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Review of the mineralogy of the Cretaceous-Tertiary boundary clay: evidence supporting a major extraterrestria catastrophic event

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ABSTRACT: The proposed impact event at the end of the Cretaceous resulted in mass extinctions and subsequently significant variations in the geochemical and mineralogical composition of the sediments marking the K/T boundary. The impact-generated material derived from target rocks produced the ejecta layer deposits around Chicxulub crater, which were subsequently diagenetically altered to mainly smectite in marine sections and to kaolinite in continental sections. The fireball layer represents the cosmic dust dispersed and deposited globally and contains smectite derived from the alteration of microkrystites and the finest fraction. The lowermost Danian clay layer, recognized in marine sections, resulted from the sudden decrease in ocean productivity and represents a reduced sedimentation deposit. Its clay mineral associations depend on local environmental conditions and diagenetic processes. Overall, the diagenetic alteration of the boundary materials resulted in a significant modification of original signatures. The composition of the clay mineral phases can, however, still be evidence of the nature of the precursor materials providing evidence for an extraterrestrial impact event.

KEYWORDS: Chicxulub, K/T, clay minerals, ejecta layer, fireball layer, clay boundary layer, impa glasses, microkrystites, diagenesis, DSDP, ODP.

The Cretaceous-Tertiary boundary (K/T) event remains one of the most controversial subjects in Earth Sciences, due both to the great biological crisis marking the end of the Cretaceous (~65 Ma) and to the geochemical and mineralogical anomalies associated with the sediments of this age. Renewed discussion on the origin of the K/T event arose ~20 years ago with the discovery of Ir anomalies in the sediments marking the K/T boundary at Stevns Klint (Denmark), Gubbio (Italy) (Alvarez *et al.*, 1980) and Caravaca (Spa (Smit & Hertogen, 1980).

Since Alvarez *et al.* (1980) proposed the imp theory to explain the mass extinction at the end the Cretaceous, several lines of evidence have be cited to support their model, including noble me anomalies (*cf.* Smit & Hertogen, 1980; Kyte *et* 1980, 1985; Martínez-Ruiz *et al.*, 1992), discovery of shocked minerals (*cf.* Bohor, 199 Ni-rich spinels (*cf.* Kyte & Smit, 1986; Bohor Foord, 1987; Izett, 1987; Bohor, 1990; Robin *et* 1991), and the presence of spherules that may impact-related (Smit & Klaver, 1981; Montanari *al.*, 1983; Montanari, 1991; Smit *et al.*, 19

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Pollastro & Bohor, 1993; Martínez-Ruiz *et al.*, 1997). However, this hypothesis has not been universally accepted, and some authors (*cf.* Officer & Drake, 1985; Courtillot *et al.*, 1986, 1988; Courtillot & Cisowski, 1987) proposed that intense volcanic activity at the end of the Cretaceous could have created adverse environmental conditions producing the same effects as those caused by a supposed meteorite impact.

The catastrophic K/T event resulted in major palaeoceanographic changes leading to significant variations in the chemistry of the terminal Cretaceous ocean water as revealed by trace-element composition and significant variations in the isotope composition of C, O and Sr. The carbon isotope surface-to-bottom water gradient, for instance, collapsed to zero or even reversed as a consequence of reduced productivity (Hsü & McKenzie, 1985, 1990). Thus, a large negative anomaly in $\delta^{13}C$ values marks the K/T boundary in marine sections worldwide. Variations in $\delta^{18}O$ values have typically been interpreted as the result of initial cooling followed by gradual warming across the K/T boundary (*cf.* Zachos *et al.*, 1989). However, several factors other than temperature can affect the oxygen isotope composition, and there is no general agreement about the magnitude of the $\delta^{18}O$ variations (*cf.* Perch-Nielsen *et al.*, 1982; Margolis *et al.*, 1987). Ocean fluctuations in $^{87}Sr/^{86}Sr$ resulted in a spike that has been attributed to an increased input of radiogenic Sr produced by acid rain after the impact (Martin & MacDougall, 1991; Martínez-Ruiz, 1994), explosive volcanism (Javoy & Courtillot, 1989) or erosion as a consequence of the transgression (Officer *et al.*, 1987).

The vast literature on this topic (numbering thousands of contributions) prevents our mentioning all the sites and geochemical anomalies reported thus far. In particular, the Deep Sea Drilling Project (for example, DSDP Site 524 in the South Atlantic and Hole 577 in the Pacific) and the Ocean Drilling Program (ODP Sites 689-690 in the Southern Atlantic, ODP Holes 603B and 390A, and ODP Legs 165, 171B and 174AX in the North Atlantic margin) have contributed to our knowledge through the recovery of expanded K/T boundary sequences. Despite all the advances made from numerous studies of this devastating impact and its environmental consequences, more work is undeniably needed for a complete understanding.

With this review article, our aim was to summarize the clay mineralogical data published on the K/T boundary and demonstrate t
information supports the extraterrestrial
hypothesis.

K/T BOUNDARY LITHOLO

Most of the published data provide co
evidence supporting the extraterrestrial hy
first proposed in the 1980s, as well as the
of the impact site at the Chicxulub crate
Yucatán Peninsula of Mexico. Evidence
occurrence of the K/T crater at this loc
apparently overwhelming, as demonstra
impact signatures recognized in sequenc
the Gulf of Mexico area, as well as
measurements and drill-core data (Hildel
al., 1991; Koeberl & Sigurdsson, 1992; Sha
al., 1993; Alvarez *et al.*, 1995; Schultz &
1996; Smit, 1999).

The K/T boundary layer deposits are pa
ejecta blanket from this impact crat
Chicxulub impact produced distinctive
material (*cf.* Alvarez *et al.*, 1995; Pier
Melosh, 1999), mostly derived from the
front of the melted target rocks deposite
proximity of the crater site (the ejecta layer)
vertically expanding hot vapour plume of v
bolide with entrained melted target rocks
dispersed and deposited globally (the fireba
Thus, locations proximal to Chicxulub show
contributions of the ejecta blanket derived
target rocks, whereas distal sections contai
component of extraterrestrial material (Fig.
distance from Chicxulub is, therefore, t
factor controlling the lithology, thickn
mineralogical and geochemical compos
K/T boundary deposits.

Proximal sites (*cf.* Yucatán, Belize, S
NE Mexico, Central Mexico, Guatemala,
USA, Haiti, DSDP/ODP sites; Fig. 1a)
1–11 m thick complex clastic deposits tra
by gravity flows, landslides and tsunamis.
of proximal ejecta can be divided in
subzones: (1) a continuous ejecta blanket e
radially up to some 600 km on the
peninsula consisting of polymictic me
microbreccias composed of moderately
clasts of extremely variable size: (2) a
area extending south of the crater to ~
characterized by carbonate megabreccias; a
third subarea occurring around the Gulf of
and in the Caribbean characterized by thick

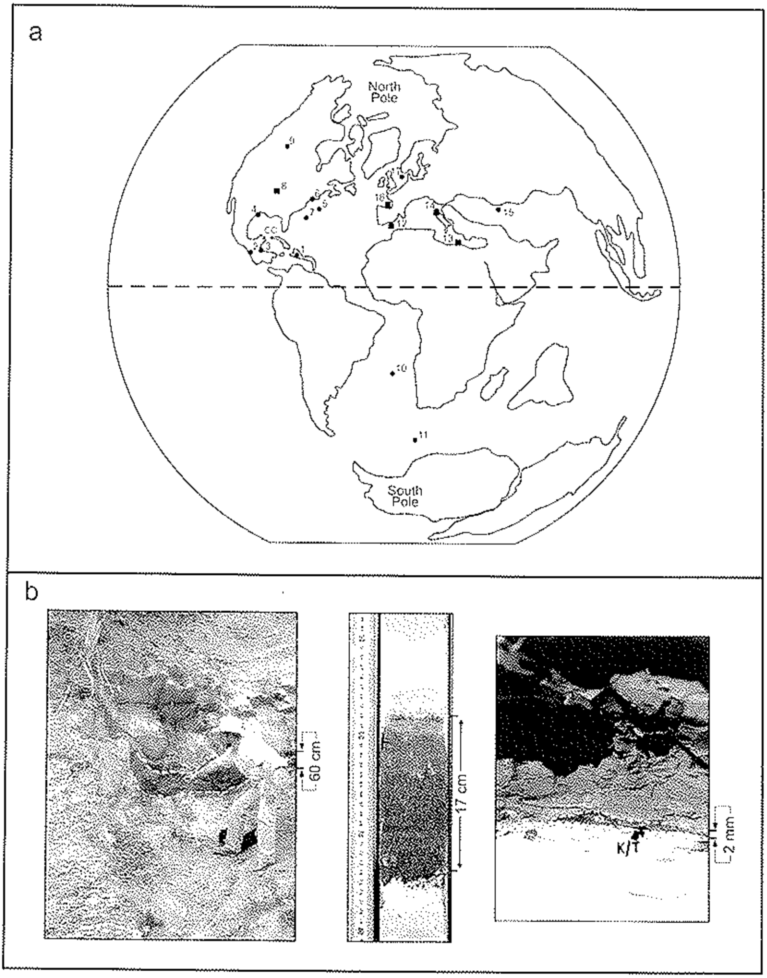

FIG. 1. (a) Palaeogeographical map of the Late Cretaceous (modified from Stanley, 1986) showing the location the K/T revised sections. 1. Haiti, 2. Guatemala, 3. Belize, 4. El Tecolote, 5. DSDP 603B, 6. Bass River, 7. Bla Nose, 8. Western Interior of North America sections, 9. Frenchman river, 10. Walvis Ridge, 11. Maud Ridge, Agost and Caravaca sections, 13. Tunisian sections, 14. Italian sections, 15. Koshak, 16. Basque-Cantabri sections, 17. Stevns Klint. CC: Chicxulub crater. (b): Photographs showing the thickness of the K/T bounda layer in El Ceibo section (left), Blake Nose-ODP Leg 171B Hole 1049A (centre) and Agost section (right).

deposits overlain by ballistically transported debris and melt spherules (*cf.* Pope *et al.*, 1996; Claeys *et al.*, 1998; Smit, 1999).

Further away, ~ 2000 km to the northeast on the North American margin, the K/T boundary is marked by an ejecta layer from 9 cm up to 17 cm thick (Fig. 1b), mainly consisting of spherical and oval-shaped spherules (*cf.* ODP Leg 171B, Bass River ODP Leg 174AX, and DSDP Leg 603B; Fig. 1a). At the Blake Nose Site 1049, the ejecta is capped by a 3 mm thick orange Fe oxide deposit that initially appeared to be the fireball lay (Norris *et al.*, 1998) equivalent to the uppermo layer found in the K/T boundary sequence in th Western Interior of North America (Pollastro Bohor, 1993). A geochemical and mineralogic study of this orange layer revealed, however, that resulted from the diagenetic remobilization of F with a non-enhanced extraterrestrial-element flu (Martínez-Ruiz *et al.*, 2001b). Moreover, th spherule bed also contains some lithic fragment Cretaceous foraminifera and clasts of Cretaceou material, which indicate reworking of the spherule bed material. This observation is further supported by the variable thickness of the spherule bed in the three holes drilled at Site 1049 in the Blake Nose Plateau (Klaus *et al.*, 2000).

At locations 2500–4000 km from the Chicxulub crater in the Western Interior of North America (*cf.* Madrid, Starkville, Sugarite, Raton; Fig. 1a), the K/T boundary interval consists of a 3 cm thick, two-layered, clay-rich unit commonly overlain by a thin (10–20 cm) bed of lignite. Mineralogical, textural and chemical evidence support the interpretation that this K/T boundary sequence represents the altered fallout ejecta from the Chicxulub impact. Its dual nature also supports different ejection and dispersal mechanisms of the ejecta material (*cf.* Pollastro & Pillmore, 1987; Pollastro & Bohor, 1993).

The most distal sites (>4000 km, Fig. 1a), such as those from the Mediterranean (*cf.* Agost and Caravaca in Spain, El Kef and Elles II in Tunisia, Petriccio and Gubbio in Italy) and NE Atlantic regions (Zumaya, Monte Urko, Sopelana and Biarritz in the Basque-Cantabrian Basin, and Stevns Klint in Denmark) are characterized by 2–3 mm thick laminae diagenetically altered and enriched in Platinum Group Elements (PGE), microkrystites and shocked minerals (Fig. 1b). In some Mediterranean sections, such as Agost, Caravaca (*cf.* Martinez Ruiz *et al.*, 1997; Smit, 1999) and El Kef, the K/T boundary layer is very well preserved (Lindinger, 1988; Adatte *et al.*, 2002; Bensalem, 2002) and the spherules are very abundant. In contrast, in the Basque-Cantabrian basin, spherules are not as abundant and the K/T boundary layer is poorly preserved mainly due to local tectonic processes (Ortega-Huertas *et al.*, 1995, 1998). At Stevns Klint (Denmark), the K/T boundary is marked by a red rust basal layer overlain by a black marl layer (*cf.* Schmitz, 1985; Elliott, 1993). In all these distal sections, this red layer is equivalent to the uppermost layer of the two-layered clay unit described for the Western Interior of North America sections (Pollastro & Bohor, 1993).

K/T BOUNDARY CLAY-MINERAL ASSOCIATIONS

The deposition of the material ballistically ejected from the Chicxulub crater resulted in a layer, commonly named the ejecta layer, which separates Cretaceous from Tertiary sediments. Thi
contains a major contribution of targ
material and is deposited in sections aro
Chicxulub crater (*cf.* Gulf of Mexico). O
the ejecta layer is an ~3 mm thick layer, k
the fireball layer, which represents the cos
dispersed and deposited globally. It
preserved at distal sections. Above the
layer, the sudden decrease in ocean product
a consequence of the catastrophic event at
of the Cretaceous, resulted in the depositio
lowermost Danian clay layer, which also m
K/T boundary in most of the sections. Most
commonly use the term clay boundary layer
to one or all of the aforementioned layers.
we use the term clay boundary layer to refe
the lowermost Danian clay layer in
sequences. The main clay-mineral asso
characteristic of representative K/T secti
given in Table 1.

Clay ejecta layer and/or fireball layer

Gulf of Mexico. The ejecta layer (i.e. t
liquid and vaporized rock ejected ballistica
an impact crater) at proximal sites in the
Mexico area comprises materials of quite
composition, ranging from pure carbonate t
melt and mixtures of these two end-memb
indicates that the melt zone during impact
deep in the crystalline basement but
completely homogenized (*cf.* Kettrup *et al.*
At the various Gulf of Mexico sites, the
clay-mineral associations result from the a
of variable silicate/carbonate mixtures. Thu
Guatemala sections (El Caribe, El Ceibo) t
layer is composed of glass spherules altered
crystallized Ca-Mg-(Na)-rich smectite (Deb
al., 1999). At the Belize site (Albion Island
the ejecta layer derives from the outer porti
continuous ejecta blanket of the Chicxulu
The smectite, which is present in the brecc
and clay-forming spheroids, results f
alteration of impact-generated material (Po
1999). These authors report that the gr
spheroids are compositionally similiar to th
palagonites formed from K/T bounda
spherules. In the Haiti section, the eje
consists of a basal layer very rich in sme
spherules, overlain by a unit consisting of a
of smectite spherules in a carbonate/smectit
Spherical to ellipsoidal smectite bodies der

TABLE 1. Main clay mineral associations.

Location	Section	Type of layer	Clay mineral associations	Reference
Gulf of Mexico	Haiti	EL	S	1, 2, 3
	Guatemala	EL	S - (K)	4.5
	Belize	EL	S	6
	El Tecolote	EL	Ch - (I - I-S - Ch-C)	7
North American Margin	DSDP 603B	EL	S	8
	Bass River	EL	S	9
	Blake Nose ODP Leg 171B	EL	S	10
Western Interior	Madrid, Starkville, Sugarite, Raton,	EL	K	11, 12, 13
of North America	Madrid, Starkville, Sugarite, Raton,	FL	S	11, 12, 13
Western Canada	Frenchman River	FL	S - (K)	14
Southeastern Atlantic	Walvis Ridge Sites 525-529	CBL	S - I - Ch - (I-S - K)	15
	Walvis Ridge Site 524 Leg 73	CBL	S - (I - K)	16
Southern Ocean	Maud Ridge Sites 689-690	CBL	S - I - Ch - (I-S - K)	15
Mediterranean Domain	Agost, Caravaca	FL	S	17, 18
	Agost, Caravaca	CBL	S - K - I	17, 18
	El Kef	FL	S - (K - I - Ch)	18
	El Kef	CBL	S - K - (I)	18
	Elles II	FL	S - (K - I - Ch)	19
	Elles II	CBL	K - (S - Ch - I)	20
	Gubbio	FL?-CBL?	I - K - (I-S)	21
	Gubbio	CBL	K - S - Ch - I - I-S	15
	Petriccio	FL	S - (I - K)	18
	Petriccio	CBL	I - S - (K)	18
Boreal Paratethys	Koshak	CBL	I - (S - K - Ch)	22
NE Atlantic	Basque-Cantabrian Basin	FL	I - (I-S - K - Ch)	18
	Basque-Cantabrian Basin	CBL	I - Ch; I - I-S - K; I - I-S - Ch	17,18
	Stevns Klint	FL	S	23, 24, 25, 26
	Stevns Klint	CBL	S - I-S - (I)	24, 25

S = smectite
I = illite
I-S = illite-smectite mixed layer
Ch = chlorite
K = kaolinite
Ch-C = chlorite-corrensite mixed

EL =Ejecta Layer
FL = Fireball Layer
CBL = Clay Boundary Layer

1. Izett *et al.* (1991)
2. Kring & Boynton (1991)
5. Debrabant *et al.* (1999)
6. Pope *et al.* (1999)
7. Mata *et al.* (2001)
8. Klaver *et al.* (1987)
9. Olsson *et al.* (1997)
10. Martínez-Ruiz *et al.* (2001a)
13. Pollastro & Bohor (1993)
14. Lerbekmo *et al.* (1987)
15. Robert & Chamley (1990)
16. Hsü *et al.* (1982)
17. Ortega-Huertas *et al.* (1995)
18. Ortega-Huertas *et al.* (1998)
21. Rampino & Reynolds (1983)
22. Pardo *et al.* (1999)
23. Kastner *et al.* (1984)
24. Elliott *et al.* (1989)
25. Elliott (1993)
26. Bauluz *et al.* (2000)

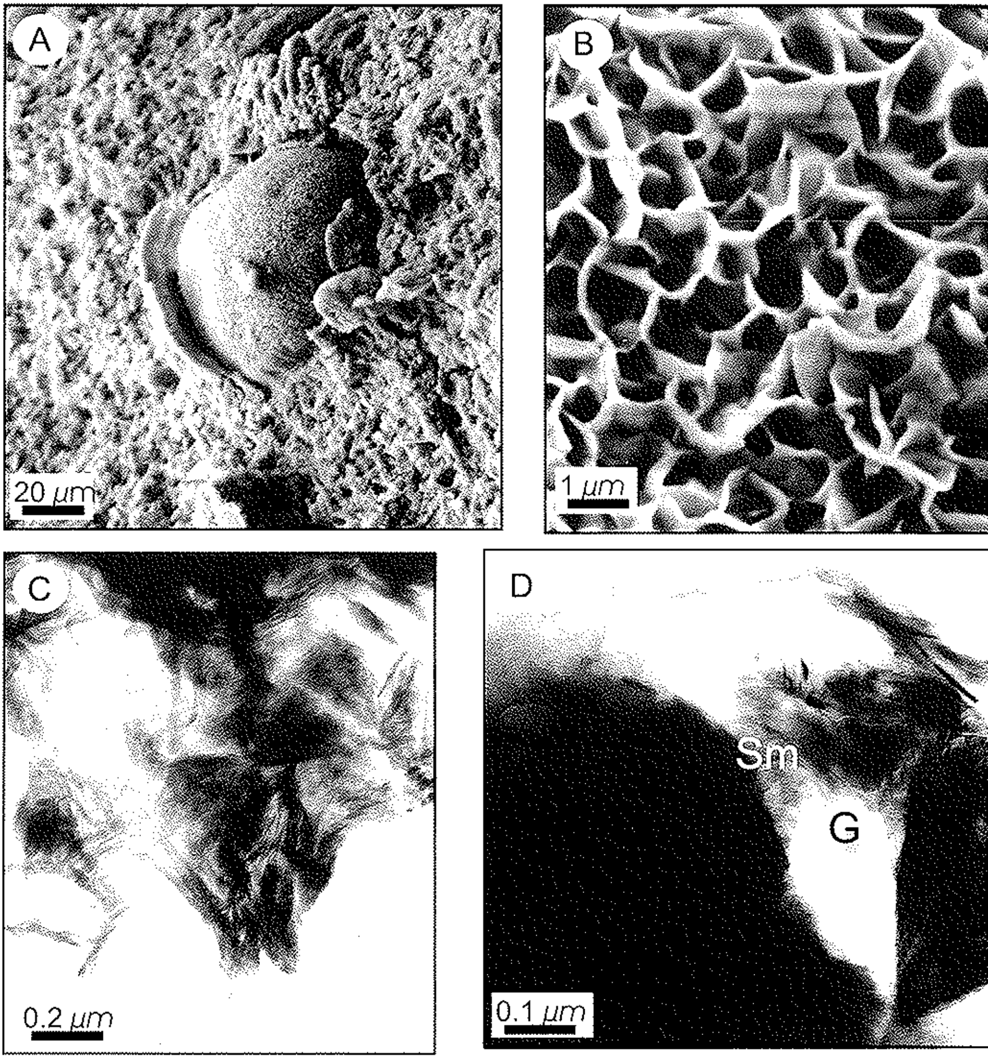

FIG. 2. Electron micrographs from Blake Nose (Site 1049) spherule bed. (a) SEM image of smectite s (b) SEM higher-resolution micrograph of the smectite. (c) TEM micrograph of smectite. (d) TEM image (G) altering to smectite (S).

impact-glass alteration (Izett *et al.*, 1991; Kring & Boynton, 1991; Koeberl & Sigurdsson, 1992). Soria *et al.* (2001) and Mata *et al.* (2001) have analysed the clay mineralogy of the ejecta layer in the El Tecolote section (NE Mexico) and report that chlorite is the main phyllosilicate, resulting from spherule alteration. Illite, illite-smectite mixed layers (I-S) and chlorite-corrensite mixed layers are also present in the matrix of the spherule layer. Chlorite in the spherules occurs as radial aggregates with individual defect-free crystals.

North American Margin. On the North A margin, the ejecta layer mostly consists c spherules composed of smectite (Fig. 2a,b,c is derived from the diagenetic alteration of glass. At Blake Nose, different smectite c tions result from the alteration of dark-gr pale-yellow spherules derived from d precursor glass types, which are richer in Ca, respectively. The alteration of Si-ric produces smectites richer in Fe, whereas glass results in smectites richer in Ca. Trans electron microscope (TEM) analyses normalized to $O_{10}(OH)_2$, reported by Martínez-Ruiz *et al.* (2001a), revealed that smectite compositions are also variable within the same spherule. In dark green spherules, the composition is Si: 3.57–3.77; Al^{IV}: 0.23–0.43; Al^{VI}: 1.71–1.91; Mg: 0.41–0.53; Fe: 0.64–0.81; Ti: 0.03–0.04; K: 0.22–0.49; Ca: 0.00–0.03; and Na: 0.08–0.27. In pale yellow spherules, the composition is Si: 3.56–3.76; Al^{IV}: 0.24–0.44; Al^{VI}: 1.04–1.35; Mg: 0.39–0.50; Fe: 0.37–0.48; Ti: 0.00–0.03; K: 0.05–0.21; Ca: 0.00–0.11; and Na: 0.07–0.48. These authors report that smectite morphologies are similar to those of smectites originating from the alteration of volcanic glass, such as hair-like smectites. The mineralogy and morphologies of the Blake Nose spherules are similar to those reported by Klaver *et al.* (1987) from DSDP Hole 603B and by Olsson *et al.* (1997) from Bass River sections. All of these spherules represent the same diagenetically altered impact ejecta from the Chicxulub crater.

Western Interior of North America. In the non-marine sections of the Western Interior of North America, a two-layered clay unit (ejecta layer + fireball layer) recording mineralogical and textural evidence of a catastrophic event, is preserved. The lower claystone layer ('melt ejecta' – ejecta layer) is mainly kaolin minerals, derived from silicic glass formed from melted target rocks. Pollastro & Bohor (1993) noted the presence of submicrometer-sized spherules or spherulitic aggregates of halloysite in Raton Basin, Brownie Butte and Morgan Creek sections. The original vitric framework of the lower claystone layer at these sites has been completely altered to microspherulitic kaolin (Pollastro & Bohor, 1993). Larger spherules are often abundant in the lower claystone layer. Most of these are altered to kaolin minerals, but some are altered to the hydrated aluminophosphate minerals goyazite or florencite (Triplehorn & Bohor, 1983). The upper laminated layer (fireball layer) consists mostly of altered vitric dust and abundant shocked minerals. The fireball layer is mostly altered to smectite from a mafic glass condensed from the vaporized chondritic bolide, along with some kaolinite formed from blebs of melted silicic target material entrained in the vapour plume cloud during ejection (Pollastro & Bohor, 1993).

Mediterranean Domain. In the Agost, Caravaca, Petriccio, El Kef and Elles II sections in the Mediterranean Domain, the fireball layer consists of almost pure smectite with minor amounts of illite, kaolinite and chlorite (Table 1). The smect derives from the alteration of distal ejecta mater (Martínez-Ruiz *et al.*, 1997; Smit, 1999). Orteg Huertas *et al.* (1998) reported the following fireb layer smectite composition normalized to O_{10}(OI obtained by TEM (standard deviation in paren eses): Agost section (average formula based on microanalyses) Si: 3.60 (0.01), Al^{IV}: 0.40 (0.0 Al^{VI}: 1.40 (0.03), Mg: 0.20 (0.05), Fe: 0.48 (0.0 Ti: 0.00, K: 0.35 (0.02), Ca: 0.05 (0.02); Carava section (average formula based on 49 analyses) 3.66 (0.06), Al^{IV}: 0.34 (0.3), Al^{VI}: 1.50 (0.03), M 0.21 (0.04), Fe: 0.38 (0.02), Ti: 0.03 (0.09), K: 0 (0.02), Ca: 0.00; Petriccio section (average form based on 29 analyses) Si: 3.64 (0.04), Al^{IV}: 0 (0.02), Al^{VI}: 1.38 (0.03), Mg: 0.31 (0.02), Fe: 0 (0.02), Ti: 0.03 (0.01), K: 0.27 (0.01), Ca: 0 (0.02); and El Kef section (average formula ba on 31 analyses) Si: 3.63 (0.06), Al^{IV}: 0.37 (0.0 Al^{VI}: 1.57 (0.03), Mg: 0.19 (0.03), Fe: 0.35 (0.0 Ti: 0.03 (0.02), K: 0.11 (0.01), Ca: 0.13 (0.02). T (Al+Fe)/Mg ratio identifies these smectites as be dioctahedral, belonging to the beidellite-nontron series (following the chemical criterion of Caill *et al.* (1982): nontronite, $Fe^{3+} > 0.5$; beidellite, F < 0.5). The smectite layer also contains abund spherules (200–400/cm^3) diagenetically altered K-feldspar or Fe oxide (mostly goethite) (Martín Ruiz *et al.*, 1997). The alteration of these spheru contributed to the increase in smectite in the firel layer. In fact, the lower proportion of spherules the Caravaca section relative to the Agost sect indicates that the former has been almost tota altered, which would explain the greater proport of smectite in the fireball layer of the Carav section. Smectite also derives from the alteration the finest cosmic dust, which is the m contribution to distal ejecta deposits. In Gubbio section, the boundary-layer clays cont fewer expandable minerals and have a composit apparently dominated by detrital illite and kaolin (Rampino & Reynolds, 1983).

NE Atlantic. In the Basque-Cantabrian Basin, spherules are less abundant (5–20/cm^3) because fireball layer is not as well preserved as in Mediterranean sections due to tectonic deformat Furthermore, the fact that smectite is not detected the fireball layer of any of the Basque-Cantabr sections may be a consequence of the extens diagenetic evolution undergone by these sequen as indicated by the presence of R1 I-S mixed-lay and even authigenic chlorite. However, the oc sional presence of nontronite spherules in the Monte Urko and Biarritz sections could be proof of the existence of authigenic smectites originating from the submarine alteration of spherules (Ortega-Huertas *et al.*, 1998). Thus, the alteration of these spherules must have followed the same general pattern as in the Mediterranean Domain. At Stevens Klint (Denmark), Kastner *et al.* (1984) found that the fireball layer was made up exclusively of pure magnesian smectite $(Si_{3.96}Al_{0.04})(Al_{1.29}Fe_{0.24}Mg_{0.69})O_{10}(OH)_2(K_{n.d.}Na_{n.d.}Ca_{0.15})$ (n.d.: not determined), whereas illite, illite-smectite mixed layers and quartz are present in the sediments above and below the fireball layer. These authors proposed that the authigenic smectites originated from the alteration of glass spherules in a marine environment and at a low water/rock ratio. Elliott (1993) found Mg-smectite $(Si_{4.01})(Al_{1.31}Fe_{0.13}Mg_{0.64})O_{10}(OH)_2(K_{0.03}Na_{0.26}Ca_{0.11})$ in the FL (layer IIIa) at Stevns Klint, Nye Klov and Karlstrup Quarry. He suggests that the anomalous concentrations of siderophile elements in the Mg-smectite of the fireball layer could have been incorporated in the smectite by exchange with sea water enriched in these elements or with trace fine-grained minerals. The TEM studies by Bauluz *et al.* (2000) indicate that the smectite composition $(Si_{3.86}Al_{0.14})(Al_{1.19}Fe_{0.17}Mg_{0.70})O_{10}(OH)_2(K_{0.07}Na_{0.06}Ca_{0.35})$ of Stevns Klint is unusual in that it has been enriched in both octahedral Al and Mg. They also point out the existence of abundant 10–20 nm diameter Fe oxides with 10% Ni and minor Zn intergrown with smectite. They interpret these domains as altered meteorite fragments, which formed when impact glass was transformed to smectite (Bauluz *et al.*, 2000).

Clay boundary layer

At distal Mediterranean Domain and NE Atlantic marine sections, the K/T boundary is clearly marked by a lowermost Danian clay boundary layer, which resulted from the significant decrease in ocean productivity and was deposited above the fireball layer. The clay boundary layer represents a reduced sedimentation deposit and records the faunal crisis resulting from the impact event. It may also contain some extraterrestrial contamination (*cf.* fine glass particles, platinum group elements). As clay mineral associations are potentially sensitive to environmental modifications, including climatic change, erosion, tectonic activity, variations in oceanic circulation, and di processes, (Chamley, 1989), they can, tl reflect the environmental conditions pr during deposition of the clay boundary lay

Mediterranean Domain. The Medite sections are characterized by a smectite-k illite association (Table 1), with smectite dominant mineral. Ortega-Huertas *et al.* reported the following average Danian smec line) and illite (down) compositions obta TEM:

Agost $(Si_{3.57}Al_{0.43})(Al_{1.30}Fe_{0.52}Mg_{0.30}$
$O_{10}(OH)_2(K_{0.}$
$(Si_{3.44}Al_{0.56})(Al_{1.18}Fe_{0.44}Mg_{0.26}$
$O_{10}(OH$

Caravaca $(Si_{3.69}Al_{0.31})(Al_{1.39}Fe_{0.50}Mg_{0.19}$
$O_{10}(OH)_2(K_{0.}$
$(Si_{3.50}Al_{0.50})(Al_{1.56}Fe_{0.17}Mg_{0.17}$
$O_{10}(OH$

Petriccio $(Si_{3.61}Al_{0.39})(Al_{1.57}Fe_{0.42}Mg_{0.21}$
$O_{10}(OH)_2(K_{0.}$
$(Si_{3.31}Al_{0.69})(Al_{1.69}Fe_{0.21}Mg_{0.21}$
$O_{10}(OH$

El Kef $(Si_{3.66}Al_{0.34})(Al_{1.54}Fe_{0.44}Mg_{0.19}$
$O_{10}(OH)_2(K_{0.1}$
$(Si_{3.26}Al_{0.74})(Al_{1.47}Fe_{0.63}Mg_{0.05}$
$O_{10}(OH$

From a mineralogical and chemical com point of view, the clay mineral associa Mediterranean Domain sections is the same uppermost Maastrichtian and lowermost deposits (clay boundary layer). In the Ag Caravaca sections (Betic Cordillera), tl boundary layer smectites are detrital, i from the erosion of soils developed in surr areas. The source was most likely the Preb of the External Zones of the Betic Cordille warm humid conditions, as indicated presence of Al-rich beidellite, their comp similarity with smectites from recent soils a fleecy-type morphology (Ortega-Huertas 1998). In addition, these smectites could be derived from the alteration of volcanic rock the similarity in chemical compositio smectites of this origin from other locati from this geological context (López Galind and their lath-like micromorphology, which them compatible with this interpretation (C *et al.*, 1985). Kaiho *et al.* (1999) reported an increase in the kaolinite/illite ratio in the lower part of the clay boundary layer in the Caravaca section and suggested a gradual increase in atmospheric temperature and rainfall in the low latitude Northern Hemisphere beginning between 0 and ~0.4 kyr after the boundary and lasting for >~3 kyr afterwards.

In the El Kef section, the large smectite and kaolinite contents and the extreme scarcity of illite and chlorite can be interpreted as evidence that soil derivation dominated over inheritance from crystalline rocks (Robert & Chamley, 1990; Ortega-Huertas *et al.*, 1998). Robert & Chamley (1990) reported a relative increase in kaolinite/smectite and illite/smectite ratios in the lower part of the clay boundary layer in this section, which can be explained by increased humidity, a sea-level fall, an uplift of the continental margin, or a rejuvenation of distant continental areas. Recently, Adatte *et al.* (2002) reported on the clay mineral assemblages of the clay boundary layer in different sections from Tunisia (El Kef, Elles I, Elles II, Seldja, El Melah, Ain Settara), with kaolinite being the most abundant clay mineral. Smectite, chlorite and illite are minor components in all sections, except in El Melah where smectite is absent probably due to post-depositional burial linked with increased tectonic activity. The kaolinite/smectite ratio increases in the clay boundary layer of the El Kef and Elles sections, indicating alternations between warm humid and seasonal temperate climate.

In the Petriccio section of Central Italy, the significant proportion of illite implies that, in addition to the inheritance of soil smectite and kaolinite, there was also erosion involving the crystalline rocks of the source area (Ortega Huertas *et al.*, 1998). The clay mineral association in the clay boundary layer of the Gubbio section is characterized by detrital illite, kaolinite and small amounts of I-S mixed layers (Table 1), which could represent a minor volcanogenic component converted to smectite-illite by diagenesis, or it could be a terrigenous weathering product (Rampino & Reynolds, 1983). Robert & Chamley (1990) noted a clay mineral association of kaolinite-smectite-chlorite-illite-I-S mixed layers in this section. The increase in kaolinite contents together with rock-derived minerals just below the K/T boundary or in the K/T boundary layer itself is interpreted by these authors as resulting from active erosion due to either tectonic rejuvenation or sea-level drop.

NE Atlantic. In the clay boundary layer of t
Basque-Cantabrian Basin sections, Ortega-Huert
et al. (1995, 1998) reported diverse clay-miner
associations [(illite-chlorite in the Monte Ur
section; illite-R1 I-S mixed-layer-kaolinite in t
Sopelana, Biarritz and Hendaye sections; and illi
R1 I-S mixed-layer-chlorite in the Zumaya secti
(Table 1)] and the following chemical compositi
for illite:

Monte Urko $(Si_{3.31}Al_{0.69})(Al_{1.63}Fe_{0.21}Mg_{0.20})$
$O_{10}(OH)_2(K_{0.}$
Sopelana $(Si_{3.26}Al_{0.74})(Al_{1.27}Fe_{0.15}Mg_{0.69}Ti_{0.15})$
$O_{10}(OH)_2(K_{0.}$
Biarritz $(Si_{3.31}Al_{0.69})(Al_{1.71}Fe_{0.22}Mg_{0.20}Ti_{0.02})$
$O_{10}(OH)_2(K_{0.}$
Hendaye $(Si_{3.20}Al_{0.80})(Al_{1.76}Fe_{0.22})$
$O_{10}(OH)_2(K_{1.}$
Zumaya $(Si_{3.34}Al_{0.66})(Al_{1.74}Fe_{0.30}Mg_{0.17}Ti_{0.02})$
$O_{10}(OH)_2(K_{0.}$

These compositions correspond to detrital mic
close to or in some cases coinciding with muscov
(Hendaye section), with a significant phengi
trend in the Zumaya and Sopelana sections. Wi
regard to the R1 I-S mixed layers, an homogeneo
chemical composition can be inferred from the S
Al^{total} *vs.* (K+Ca) varying from 1.5 to 2.5 and 0.
to 0.66, respectively. Where present, detrit
chlorite is not a very abundant mineral in the cl
boundary layer of these sections. Its compositi
mostly corresponds to chamosite (Fe: 1.87–2.
a.p.f.u.; Mg: 0.95–1.57 a.p.f.u.) showing chemic
characteristics representative of contamination l
corrensite or smectite interlayers, high Si conte
(2.50–3.05 a.p.f.u.), and Al^{VI} contents (1.73–2.
a.p.f.u.) much higher than Al^{IV} contents (0.95–1.
a.p.f.u.), and a total octahedral population mu
lower than 6 cations a.p.f.u. (5.24–5.71) (Orteg
Huertas *et al.*, 1998). These authors proposed th
the micas and chlorite in the Basque-Cantabri
Basin are detrital, derived from the erosion of ro
substrata, whereas kaolinite is inherited from so
that developed in the warm and humid climate th
prevailed in peri-Atlantic domains during t
Cretaceous and most of the Tertiary (Chamle
1989). The abundance of kaolinite in the Sopela
Biarritz and Hendaye sections is a consequence
the relative proximity of emergent areas exposed
erosion which, according to Mathey (1988), cou
have been located nearby on the eastern a
western platforms of the Cantabrian Sea.
general, as proposed by Ortega-Huertas *et*

(1995), clay sedimentation in the Basque-Cantabrian Basin was controlled by tectonic processes occurring during the Maastrichtian and basal Danian that were responsible for the supply of illite (with a clear increasing trend in the basal clay boundary layer) and chlorite and the absence of detrital smectites. The presence of significant amounts of R1 I-S mixed layers in the Sopelana and Zumaya sections and, to a lesser extent, at Biarritz and Hendaye could be the result of burial diagenesis, which would explain the absence of smectite as an independent mineral phase in these sections. This interpretation agrees with that of Aróstegui *et al.* (1991) and Nieto *et al.* (1996) for other sequences of the Basque-Cantabrian Basin.

The clay mineralogy of the clay boundary layer (layer IIIb, Schmitz, 1985) at Stevns Klint is dominated by Mg-smectite. It was deposited above the red-rust layer referred to as the 'impact layer' (fireball layer). Its composition is similar to the Danian marl from the Dania Quarry (Mg-smectite-I-S mixed-layer-illite) and to the clay mineralogy reported for Maastrichtian marl at Kjolby Gaard (Rampino & Reynolds, 1983).

Boreal Paratethys. According to Pardo *et al.* (1999), at the time of the K/T boundary, the Koshak section (Fig. 1a) was located on a relatively shallow open marine platform. The most common clay mineral is illite, which varies between 50 and 85%. Just above the K/T boundary, smectite and kaolinite show a slight increase. The overall high illite contents are consistent with a generally cool high-latitude climate for the Koshak region, with low humidity but high physical erosion. The increase in the smectite or kaolinite/chlorite + illite ratio suggests short warm periods at or just above the K/T boundary.

Southeastern Atlantic (Walvis Ridge) and Southern Ocean (Maud Ridge). Hsü *et al.* (1982) and Robert & Chamley (1990) report on the clay mineral associations across the K/T boundary in the Southern Hemisphere (Fig. 1). On the Walvis Ridge, the boundary occurs in a background of active tectonics. In contrast, no significant tectonic activity was recorded in the Maud Rise area. At both Walvis Ridge (DSDP Leg 73 Site 524) and Maud Ridge (ODP Leg 113 Sites 689-690), the clay fraction just above the K/T boundary (clay boundary layer) is characterized by an important increase in smectite. At both of these areas, no significant influence of extraterrestrial material has been reported. On Walvis Ridge (DSDP Leg 73 Site
524) the boundary occurs in marly turbidit
charcterized by an abrupt decrease in
content. The clay composition of the clay bo
layer is mainly Fe-smectite. There is no sig
change in the clay association below and ab
clay boundary layer (Hsü *et al.*, 1982). On
Ridge (DSDP Leg 74 Sites 525-529), an inc
kaolinite is also observed in the clay bo
layer, which could indicate a period of
temperature and humidity (Robert & C
1990). These authors, however, consider t
kaolinite is essentially derived from the erc
rocky substrate on the basis of its associati
illite and chlorite. The increase in smectite p
represents the higher supply of volcar
smectite from nearby subaerially exposec
The presence of broken particles of volca
smectite, mixed with smectite from other
suggests that the increase in volcanogenic p
at the clay boundary layer is not directly re
increased volcanic activity, but rather result
reworking. Tectonic instability at Maud
(ODP Leg 113 Sites 689 and 690) cou
explain the increased erosion of volca
smectite, which could account for the incr
soil-derived minerals (illite, kaolinite).

North American Margin. In the Blak
section, the lowermost Danian deposits ar
acterized by high calcite contents (85%) anc
clay boundary layer, such as that recognize
most distal marine sections. In the inter
above the K/T boundary, the clay r
associations are dominated by inherited s
(70–85%) and minor quantities of illite (~5
and kaolinite (~5–10%). The TEM analy
Martínez-Ruiz *et al.* (2001c) revealed the fo
compositional range for this smectite: (S
$Al_{0.12\text{-}0.64})(Al_{1.18\text{-}1.72}Fe_{0.19\text{-}0.46}Mg_{0.}$
$O_{10}(OH)_2(K_{0.06\text{-}0.24}Ca_{0.00\text{-}0.10}Na_{n.d.})$ (n.d.: nc
mined). Its beidellite nature is conclusive,
pedogenic origin and, therefore, indicates rc
warm and hydrolysing continental condition
the K/T boundary.

DIAGENETIC ALTERATION
PRESERVATION OF PRECUR
MATERIAL

The sedimented impact-generated materia
target-rock derived and cosmic dust, as
Cretaceous and Tertiary sediments, ha
subjected to significant diagenetic alterati

may have led, in many cases, to a severe modification of the original geochemical signatures and indicators of palaeo-depositional conditions at 65 Ma. Nonetheless, when carefully evaluated, distinctive proxies can be inferred for palaeoenvironmental reconstructions for that period. For this purpose, an evaluation of the diagenetic processes and alteration of original phases is required to determine the precursor minerals. In the K/T boundary sediments, the classic indicators for extraterrestrial contamination, such as impact glasses and microkrystites, are usually altered and the original material has been replaced by secondary diagenetic phases. Original trace-element concentrations, such as those of the platinum group elements (PGE) or rare earth elements (*REE*), have also been modified as a result of diagenetic alteration. The discrimination of original *vs.* diagenetic signatures, therefore, needs to be addressed to establish if the geochemical evidence supporting an extraterrestrial event exists.

Alteration of impact glasses and microkrystites. The K/T boundary spherules are restricted to the ejecta layer and fireball layer. Two main types of impact spherules have been reported, which occur in different strewn fields (*cf.* Bohor & Betterton, 1990; Smit *et al.*, 1992; Bohor & Glass, 1995).

One type, restricted to the ejecta layer, is interpreted as originally being composed of target-rock melt glass, with a radial distribution around the impact crater in the Caribbean area (*cf.* Smit *et al.*, 1992). Although several authors have referred to these glass spherules as 'tektites' or 'microtektites', some of them may differ from 'tektites', which are generally chemically homogeneous on a 10–100 μm scale, are almost water-free and may show signs of glass flow (*cf.* Koeberl, 1990). In this paper, we use the term impact glass, according to Koeberl & Sigurdson (1992), in reference to spherules from the ejecta layer. The original impact-generated glass is expected to be compositionally variable since it was only briefly molten and there was not enough time for mixing and homogenization of the composition (*cf.* Alvarez *et al.*, 1992). This resulted in different compositions of impact glasses (*cf.* black andesitic glass and honey-coloured CaO-rich glass from Haiti, Sigurdsson *et al.*, 1991; Koeberl & Sigurdsson, 1992), and also in different smectite compositions within the ejecta layer of some sections, *cf.* Blake Nose (Martínez-Ruiz et al., 2001a). However, the end-mineral phase product of alteration of the original glass mostly
depends on local diagenetic conditions and diffe
from place to place, i.e. smectite or chlorite (Gu
of Mexico, North American Margin), or kaolin
(Western Interior of North America) (Table 1).

At Blake Nose ODP Site 1049 (North Americ
Margin), TEM observations show glass relict
smectite spherules (Fig. 2d) and Martínez-Ruiz
al. (2001a) reported smectite growing from the S
rich glass. These observations also reveal palygo
kite forming from a smectite precursor. Zeolit
(clinoptilolite) originate from the diagenetic rea
tion involving glass alteration. Both minera
indicate a high-silica source and alkaline conditio
which favour the precipitation of chain-structu
silicates. A Ca-rich glass precursor is also impli
by the composition of yellow spherules from th
section, which agrees with the geochemistry of t
above-mentioned Haitian impact glasses and t
pre-impact stratigraphy at the Chicxulub region (
Kring & Boynton, 1991). Despite alteration, t
composition of clays derived from the original gla
is still informative and provides evidence of t
precursor material. In the El Tecolote section, Ma
et al. (2001) suggested that the high diagene
grade resulted in the complete alteration of Si-ri
glass to chlorite. In contrast, in the Western Inter
of North America, Pollastro & Bohor (1993) repo
that silicic impact glasses were probably altered
kaolinite in the acidic, organic carbon-rich wate
of ancient peat swamps.

The second type of spherules which have
quench-crystal texture, are confined to the fireb
layer, are globally distributed, and are referred to
microkrystites (Glass & Burns, 1987; Smit *et a*
1992). These microkrystites may or may not
altered; in most cases, they are altered to authiger
phases whose composition varies from section
section. For instance, in sections from the Itali
Apennines, they are altered to K-feldspar, smecti
glauconite and goethite (Montanari, 1991).
Zumaya (Basque-Cantabrian Basin), they a
altered to pyrite, in Agost (Betic Cordillera)
Fe oxides and K-feldspar, and in Caravaca (Be
Cordillera) to K-feldspar (*cf.* Smit *et al.*, 199
Martínez-Ruiz *et al.*, 1997). When altered,
mineral composition of such authigenic phases do
not represent direct evidence of the precurs
material, since the local Eh and pH conditio
seem to be the main factor controlling the e
diagenetic product. However, quench/fibrorad
textures and morphologies provide evidence
their extraterrestrial origin. Moreover, K-felds

spherules from the Agost and Caravaca sections contain C-rich cores enriched in Ir, Pt, Pd and Ni that could represent a relict of the extraterrestrial material (Martínez-Ruiz *et al.*, 1997). Unaltered clinopyroxene microkrystites were recovered at Shastky Rise in the Pacific (Smit *et al.*, 1992). Based on the mafic composition of the C-rich cores of K-feldspar spherules, Martínez-Ruiz *et al.* (1997) suggest that the original precursor must have had a mafic composition. In any case, the composition of the microkrystites may depend on the place where they originated in the ejected vapour cloud and oxygen fugacity (*cf.* Smit *et al.*, 1992). A mafic composition for the fireball layer precursor material has also been proposed by Pollastro & Bohor (1993) for the Western Interior of North America sections. Here, the fireball layer was mostly altered to smectite, in contrast to the ejecta layer, which was altered to kaolinite. Acidic and organic carbon-rich waters in these peat swamps would have favoured the alteration to kaolinite. Thus, the compositional differences for material deposited in similar environments may reflect a silicic *vs.* mafic precursor. The smectite composition of the fireball layer in the most distal sections, such as those from Tunisia, Agost and Caravaca, also indicate that an original mafic composition may have influenced the end diagenetic product. In these sections, smectite resulted from the alteration of the finest cosmic dust and probably from the progressive alteration of microkrystites.

Alteration of primary geochemical signatures. The diagenetic processes involving the alteration of the impact-generated material also led to a severe modification of the original chemical composition. Since Ir and other PGE have traditionally been used to support the extraterrestrial contribution theory, PGE concentrations should be considered on the basis of an accurate evaluation of diagenetic processes. In fact, differences in PGE concentrations in sections, such as Agost and Caravaca (Martínez-Ruiz *et al.*, 1992, 1999), located at a short distance from each other and assumed to have had similar contributions of the impact-generated material, may have resulted from different diagenetic evolutions of the original ejecta layer material. Different proxies such as extensive pyrite formation or elevated authigenic uranium concentrations indicate very strong reducing conditions at the Agost section, which may have resulted in Ir remobilization and, therefore, lower Ir content at the Agost than in the Caravaca section.
Furthermore, the elevated PGE and other
elements in the clay boundary layer from A
Caravaca may also have resulted partial
diagenetic remobilization (Martínez-Ruiz
1999).

Another important effect of the dia
alteration of the impact-generated materia
significant *REE* depletion in the ejecta la
fireball layer relative to overlying and un
sediments. Initially, the low *REE* content in
boundary materials was explained as a resu
impact in oceanic crust (*cf.* Smit & ten Kat
Hildebrand & Boynton, 1987). Neverthele
remobilization during diagenesis has been
(*cf.* Taylor & McLennan, 1988). Izett
demonstrated, comparing impact glass co
smectite alteration rims, that *REE* remob
could explain the low *REE* abundances.
suggested that *REE* may not reflect the n
the precursor material. However, certa
patterns could be informative. Thus, a
Nose, *REE* patterns are similar to thos
upper crustal rocks and to those from Cr
and Tertiary sediments (Martínez-Ruiz *et a*
and, despite alteration and depleted concen
the C1-normalized patterns are indicative o
rock origin. Koeberl & Sigurdsson (19
reported *REE* C1-normalized patterns from
tites derived from Haitian impact glasses, w
almost flat. Such patterns are not recog
Blake Nose, where *REE* C1-normalized
still indicate the target-rock derivation of th
layer.

At the most distal sections, the *R*
normalized patterns from the fireball mate
indicate significant *REE* depletion (Fig
Ortega-Huertas *et al.*, 1998). At the Agost
the *REE* C1-normalized patterns of in
microkrystites are essentially flat and
significantly from those of the surr
Cretaceous and Tertiary sediments (F
Martínez-Ruiz *et al.*, 1999). Although di
may have been an important controlling f
the *REE* concentrations, variable patter
support the suggestion of a different natur
original material, and are consistent w
probable mafic composition of the
precursor.

In summary, a proper evaluation of the a
of the boundary materials is essential to as
extraterrestrial contribution, as well as to c
nate original and secondary signatures. No

tion of extraterrestrial fluxes should be based solely on altered geochemical records.

CONCLUSIONS

The detailed analysis of the K/T boundary clay-mineral associations permits differentiation between: (1) the ejecta layer, with a major contribution of target-rock material deposited around the Chicxulub crater; (2) the fireball layer, which is well preserved at more distal sections and represents the cosmic dust dispersed and deposited globally; and (3) the lowermost Danian clay layer, which was deposited under a decrease in ocean productivity after the impact event.

Smectite is the main clay mineral in the ejecta layer in the Gulf of Mexico, except in the El Tecolote section where chlorite is the predominant phyllosilicate, and in the North American Margin sections. In the Western Interior of North America, kaolinite is the main clay mineral. All of these clay minerals were produced by the diagenetic alteration of target-rock-derived materials. At Blake Nose, the alteration of Si-rich glass produced smectites richer in Fe, whereas alteration of Ca-rich glass resulted in smectites richer in Ca.

The fireball layer mainly consists of smectite derived from the alteration of microkrystites and the finest fraction, which contains a major contribution of extraterrestrial material. In the Mediterranean Domain, the smectite belongs to the beidellite-nontronite series. At Stevns Klint section, the fireball layer was exclusively made up of pure magnesian smectite. Anomalous concentrations of typical extraterrestrial elements in the smectitic fireball layer support the cosmic contribution. In the Basque-Cantabrian Basin, smectite is not preserved as a consequence of the considerable diagenetic evolution. The main clay mineral association is dominated by illite with minor quantities of R1 I-S mixed-layer-kaolinite-chlorite.

The clay boundary layer represents a reduced sedimentation deposit and the clay mineral associations depend on the local environmental conditions such as climatic change, erosion, tectonic activity and diagenetic processes. In the Betic Cordillera, Tunisian and Denmark sections, this layer is mainly composed of smectite inherited from the erosion of soils developed in surrounding areas and/or derived from the alteration of volcanic rocks. The increase of kaolinite content in the clay boundary layer from the Caravaca and Tunisian sections could indicate enhanced temperature and rainfall at this time. the Italian Apennines and in the Basque-Cantabri Basin sections, diverse clay mineral associations a present, mostly dominated by illite.

The alteration of impact-generated materia (impact glasses, microkrystites and fine fraction to clay minerals involved a significant modificati of original signatures. However, the mineral a chemical compositions of the alteration produc can still provide information on the nature of t precursors. For example, the smectite compositi of the fireball layer has been cited as evidence the mafic character of the progenitor. T composition of the smectite at Blake Nose can also related to different types of glass precursors. addition, the *REE* C1-normalized patterns supp the terrestrial nature of the parent rocks. Moreov the enrichment in extraterrestrial elements, such Ni, in smectites from the fireball layer provi further evidence for the extraterrestrial contributi in this layer.

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