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Climate, tectonics and meteoritic impact expressed by clay mineral sedimentation across the Cretaceous-Tertiary boundary a Blake Nose, Northwestern Atlantic

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ABSTRACT: The ODP Leg 171B drilled a transect of four sites at Blake Nose in the NW Atlantic providing an excellent record of the K-T boundary. At the deepest, Site 1049, the boundary is marked by a 9–17 cm thick layer formed mostly of green spherules composed of Fe-rich smectite resulting from the diagenetic alteration of tektites and impact glasses. Minor amounts of authigenic zeolites and palygorskite also occur. This association represents a notable break in the clay mineral composition of Cretaceous and Tertiary sequences. The clay mineral assemblages of the Cretaceous and Tertiary sediments are dominated by inherited clays. Aluminium-rich smectite of pedogenic origin is abundant in both Cretaceous and Tertiary sediments, indicating a relatively warm and hydrolysing climate across the K-T boundary. At Hole 1049A, where the oldest sediments of the interval were analysed, an increase in kaolinite and smectite down core suggests tectonic rejuvenation and distal transport of illite and kaolinite, probably accompanied by more hydrolysing conditions during the late Maastrichtian.

KEYWORDS: Blake Nose, smectites, spherules, impact, Chicxulub, diagenesis.

The Cretaceous-Tertiary (K-T) boundary is associated with geochemical and mineralogical anomalies attributed to the Chicxulub impact event at the end of the Cretaceous. In the last two decades, an intense debate has focused on the meaning of these anomalies and their relationship to recent evidence for the occurrence of an impact feature at Chicxulub, in the Yucatan Peninsula of Mexico. Support for a crater at this location seems overwhelming, including impact signatures recognized in sequences from the Gulf of Mexico area, as well as gravity measurements and drill-core data (Hildebrand & Boynton, 1990; Sigurdsson *et al.*, 1991a,b; Smit *et al.*, 1992; Koeberl & Sigurdss 1992; Alvarez *et al.*, 1995). Reanalysis of Deep S Drilling Project Sites 536 and 540 in the Gulf Mexico led to the new interpretation that so deposits in this area are part of the ejecta blan (Alvarez *et al.*, 1991). More recently, Oce Drilling Program (ODP) Legs 161 and 17 (Norris *et al.*, 1998) attempted to sample K boundary deposits in the area of the Blake Nose order to extend our knowledge of the ejecta blank

A major objective of ODP Leg 171B, the subj of this paper, was to obtain sediment samples fr shallow sites along a transect from the Blake N area of the Blake Plateau to the edge of the Bla Escarpment (Fig. 1) in order to interpret the verti structure of the western North Atlantic Oce during the Cretaceous and Palaeocene. At Bla

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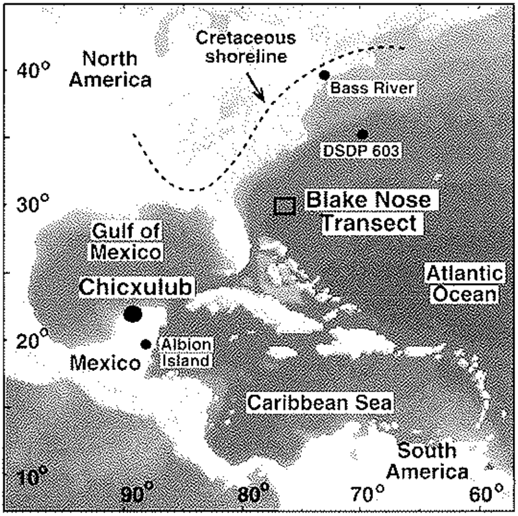

FIG. 1. Location of the Blake Nose transect and some other K-T boundary sections: Bass River, DSDP Site 603 and Albion Island.

Nose, most of the plateau is covered with Mn-phosphorite nodules and pavements that have preserved the underlying sediments from substantial erosion (Norris *et al.*, 1998, 1999; Klaus *et al.*, 2000). The programme provided an excellent opportunity to recover sections through the Cretaceous-Palaeocene boundary (Norris *et al.*, 1998).

Analysis of the boundary deposits should permit ejecta fallout patterns and the settling of the dust cloud to be reconstructed. The mineral composition of the K-T boundary interval may provide information on continental erosion and weathering as well as on depositional mechanisms and authigenic processes. This paper provides the first mineral data on the K-T boundary interval from sites drilled by ODP Leg 171B and uses them to reconstruct sedimentation regimes and constrain depositional conditions, including those of the fallout material.

MATERIALS AND METHODS

Samples from the K-T boundary interval at Blake Nose were collected from Holes 1049A, 1049B, 1050C and 1052E. In Holes 1049A and 1049B, a spherule bed occurs at the biostratigraphic boundary between the Cretaceous and Palaeocene (Fig. 2). This bed overlies slumped uppermost C
materials and is overlain by a lo
Palaeocene ooze with a foraminiferal as
indicative of the P-alpha Zone (Norris *et*
1999). The spherule bed is 17 cm thick
and 9 cm thick in 1049B (Fig. 2), bu
preserved in Holes 1050C or 1052E. Ho
the core from 1052E some burrows fi
spherule material have been recognized.

Continuous samples were collected
intervals from the zones containing t
layer in 1049A (125.69–126.23 mbsf) a
(111.00–111.32 mbsf). They were drie
genized and ground gently in an agate m
mineralogical analyses using the method
below.

X-ray diffraction (XRD)

A representative fraction of the samples
for the mineralogical study of the bulk s
and another was used for the extraction
of the clay fraction. The XRD pat
quantitative mineralogical analyses (bul
alogy and <2 μm clay fraction) were obtai
a Philips PW 1710 diffractometer (with
divergence slits) at the Department of M
and Petrology, University of Granada, Sp
minerals were extracted by centrifugat
removing carbonates with acetic acid an
sive washing. The mineral intensity
calculated for this equipment and the ins
conditions are detailed in Ortega Huert
(1995).

Electron microscopy

Morphological studies were performed
ning electron microscopy (SEM) with
DSM 950 (at the Centro de Instru
Científica, University of Granada,
Quantitative microanalyses of clay mine
obtained using a Philips CM-20 tra
electron microscope (TEM) equipped
EDAX microanalysis system. The d
collected in scanning TEM mode only fr
of particles using a 70 Å diameter b
200 × 1000 Å scanning area and a short
time to avoid alkali loss (Nieto *et a*
Smectite formulae were normalized to 11
Beidellite and nontronite were diffe
following the method of Caillère *et al.* (1

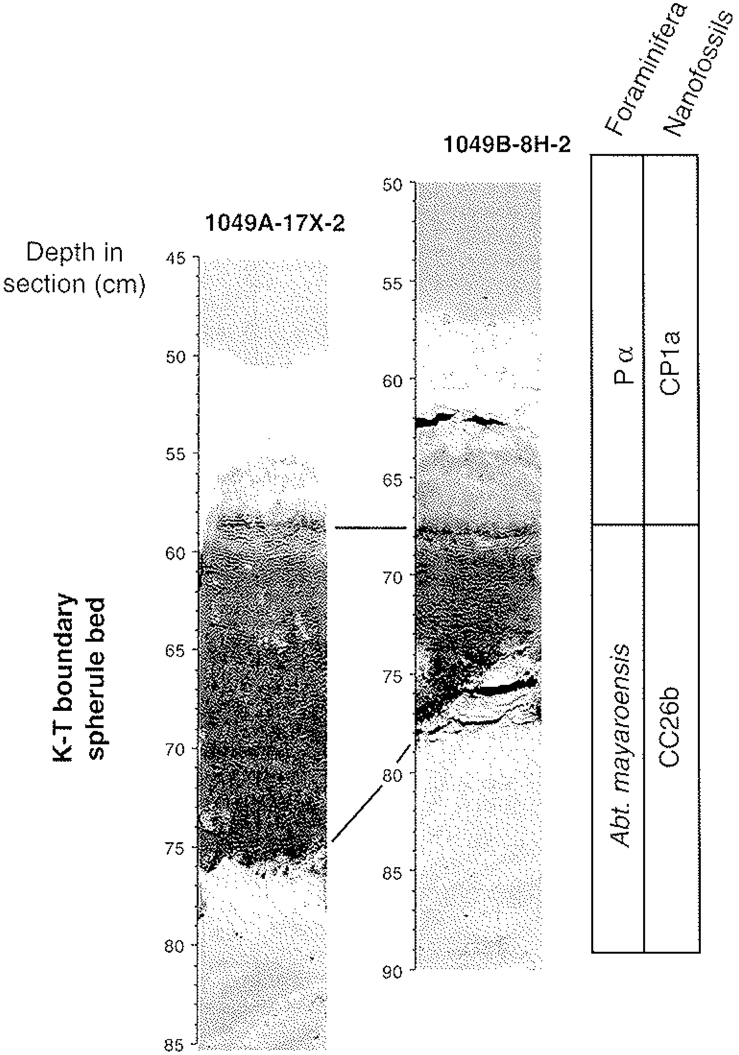

FIG. 2. Core photographs from the K-T boundary layer at Holes 1049A (125.91–126.05 mbsf) and 104 (111.18–111.24 mbsf) showing the variable thickness of the spherule bed and the presence of some clasts Cretaceous material within this bed.

RESULTS

Table 1 and Figs 3 and 4 summarize the XRD results for Holes 1049A, 1049B, 1050C and 1052E. The lithology of the cored interval is similar at all locations, except that the K-T boundary layer is preserved only in 1049A and 1049B. Cretaceous and Tertiary sediments above and below the boundary layer, as well as at Holes 1050C and 1052E, are a light greenish-grey nanofossil-foraminiferal ooze (Norris *et al.*, 1998). The K boundary layer consists of green spherical a oval-shaped spherules, the size of which usua ranges from 100 to 1000 µm, and also contai some Cretaceous planktonic foraminifera and cla of Cretaceous material.

The boundary layer is mostly composed of cla and minor amounts of calcite (Table 1). Zeolit quartz and small amounts of rutile, biotite and so lithic fragments are also present. The clays a

TABLE 1. XRD data of the interval analysed at Holes 1049A, 1049B, 1050C and 1052E: Range p
(wt.%) of the main mineral components in the bulk sediments (clay minerals, quartz and calcite)
minerals in the <2 μm fraction (smectite, illite and kaolinite). n = number of samples.

Core	Depth (mbsf)	Clay minerals	Quartz	Calcite	Smectite	Illite
171B-1049A-						
16X (Tertiary) (n = 76)	115.02–124.05	<5–45	<5–15	43–98	73–97	<5–19
17X (Tertiary) (n = 226)	124.25–125.87	9–30	<5–7	65–87	56–90	<5–30
17X (K-T) (n = 8)	125.91–126.05	75–95	<5	5–12	96–99	<5
17X (Cretaceous) (n = 46)	126.07–128.36	8–31	<5	67–90	<5–98	<5–44
18X (Cretaceous) (n = 8)	134.45–139.75	<5–18	<5–9	79–97	<5–15	27–70
171B-1049B-						
8H (Tertiary) (n = 30)	109.05–111.14	<5–42	<5–7	53–98	25–90	7–64
8H (K-T) (n = 4)	111.18–111.24	90–87	<5	8–12	95–97	<5
8H (Cretaceous) (n = 4)	111.26–111.32	<5–12	<5	85–98	45–83	10–37
171B-1050C-						
9R (Tertiary) (n = 68)	394.50–401.30	<5–48	<5–8	47–98	67–98	<5–21
10R (Tertiary) (n = 23)	404.17–405.93	<5–31	<5–8	67–97	47–87	<5–21
10R (Cretaceous) (n = 8)	405.97–406.38	<5–16	<5–6	77–97	82–94	<5–8
11R (Cretaceous) (n = 42)	408.70–412.80	<5–41	<5–7	54–97	69–94	<5–17
171B-1052E-						
17R (Tertiary) (n = 38)	290.51–300.25	<5–44	<5–15	51–98	22–99	<5–20
18R (Tertiary) (n = 26)	300.39–302.41	<5–26	<5–7	53–98	76–96	<5–9
18R (Cretaceous) (n = 6)	302.46–302.98	7–13	<5–6	78–94	76–96	<5–12
19R (Cretaceous) (n = 13)	309.80–311.60	<5–16	<5–7	79–97	59–80	9–25

mostly smectite (Table 1) derived from the diagenetic alteration of impact spherules (Fig. 5) (Martínez-Ruiz *et al.*, 2000) with traces of illite, palygorskite and kaolinite.

The Cretaceous and Tertiary sediments contain carbonates, clay minerals, and quartz, with minor quantities of feldspars and traces of heavy minerals and pyrite. Feldspar recognized using XRD is

always <5 wt.%, while trace minerals
identified by using the SEM. Calcit
dominant carbonate phase, but small qua
dolomite are occasionally present. On
within the boundary layer (sample 1049
02, 60–62 cm), contains 12 wt.% dolomit
usually ranges from 50 to 95 wt.% in
samples and from 65 to almost 100

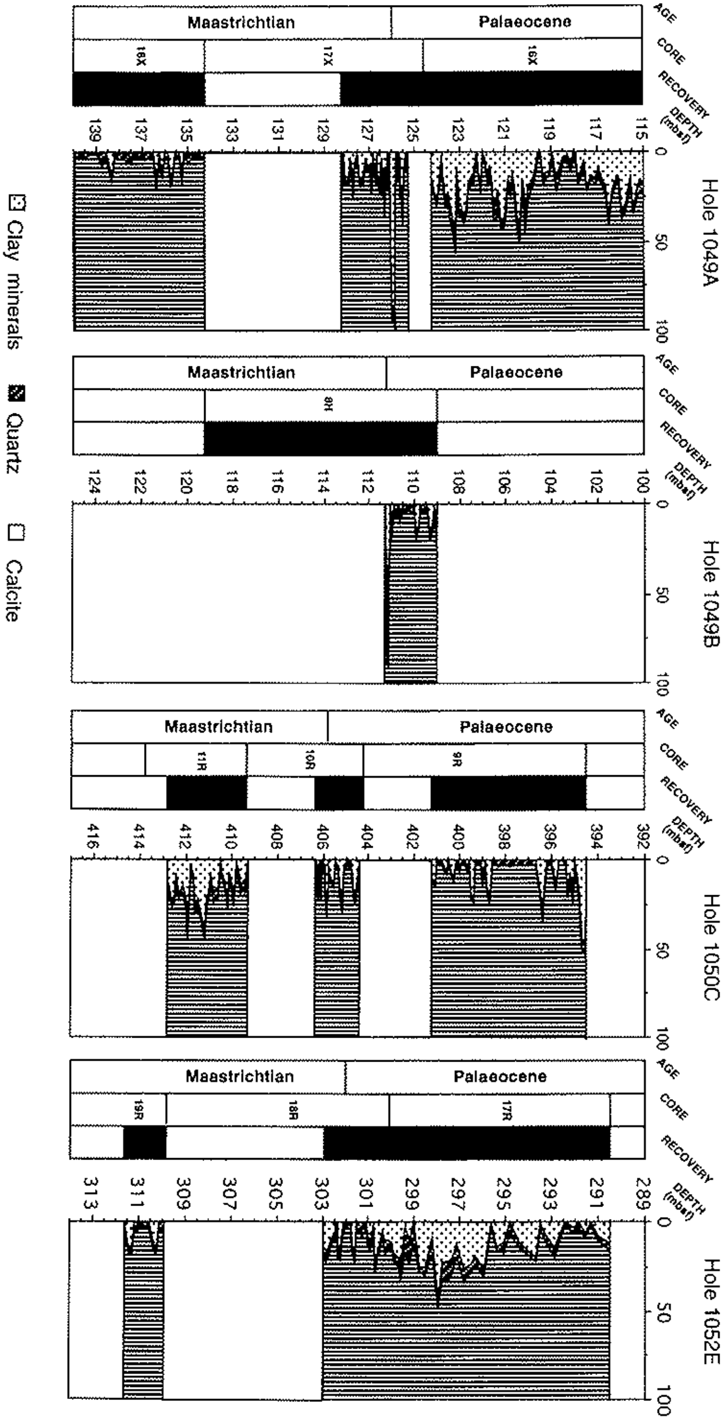

FIG. 3. Bulk mineral composition of the analysed intervals from Holes 1049A, 1049B, 1050C and 1052E. The a
of the sediments and core recovery are also shown.

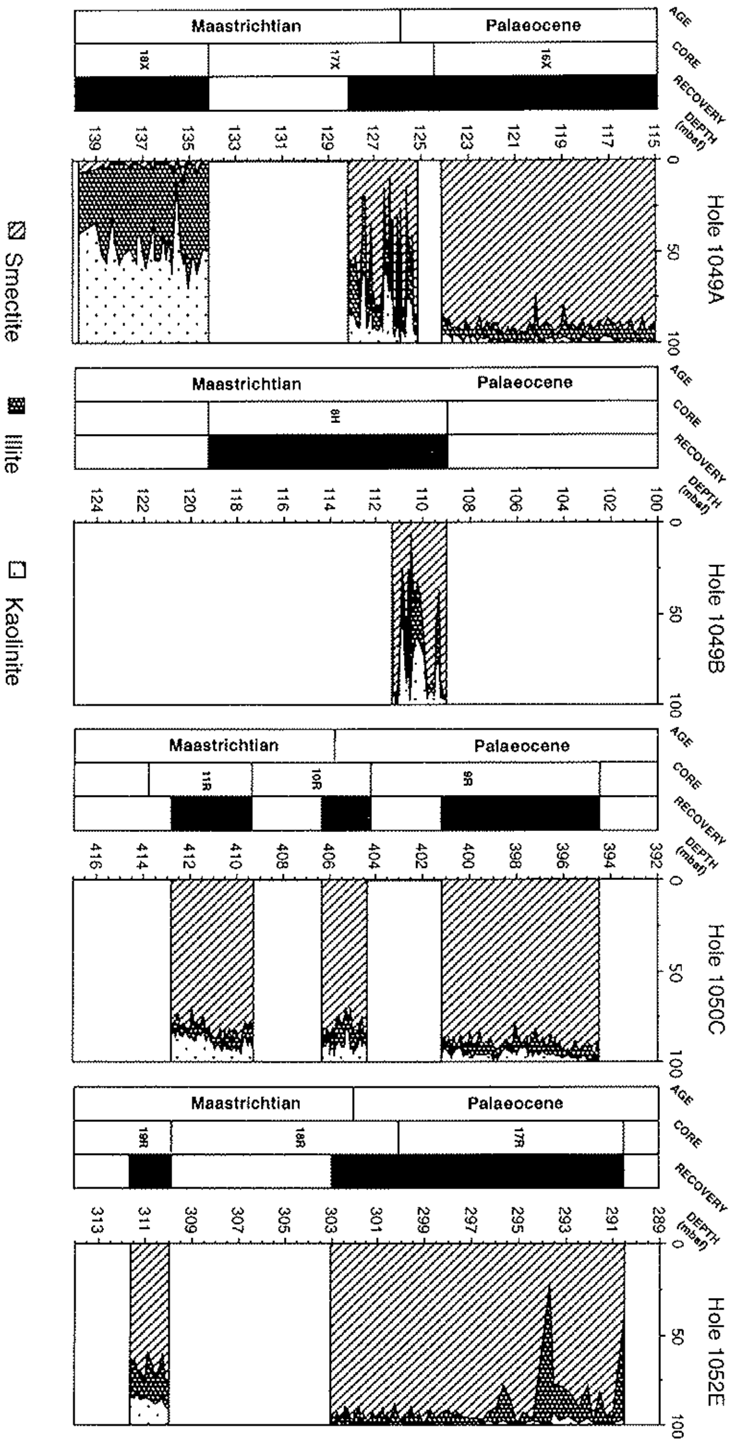

FIG. 4. Clay mineral composition of the analysed intervals from Holes 1049A, 1049B, 1050C and 1052
of the sediments and core recovery are also shown.

Cretaceous samples. Quartz is usually <5 wt.% in Cretaceous samples and its proportions range from <5 up to 15 wt.% in Tertiary samples. Clay minerals are also more abundant in Tertiary samples (<5 up to 50 wt.%) and some cyclic variations in abundance are observed in the early Palaeocene (Fig. 3). In Cretaceous samples, clay proportions range from <5 up to 30 wt.%.

The relative proportions of clay minerals are also given in Table 1 and Fig. 4. Smectite is dominant in most of the samples except for the lowermost part of the Cretaceous interval analysed in 1049A, where kaolinite and illite are more abundant (Fig. 4). In samples from 1052E, a down core increase in illite and kaolinite is also observed (Table 1, Fig. 4).

In most of the Tertiary clay-sized fraction samples, the smectite contents reach ~90 wt.%, illite is ~10 wt.%, and kaolinite is usually <5 wt.%, with the exception of one interval in 1049A (125.39–125.66 mbsf), where illite and kaolinite increase and smectite decreases to ~50–60 wt.%. Minor amounts of chlorite (<5 wt.%) were found in occasional samples, appearing to be more common in Cretaceous samples, but not abundant enough to be quantified by XRD.

Stereomicroscope and SEM observations revealed different types of spherules: pale yellow, light green and dark green spherules with smooth, rough or nodular surfaces (Fig. 5). The original material has been altered to smectite (Martínez-Ruiz *et al.*, 2000). The TEM microchemical analyses revealed the smectites to be Al-beidellites in Cretaceous and Tertiary samples (Table 2, Fig. 6).

DISCUSSION

Blake-Nose clay mineralogy across the K-T boundary

The variable thickness of the spherule bed at Blake Nose suggests reworking of the original material and therefore precludes any possible interpretation of the original stratigraphy. However, its presence indicates that a large volume of ejecta material reached the plateau during the Chicxulub impact. The various morphologies (Fig. 5) and the composition (Fig. 6a) of the spherules (Martinez-Ruiz *et al.*, 2000) support their origin from the alteration of a variety of impact glasses and tektites such as those reported in the Gulf of Mexico area. They are also similar to those from other locations on the North American marg such as near Bass River (Olsson *et al.*, 1997) a DSDP Hole 603 B (Fig. 1) (Klaver *et al.*, 1987). A of them represent impact ejecta from the Chicxul crater altered by diagenetic processes.

The presence of palygorskite and zeolites in th layer also suggests that its composition was affect by diagenetic alteration. The TEM observatio revealed palygorskite forming from a smecti precursor. The occurrence of authigenic palygor kite indicates a high-silica source and alkali conditions, which favour the precipitation of chai structure silicates (Beck & Weaver, 1978; Sing 1979). Abundant dolomite and calcite (Pope *et a* 1999) in unaltered ejecta material similar to tho found on Albion Island (Fig. 1) suggest th dolomite may also be involved in the origin palygorskite as described in other sedimenta environments (Jones & Galán, 1988).

Zeolites are typical of the low-temperatu alteration processes of volcanic material, and this case from the glassy material produced duri impact. They formed after neutralization of t large volumes of acid generated during the impa (e.g. Retallack, 1996) from the impact ejecta. T parent materials for these alteration produc represent a notable break in the mineral compo tion of the Cretaceous and Tertiary sequences a confirm the rapid deposition of 'exotic' material the Blake Nose Plateau.

Variations in the bulk mineral compositi (Fig. 3) and clay mineralogy (Fig. 4) of t normal sediment supplied to the area can interpreted in terms of palaeoenvironmental cond tions. Previous work by Chamley *et al.* (198 revealed that the clay mineral changes main reflect events on the American continent as w as the alteration of the impact-generated mater (Debrabant *et al.*, 1999). Diagenetic processes h only a very slight effect on Cretaceous and Tertia sediments, and no changes in smectite abundan can be linked to the depth of burial. In contrast w the boundary layer, the clay mineral assemblages not represent authigenic material but rather inherit material derived from the nearby continent.

The smectite in the Cretaceous and Tertia sediments is Al rich and supports a pedoge origin. Warm climate conditions and tecto stability during the Cretaceous favoured the dev opment of thick continental soils which led to t abundance of Al-Fe smectites in Cretaceous se ments from Atlantic and Tethyan domai

TABLE 2. Representative analytical electron microscopy data from smectites of the Cretaceous and
sediments normalized to $O_{10}(OH)_2$. (See Fig. 2 for location of samples).

Samples	Si	Al^{IV}	Al^{VI}	Mg	Fe	Ti	Σ^{VI}	K	Ca
171B-1049A- 17X-2 54-56	3.36	0.64	1.72	0.20	0.19	0.00	2.11	0.24	0.00
	3.79	0.21	1.45	0.19	0.39	0.00	2.03	0.09	0.07
	3.74	0.26	1.29	0.39	0.46	0.00	2.14	0.06	0.10
	3.75	0.25	1.18	0.49	0.46	0.00	2.13	0.08	0.08
	3.88	0.12	1.28	0.40	0.43	0.00	2.11	0.16	0.05
17X-2 68-70 **(K-T)**	3.63	0.37	1.31	0.84	0.17	0.00	2.32	0.08	0.06
	3.94	0.06	1.64	0.38	0.11	0.00	2.13	0.02	0.01
	3.95	0.05	1.52	0.35	0.16	0.06	2.09	0.07	0.01
	3.75	0.25	1.44	0.53	0.20	0.03	2.20	0.09	0.06
17X-2 78-80	3.76	0.24	1.37	0.46	0.34	0.00	2.17	0.03	0.10
	3.73	0.27	1.34	0.34	0.42	0.00	2.10	0.05	0.15
17X-2 90-92	3.58	0.42	1.28	0.46	0.48	0.00	2.22	0.02	0.08
	3.39	0.61	1.62	0.32	0.32	0.00	2.26	0.10	0.30
	3.61	0.39	1.37	0.45	0.36	0.00	2.18	0.12	0.02
	3.50	0.50	1.15	0.51	0.47	0.00	2.13	0.14	0.12
	3.58	0.42	1.24	0.36	0.47	0.00	2.07	0.11	0.00
	3.68	0.32	1.38	0.39	0.37	0.00	2.14	0.07	0.02
171B-1049B- 8H-2 54-56	3.38	0.62	1.85	0.23	0.10	0.00	2.18	0.16	0.06
	3.75	0.25	1.05	0.35	0.57	0.00	1.97	0.16	0.17
	3.69	0.31	1.39	0.30	0.35	0.00	2.04	0.11	0.20
	3.78	0.22	1.38	0.30	0.41	0.00	2.09	0.10	0.08
	3.73	0.27	1.43	0.36	0.31	0.00	2.10	0.10	0.13
	3.43	0.57	1.86	0.17	0.14	0.00	2.17	0.02	0.06
	3.59	0.41	1.43	0.36	0.36	0.00	2.15	0.17	0.09
	3.78	0.22	1.03	0.35	0.63	0.00	2.01	0.27	0.12
	3.54	0.46	1.20	0.50	0.36	0.00	2.06	0.16	0.14
8H-2 70-72 **(K-T)**	3.84	0.16	1.87	0.14	0.06	0.00	2.07	0.01	0.03
	3.83	0.17	1.70	0.39	0.06	0.00	2.15	0.01	0.04
	3.77	0.23	1.72	0.32	0.03	0.00	2.07	0.02	0.11
	3.73	0.27	1.43	0.52	0.22	0.05	2.22	0.03	0.02
8H-2 78-80	3.95	0.25	1.55	0.27	0.23	0.00	2.05	0.06	0.04
	3.71	0.29	1.38	0.42	0.37	0.00	2.17	0.14	0.04
	3.66	0.34	1.18	0.53	0.42	0.00	2.13	0.23	0.11
	3.64	0.36	1.44	0.48	0.28	0.00	2.20	0.14	0.04
	3.68	0.32	1.16	0.48	0.55	0.00	2.19	0.17	0.03
	3.61	0.39	1.41	0.41	0.33	0.00	2.15	0.16	0.08

(Chamley, 1979; Chamley & Robert, 1982). The abundance of smectite in Lower Cretaceous sediments led these authors to suggest that extensive vertisols had formed in poorly drained coastal areas as a result of tectonic stability, low continental relief and warm climate conditions. Such conditions seem to have dominated during most of the C
and according to the data reported here, a
the lowermost Palaeocene. Hence, the abu
smectite in both Cretaceous and Tertiary
indicates a relatively warm and hydrolysi
across the K-T boundary.

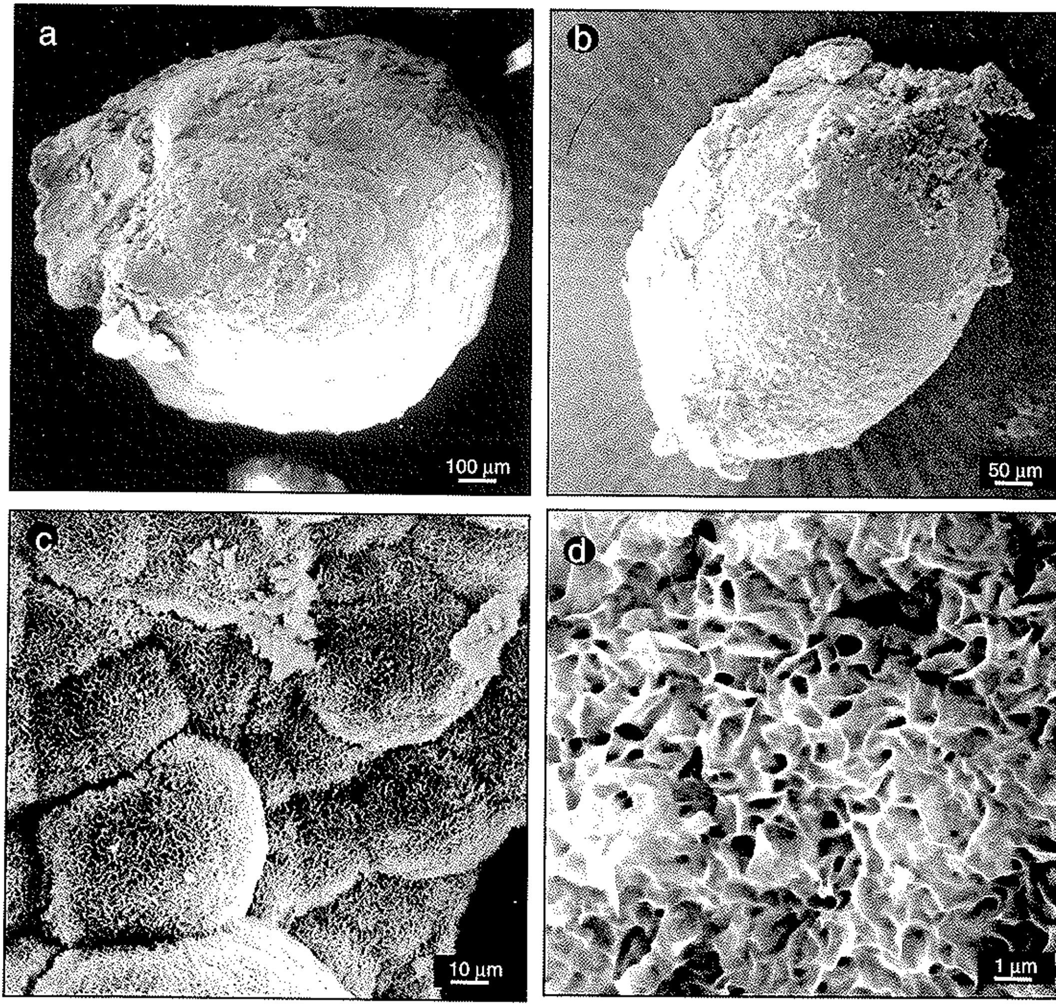

FIG. 5. Scanning electron micrographs of smectite spherules from Blake Nose at Site 1049. View of spherica (a) and oval (b) smectite spherules. (c) Surface detail of a nodular spherule. (d) Smectite morphology produce by alteration of the K-T boundary spherules.

There are some intervals characterized by an increased illite and kaolinite supply. Slumping in late Cretaceous sediments (Klaus *et al*., 2000) and the poor recovery of this time interval (Figs 3, 4) do not allow precise correlation of mineralogical changes among the different sites. At Hole 1049A, where a thicker sediment interval was sampled, a change from a smectite-rich clay association to an (illite+kaolinite)-rich association is observed down core (Fig. 4). The abundance of illite and kaolinite in these late Maastrichtian sediments suggests tha this interval corresponds to an "illite event", a proposed by Chamley *et al*. (1983). An 'illite event can be related to temporary tectonic rejuvenatio occurring on a stable continent with a warm an episodically humid climate. They are reported t occur throughout the Atlantic Ocean between th Campanian and the early Palaeocene (Chamley *e al*., 1979). The late Maastrichtian event followe the major spreading stage responsible for th

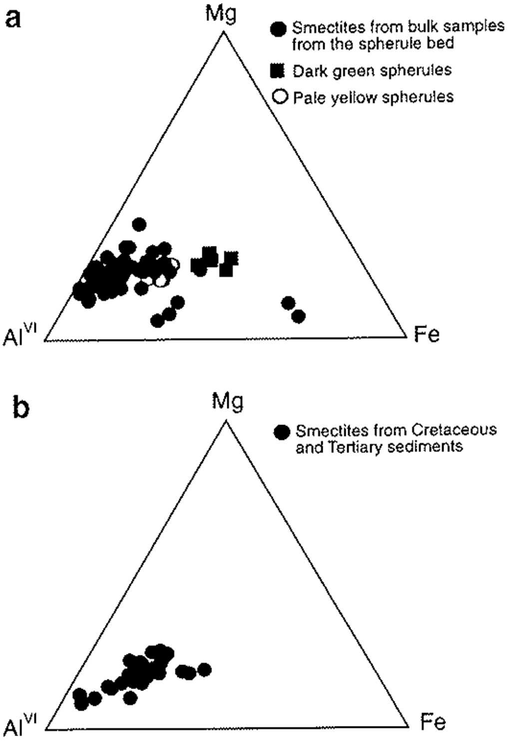

FIG. 6. Al-Fe-Mg diagrams (based on Güven, 1988) showing the smectite composition of spherule bed samples from Holes 1049A and 1049B (a) (Martínez-Ruíz *et al.*, 2000), and smectite composition from Cretaceous and Tertiary samples (b).

definitive communication between the North and South Atlantic and the development of deep-water circulation (Chamley *et al.*, 1983).

Changes in clay mineral abundance are not associated with changes in the relative abundance of minerals associated with coarser grain-size fractions. There are no significant increases in quartz or feldspar abundance in the late Cretaceous sediments during the 'illite event', thus suggesting a distal source for kaolinite and illite. The long-distance transport of kaolinite at Blake Nose implies the morphological maturation of a river basin system and/or tectonic rejuvenation (Chamley *et al.*, 1983). Although the general kaolinite+illite enrichment observed in Core 18X and the lowermost samples from Core 17X (Hole 1049A) resulted from strong tectonic rejuvenation, it was probably accompanied by increasing hydrolysis due
to the climate that reinforced the tector
Alternatively, climate could have been
factor.

Although slumping affected the u
Cretaceous sediments, the mineral cha
are recognized just below the boundary
related to climate variations as well. Th
the latest Cretaceous warming occurred
base of Chron 29 (e.g. Li & Keller, 19
could be correlated with increased kaolin
126.21–126.55 mbsf interval. The s
warming at the end of the Cretaceous wa
by a cooling interval (Stott & Kennett, 1
Keller, 1998). Warmer, wetter condition
increase in hydrolysis processes coul
more kaolinite from smectite and rei
tectonic signal.

CONCLUSIONS

(1) The K-T boundary layer at Bl
represents the impact ejecta of the
crater. The impact-generated material w
to smectite and the alteration processes
the formation of minor amounts of ze
palygorskite.

(2) The morphology and compositi
smectite-spherules support their origin
alteration of impact glasses. This spheru
confirms that large volumes of eject
reached the Blake Nose Plateau.

(3) In contrast with the authigenic cl
assemblages in the spherule bed, th
Cretaceous and Tertiary sediments are
of detrital clays inherited from the
margin. No changes linked to the depth
have been observed in these Creta
Tertiary assemblages, indicating the cla
in these sediments reflect processes takin
the American continent.

(4) Smectite dominates the clay mine
blages, being very abundant in sediments
near the boundary. Its beidellitic nature
pedogenic origin and therefore indicates
warm and hydrolysing conditions acros
boundary.

(5) An increase in kaolinite and illite c
recognized down core at the three H
Cretaceous sediments were analysed. Th
in (kaolinite+illite) probably correspon
'illite events' reported by Chamley *et al.*
this area, and suggests the late Maastri

also characterized by episodes of tectonic rejuvenation and long-distance transport of these minerals. The abundance of kaolinite suggests this tectonic rejuvenation could also have been accompanied by more severe hydrolysing conditions.

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