of palygorskite and chlorite are identified in the Betic domain. In all sections investigated the uppermost Maastrichtian and lowermost Danian sediments have very similar clay mineral associations, which show little or no difference from those of the KTB layer. The quantitative mineralogical variations in the KTB layers do, however, exist. In the Betic Cordilleras, the amount of smectite increases at the expense of kaolinite, which is attributed to both an input of volcano-derived minerals and a weathering of Fe-oxide and K-feldspar spherules. In the Basque-Cantabrian Basin, the situation is more varied: in some sections, kaolinite and R1 illite/smectite increase whereas, in others, illite increases and kaolinite decreases, or illite and chlorite are the only clay species identified. There is, therefore, no uniform pattern of mineralogic variation in the KTB sediments among the different studied sections.

The lack of an obvious trend in the KTB clay mineral associations implies that regional rather than global events, within a single terrestrial or extra-terrestrial event, are the major control on clay mineral associations. This agrees with Robert and Chamley's (1990) interpretation deduced from the study of various land and ocean KTB sections. The variability of clay mineral associations in the KTB transition are namely controlled by erosional processes occurring in the surrounding source areas and by the palaeogeography of the depositional basins. For instance, the abundance of dioctahedral smectites in the Betic Cordilleras could be related to several factors, such as volcanic activity, development and erosion of continental soils, and alteration of very abundant spherules. In the Basque-Cantabrian Basin, the tectonic instability played an important role in the supply of abundant illite and chlorite derived from rocky substrates, and of kaolinite reworked from soil formations.

The diagenetic control on the clay mineral association is especially significant in the Basque-Cantabrian Basin, as indicated by the absence of smectite, by the presence of R1 illite/

smectite mixed-layers probably derived from smectite, and by the abundance of illite. The clay diagenetic processes appear to have been more effective in the central part of this basin, marked by active sedimentation in the Plencia trough, relative to adjacent platforms, enriched in kaolinite and mixed-layers.

The values of Al/(Al + Fe + Mn) and Ce/Ce* ratios and the rare-earth elements content in the Betic Cordilleras indicate an important detrital input during the latest Cretaceous and earliest Paleocene. The detrital influence is higher and more variable in the Basque-Cantabrian Basin than in the Betic Cordilleras, where the clay sedimentation displays more regional than local characteristics.

Finally, the clay mineral and chemical successions identified at the Cretaceous–Tertiary transition and in the KTB layer in both the southern and northern Spain sections reflect various geodynamical and post-sedimentary processes, which occurred in the source and depositional areas marked by distinct geological rocks and history. In these marine clay successions, the local and regional influences determine the clay mineral associations, and thus they cannot be used as a record to distinguish global extraterrestrial or terrestrial events.

Acknowledgements

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