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Cretaceous-Tertiary boundary at Blake Nose (Ocean Drilling Program Leg 171B): A record of the Chicxulub impact ejecta

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ABSTRACT

The Ocean Drilling Program (ODP) included as one of its Leg 171B objectives the recovery of a detailed record of the Cretaceous-Tertiary (K-T) events at Blake Nose (northwest Atlantic). This aim was successfully achieved with sections across the K-T boundary recovered at Sites 1049, 1050, and 1052, and a thick spherule bed recovered at ODP Site 1049. This spherule bed varies from 7 to 17 cm in thickness at the three different holes drilled at Site 1049, and occurs at the biostratigraphic boundary between the Cretaceous and the Paleocene. Mineralogical and geochemical analyses of the Blake Nose spherule bed reveal that it is mainly composed of smectite derived from the alteration of a precursor material, mostly glass. Also present in minor proportions are dolomite, quartz, zeolites, and trace amounts of rutile and some lithic fragments. Different types of spherules, dark green, pale yellow, and light green, that can be related to different precursors were observed in the Blake Nose spherule bed. Transmission electron microscope observations showed that smectite directly replaced the original material and that dark green spherules originated from a Si-rich precursor, whereas pale yellow spherules originated from a more Ca-rich precursor. The chemical composition of the spherule-bed material at Blake Nose shows little evidence for a significant extraterrestrial contribution, suggesting that the spherule-bed material was mainly derived from the alteration of target-rock-derived material from Chicxulub crater. In addition, rare earth element C1-normalized patterns also suggest that this material was derived from upper crustal rocks.

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INTRODUCTION

The Chicxulub structure was first reported by Penfield and Camargo (1981) as a large buried impact crater, and it was suggested at that time that it could be the site of the Cretaceous-Tertiary (K-T) impact event (Byars, 1981). However, little research was devoted to this structure until evidence for thick ejecta layers and larger shocked quartz grains in the United States interior (e.g., Bohor, 1990; Sharpton et al., 1990), and evidence for tsunami deposits in Brazos River, Texas (Bourgeois et al., 1988; Smit and Romein, 1985), turned attention to a possible buried crater near the Gulf of Mexico. In the early 1990s, evidence for the temporal link of the Chicxulub structure to the K-T mass-extinction event (e.g., Hildebrand et al., 1991; Kring and Boynton, 1992; Izett, 1991; Izett et al., 1991; Sharpton et al., 1992; Swisher et al., 1992) concentrated intense research on this structure and revitalized the issue of a buried K-T impact crater to further confirm the Alvarez hypothesis (Alvarez et al., 1980). Gravity measurements and drill-core data from Chicxulub, as well as the discovery of new K-T boundary outcrops in the Gulf of Mexico area, reinforced the hypothesis of the K-T boundary impact at this site (e.g., Sigurdsson et al., 1991, 1992; Sharpton et al., 1992, 1993, 1994; Blum et al., 1993; Koeberl et al., 1994; Smit et al., 1992a, 1992b). The location of the impact would also explain the different nature of proximal and distal K-T boundary deposits and some features such as spherule size and Ir concentration (e.g., Smit, 1999). The Ocean Drilling Program (ODP) also addressed this line of research by including the K-T boundary sediments in the Gulf of Mexico and the North American Atlantic margin in its drilling objectives. At the Blake Nose Plateau, ODP Leg 171B included as one of its objectives the recovery of a detailed record of the K-T events. This aim was successfully achieved and K-T boundary materials were recovered at ODP Site 1049 in three adjacent holes: 1049A (30°08.5436'N, 76°06.7312'W), 1049B (30 + 08.5423'N, 76 + 06.7264'W), and 1049C (30°08.5370'N, 76°06.7271'W). The K-T boundary is marked in Holes 1049A, 1049B, and 1049C by a single bed of spherules, 17, 7, and 9 cm thick, respectively, capped by a limonitic layer. The excellent Cretaceous-Tertiary (K-T) boundary interval recovered provided evidence of the deposition of K-T impact-generated material at this location.

SAMPLES AND METHODS

During ODP Leg 171B five sites were cored at Blake Nose (Fig. 1); sections across the K-T boundary recovered at Sites 1049, 1050, and 1052 (Norris et al., 1998). At ODP Site 1049, a spherule bed occurs at the biostratigraphic boundary between the Cretaceous and the Paleocene. Analytical work has therefore focused on sediments from the K-T boundary interval recovered at this site because there is a complete record of the K-T event here. The uppermost Maastrichtian sediments comprise light gray nannofossil-foraminifer ooze (*Abathomphalus mayaroensis* zone and *Micula prinsii* zone) that is slumped (Norris et al., 1998, 1999; Klaus et al., 2000). A sharp contact separates this ooze from an overlying bed of spherical and oval-shaped spherules. This spherule bed varies from 7 to 17 cm in thickness at the three holes drilled at Site 1049 (Fig. 2), which suggests reworking of the ejecta material (Klaus et al., 2000). Despite this, the spherule bed confirms that the impact-generated material from the Chicxulub crater is well preserved at the Blake Nose Plateau. The spherule bed is capped by a 1–3-mm-thick orange limonitic layer, overlain by lowermost Paleocene ooze with a foraminiferal assemblage indicative of the P-alpha zone (Norris et al., 1998, 1999). The limonitic layer was initially (during on-board analysis) considered to be a candidate for the so-called fireball layer, but the usual extraterrestrial markers, such as Ni-rich spinels and a strong iridium anomaly, are conspicuously absent. The spherule bed and Cretaceous and Tertiary sediments were sampled in sections 1049A-17X-2 and 1049B-8H-2, by continuous sampling every 2 cm between 20 cm above and 20 cm below the boundary bed and samples spaced 2 cm above and below this interval. Because similar results were obtained from K-T boundary sediments from Holes 1049A and 1049B, only data from Hole 1049A are reported in tables and figures (see Table 1 for location of samples). Spherules were hand-picked under a stereomicroscope with a dry brush. Mineralogical and geochemical analyses of bulk samples and representative hand-picked spherules were done using the following methods.

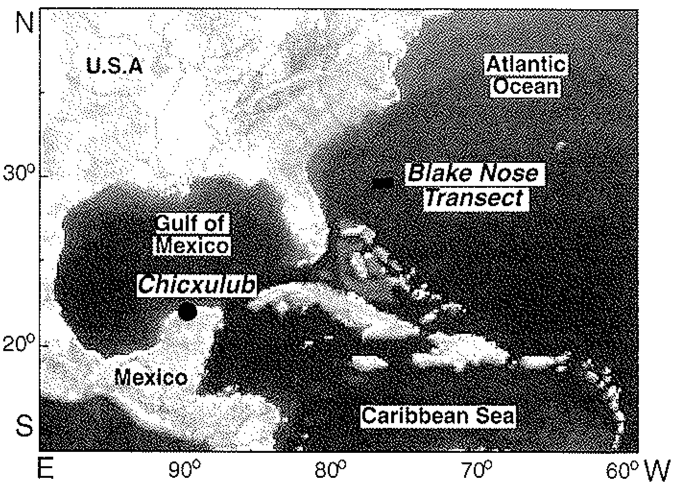

Figure 1. Location of Ocean Drilling Program (ODP) Leg 171B Blake Nose drilling transect.

X-ray diffraction

For bulk mineralogy analyses, samples were packed in Al holders for X-ray diffraction (XRD). For clay mineral analyses, the carbonate fraction was removed using acetic acid, starting the reaction at a very low concentration (0.1 N) and increasing

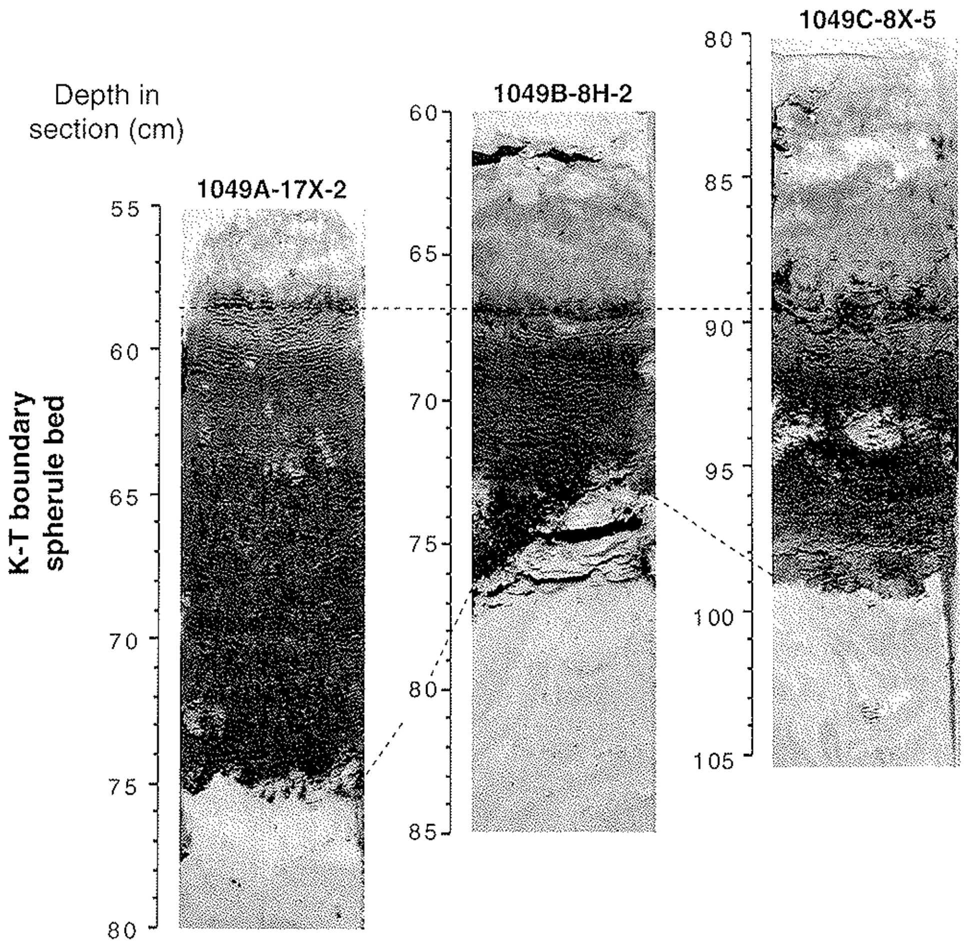

Figure 2. Core photographs of spherule bed that marks Cretaceous-Tertiary (K-T) boundary interval at three holes drilled at Site 1049.

to 1 N. Clays were deflocculated by successive washing and the <2 μm fraction was separated by centrifuging. The clay fraction was smeared onto glass slides for XRD. Diffractograms were obtained using a Philips PW 1710 diffractometer with Cu-Kα radiation. Scans were run from 2° to 64° 2θ for bulk samples and untreated clay preparations, and from 2° to 30° 2θ for glycolated, heated, and dimethyl-sulfoxide-treated samples. Semiquantitative analyses were performed on integrated peak areas using a specific computer program for the diffractometer used (Nieto et al., 1989). The estimated semiquantitative analysis error is 5%.

Electron microscopy

Morphological studies on bulk samples and hand-picked spherules were performed using binocular microscope and scanning electron microscopy (SEM; Zeiss DSM 950). Quantitative microanalyses of clay minerals were obtained by transmission electron microscopy (TEM, Philips CM-20 equipped with an EDAX microanalysis system). Quantitative analyses were obtained in scanning TEM mode only from particle edges using a 70 D diameter beam with a 200 × 1000 D scanning area and a short counting time to avoid alkali loss (Nieto et al., 1996). Smectite formulas were normalized to 11 oxygens.

Inductively coupled plasma-mass spectrometry and atomic absorption spectrometry

Samples from the spherule bed were cleaned of Cretaceous clasts under a stereomicroscope and dried, homogenized, and ground in an agate mortar for chemical analyses by inductively coupled plasma-mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS). Rb, Sr, Ba, V, Cr, Co, Ni, Cu, Zr, Hf, Mo, Pb, U, Th, and rare earth elements (REE) were analyzed by ICP-MS, and Al, K, Fe, Mn, Ca, and Mg were analyzed by AAS. Analyses were performed on bulk samples following sample digestion with HNO_3 + HF of 0.100 g of sample powder in a Teflon-lined vessel at high temperature and pressure, evaporation to dryness, and subsequent dissolution in 100 ml of 4 vol% HNO_3. ICP-MS instrument measurements were performed in triplicate using a Perkin Elmer Sciex Elan-5000 spectrometer with Rh as internal standard, and AAS

TABLE 1. X-RAY DIFFRACTION DATA OF THE CRETACEOUS-TERTIARY BOUNDARY INTERVAL AT HOLE 1049A

Core, section, interval (cm)	Depth (mbsf)	Clay minerals	Quartz (wt%)	Calcite (wt%)	Smectite (wt%)	Illite (wt%)	Kaolinite (wt%)
17X-2, 001–003	125.32	28	<5	69	83	8	9
17X-2, 004–006	125.35	28	<5	69	82	12	6
17X-2, 008–010	125.39	24	5	71	63	30	7
17X-2, 012–014	125.43	25	<5	74	56	20	24
17X-2, 016–018	125.47	27	<5	70	61	17	22
17X-2, 020–022	125.51	30	5	65	49	25	26
17X-2, 024–026	125.55	30	5	65	56	25	19
17X-2, 028–030	125.59	28	7	65	63	22	15
17X-2, 032–034	125.63	28	7	65	65	20	15
17X-2, 035–037	125.66	30	<5	66	60	29	11
17X-2, 038–040	125.69	25	<5	72	83	14	<5
17X-2, 040–042	125.71	28	<5	69	90	<5	8
17X-2, 042–044	125.73	26	<5	72	85	11	<5
17X-2, 044–046	125.75	19	<5	77	85	9	6
17X-2, 046–048	125.77	9	<5	87	84	9	7
17X-2, 048–050	125.79	11	<5	85	86	6	8
17X-2, 050–052	125.81	12	<5	84	80	13	7
17X-2, 052–054	125.83	11	<5	85	84	9	7
17X-2, 054–056	125.85	14	<5	83	88	5	7
17X-2, 056–058	125.87	12	<5	85	89	5	6
17X-2, 060–062	125.91	75	<5	12	99	<5	<5
17X-2, 062–064	125.93	92	<5	6	99	<5	<5
17X-2, 064–066	125.95	90	<5	8	98	<5	<5
17X-2, 066–068	125.97	91	<5	7	98	<5	<5
17X-2, 068–070	125.99	90	<5	8	96	<5	3
17X-2, 070–072	126.01	95	<5	5	98	<5	<5
17X-2, 072–074	126.03	91	<5	7	99	<5	<5
17X-2, 074–076	126.05	91	<5	7	99	<5	<5
17X-2, 076–078	126.07	13	<5	84	98	<5	<5
17X-2, 078–080	126.09	23	<5	75	77	15	8
17X-2, 080–082	126.11	22	<5	75	80	14	6
17X-2, 082–084	126.13	22	<5	74	82	10	8
17X-2, 084–086	126.15	21	<5	76	80	12	8
17X-2, 086–088	126.17	21	<5	76	84	13	<5
17X-2, 088–090	126.19	19	<5	79	83	10	7
17X-2, 090–092	126.21	22	<5	76	77	15	8
17X-2, 092–094	126.23	28	<5	68	45	40	15
17X-2, 096–098	126.27	30	<5	67	72	<5	24
17X-2, 100–102	126.31	30	<5	68	62	23	15
17X-2, 104–106	126.35	31	<5	68	30	30	40
17X-2, 108–110	126.39	29	<5	68	55	26	19
17X-2, 112–114	126.43	30	<5	67	50	22	28
17X-2, 116–118	126.47	28	<5	68	43	17	40
17X-2, 120–122	126.51	28	<5	68	48	12	40
17X-2, 124–126	126.55	31	<5	67	46	30	24
17X-2, 128–130	126.59	27	<5	69	68	19	13
17X-2, 132–134	126.63	28	<5	68	83	11	6
17X-2, 136–138	126.67	24	<5	75	66	13	21
17X-2, 140–142	126.71	24	<5	75	48	35	17
17X-2, 144–146	126.75	25	<5	75	81	11	8
17X-2, 148–150	126.79	20	<5	79	82	10	8

Note: Main mineral components are in the bulk sediments (clay minerals, quartz, and calcite) and clay minerals proportions are in the <2 μm fraction (smectite, illite, and kaolinite). Shaded area corresponds to the Cretaceous-Tertiary boundary layer; mbsf: meters below sea floor.

analyses were carried out with a Perkin Elmer 5100 ZL spectrometer. The quality of the analyses was monitored with laboratory and international standards from the U.S. Geological Survey (USGS). ICP-MS precision and accuracy was better than ±2% and ±5% for analyte concentrations of 50 and 5 ppm in the rock, respectively. AAS analytical error was <2%.

CRETACEOUS AND TERTIARY SEDIMENTS

The ooze immediately below the spherule bed contains planktonic foraminifera and calcareous nannofossils of late Maastrichtian age; fossils are abundant and well preserved (Norris et al., 1998, 1999). The burrow-mottled ooze overlying the spherule bed (Fig. 2) contains some reworked Cretaceous planktonic foraminifera, but typical early Danian species are also present (Norris et al., 1998, 1999). These uppermost Cretaceous and lowermost Danian materials are composed of carbonates, clay minerals, and quartz (Table 1), and minor quantities of feldspars and traces of heavy minerals and pyrite. Feldspar recognized by XRD is always <5 wt%, and trace minerals were only identified by SEM. Calcite is the dominant carbonate phase, but small quantities of dolomite are occasionally present in the burrow-mottled ooze. Clay mineral assemblages consist of smectite, which is dominant, kaolinite, and illite (Table 1). Cretaceous sediments are slump folded, although the overlying K-T boundary stratigraphy is undisturbed. The deformation of Cretaceous sediments is a general feature at proximal ejecta sites, related to the seismic energy input from the Chicxulub impact, some of it induced before the emplacement of the ejecta from this impact (Alvarez et al., 1992; Smit, 1999; Norris et al., 2000).

Although precise chemical stratigraphy of the uppermost Cretaceous sediments cannot be established due to slumping, their chemical composition is very homogeneous (Fig. 3), except for some variations related to detrital mineral abundances and redox conditions (for the chemical data, see Martínez-Ruiz et al., 2001a). Thus, some potassium-concentration fluctuations can be related to illite abundance. The slight decrease in Mn and Fe contents, and the slight increase in redox-sensitive element concentration, could be related to a change in redox conditions at the end of the Maastrichtian. The lowermost Danian stratigraphy is undisturbed. Some changes observed in the burrow-mottled ooze are mainly related to diagenetic alteration. The Mn content increases above the boundary bed, indicating diagenetic remobilization of Mn, and the Mn peak marks the penetration of the oxidation front. The REE concentrations are depleted in the spherule bed, but they are slightly enriched in the burrow-mottled ooze, which suggests reprecipitation of REEs mobilized from the spherule bed. Smit et al. (1997) reported the maximum Ir concentration in Blake Nose sediments just above the spherule bed, which may suggest that diagenetic remobilization may also have affected extraterrestrial elements, although Ni-rich spinels are abundant above the spherule bed as well (R. Rocchia and E. Robin, 1997, personal commun.).

K-T BOUNDARY BED

The spherule bed at Blake Nose (Fig. 2) consists of a coarse, graded, and poorly cemented unit. It is mostly composed of spherules, but contains Cretaceous foraminifera and clasts. Mineralogical analyses reveal that the spherule bed mostly consists of clays and minor proportions of calcite (Table 1), partially derived from the Cretaceous material. Dolomite, quartz, and zeolites are also present in minor proportions, and trace amounts of rutile, biotite, and some lithic fragments. Clays are mostly smectites; occasional traces of illite and kaolinite are probably derived from contamination by Cretaceous material. The contact of the spherule bed with sediments above and below is very sharp, suggesting very rapid deposition. The presence of Cretaceous materials within the spherule bed strongly supports downslope transport of the spherule bed material.

Spherules

Stereomicroscope and SEM observations reveal that the morphologies of the Blake Nose spherules are mainly perfect spheres with lesser proportions of oval spherules that contain bubble cavities. Sizes usually range from 100 μm to 1000 μm. Different types of spherules have been distinguished on the basis of color, morphology, and surface texture. They are light green, dark green, or pale yellow, with nodular, smooth or rough (Fig. 4) surfaces (Martínez-Ruiz et al., 2001b).

Diagenetic alteration and precursor material

X-ray diffraction scans of oriented samples reveal that the spherules are mainly composed of smectite (Table 2); there is some evidence for preserved unaltered glass relics. Moreover, TEM microanalyses show some compositional variations between dark green spherules and pale yellow spherules (Table 2). Smectites from dark green spherules are richer in Fe (Table 2), and Si/Al usually ranges from 3.1 to 3.3; however, in some Si-rich areas, the Si/Al range of 3.5 to 5 (Fig. 5A) does not correspond to a true smectite composition but to the altering glass. This suggests that a Si-rich glass has been their precursor. Smectites from pale yellow spherules have lower Si/Al, usually ranging from 2.1 to 2.5, and originated from a Ca-rich material, the Ca/Si ratio being ~6. Some calcite crystals are observed in the Ca-rich matrix that could be an original, unaltered phase. Light green spherules smectites have lower Si/Al (2–2.5) than those from dark green spherules.

The compositional differences are probably derived from different precursor glass types. Two end-member types of glass, black andesitic and CaO-poor, and honey-colored CaO-rich, are present in the proximal K-T ejecta from Haitian sections, and Mimbral, Mexico (Izett, 1991; Izett et al., 1991; Sigurdsson et al., 1991; Smit et al., 1992b; Koeberl and Sigurdsson, 1992). The differences between Blake Nose spherules therefore seem to indicate that they were derived from the alteration of compositionally different impact glasses. Variations in octahedral cations (Table 2) support a compositionally variable precursor because impact-generated glass was only briefly melted, so there was not enough time for the elements to mix and homogenize (e.g., Alvarez et al., 1992).

The smectite morphologies observed by TEM in this study are similar to those of smectites originated from the alteration of volcanic glass (e.g., De la Fuente et al., 2000) (Fig. 5A), implying that the smectite directly replaced the original glass phase. Direct formation of smectites from glass material is also consistent with the presence of altered rims where there seems

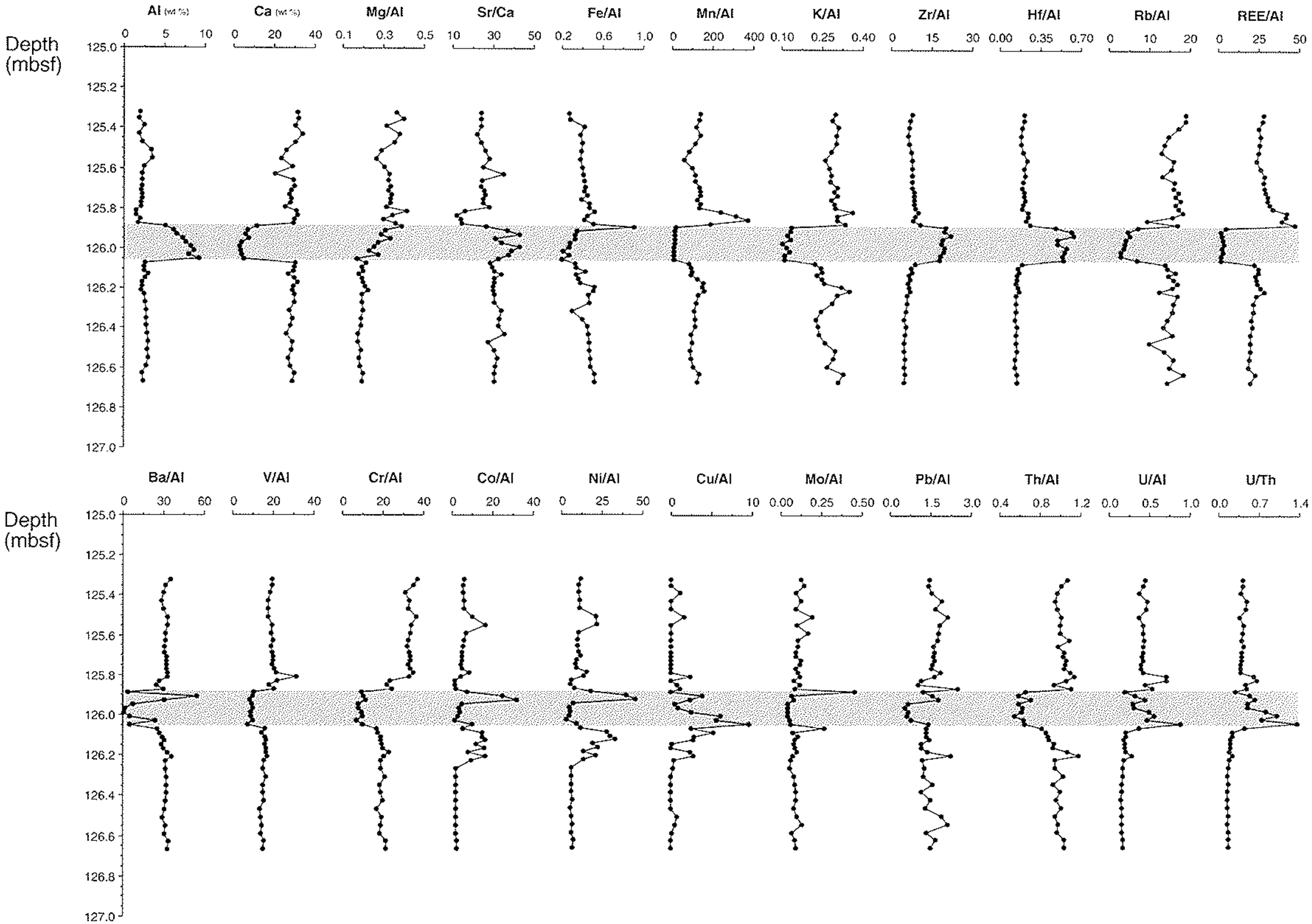

Figure 3. Geochemical data from Cretaceous-Tertiary (K-T) boundary interval at Hole 1049A. Plots show Ca and Al concentrations (wt%), Sr/Ca and Th/U ratios, Fe, K, and Mg concentrations normalized to Al and trace element/Al weight ratio ($\times 10^4$) vs. depth (for chemical data, see Martínez-Ruiz et al., 2001a). REE, rare earth elements; MBSF, meters below seafloor.

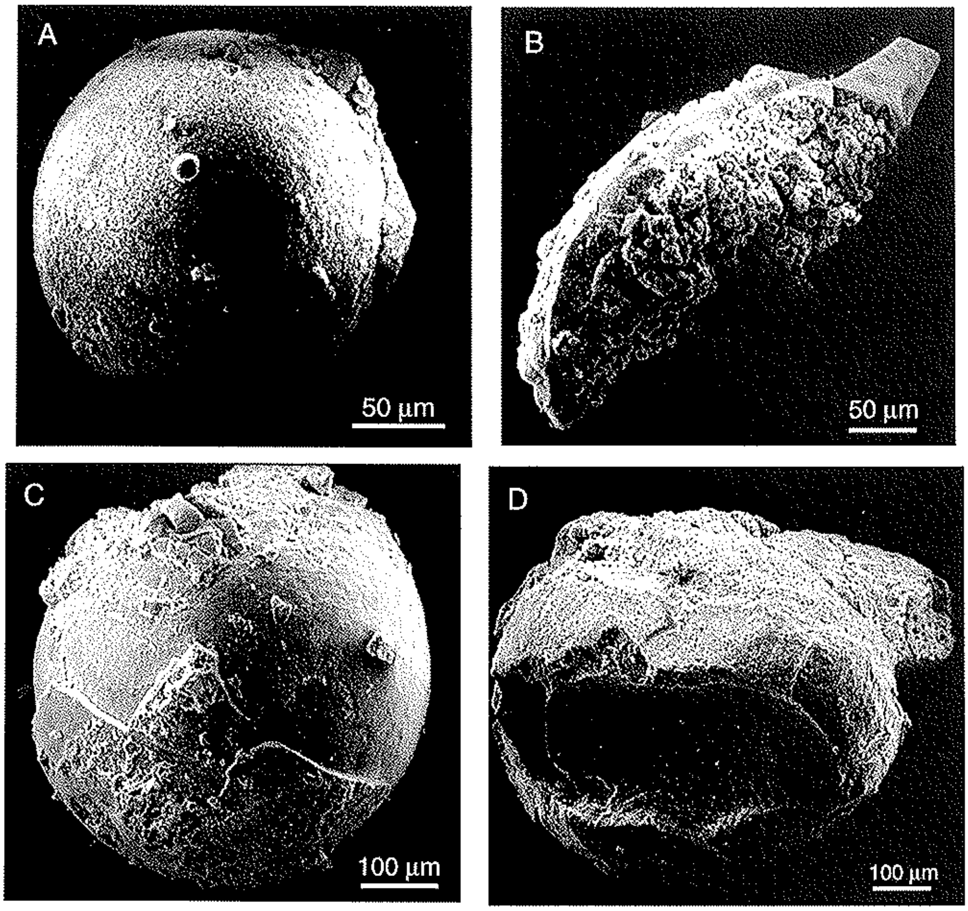

Figure 4. Scanning electron microscopy photographs of smectite spherules from Blake Nose at Site 1049. A: View of dark green spherule showing spherical morphology and nodular surface. B: View of dark green spherule with drop-shape morphology and filled with smectite aggregates. C: View of pale yellow spherule showing its spherical morphology. D: View of light green spherule showing its morphology and rough surface.

TABLE 2. REPRESENTATIVE ANALYTICAL ELECTRON MICROSCOPY DATA FROM SMECTITE SPHERULES OF THE CRETACEOUS-TERTIARY BOUNDARY BED AT HOLE 1049A

Samples	Si (a. f. u.)	Al^{IV} (a. f. u.)	Al^{VI} (a. f. u.)	Mg (a. f. u.)	Fe (a. f. u.)	Ti (a. f. u.)	Σ^{VI} (a. f. u.)	K (a. f. u.)	Ca (a. f. u.)	Na (a. f. u.)	$\Sigma^{Int.}$ (a. f. u.)
Light green spherules	3.80	0.20	1.47	0.42	0.23	0.03	2.15	0.04	0.02	0.05	0.11
	3.80	0.20	1.55	0.43	0.10	0.04	2.12	0.05	0.05	0.10	0.20
	3.71	0.29	1.53	0.55	0.09	0.06	2.23	0.06	0.02	0.21	0.29
	3.89	0.11	1.44	0.44	0.15	0.05	2.08	0.05	0.03	0.12	0.20
	3.65	0.35	1.36	0.61	0.16	0.12	2.25	0.12	0.02	0.37	0.51
	3.76	0.24	1.28	0.51	0.35	0.00	2.14	0.16	0.01	0.15	0.32
	3.70	0.30	1.50	0.47	0.19	0.00	2.16	0.07	0.04	0.15	0.26
	3.71	0.29	1.21	0.57	0.33	0.00	2.11	0.09	0.04	0.25	0.38
	3.75	0.25	1.38	0.47	0.27	0.02	2.14	0.06	0.19	0.19	0.44
	3.53	0.47	1.28	0.58	0.17	0.09	2.12	0.11	0.15	0.19	0.45
Dark green spherules	3.57	0.43	0.71	0.49	0.81	0.04	2.05	0.49	0.02	0.18	0.69
	3.67	0.35	0.77	0.41	0.81	0.04	2.03	0.41	0.00	0.12	0.53
	3.66	0.34	0.84	0.48	0.71	0.03	2.06	0.22	0.02	0.25	0.49
	3.58	0.42	0.83	0.53	0.68	0.04	2.08	0.29	0.03	0.27	0.59
	3.77	0.23	0.91	0.44	0.64	0.03	2.02	0.29	0.02	0.08	0.39
Pale yellow spherules	3.64	0.36	1.35	0.50	0.37	0.00	2.22	0.13	0.00	0.07	0.20
	3.64	0.36	1.18	0.39	0.48	0.02	2.07	0.20	0.02	0.16	0.38
	3.69	0.31	1.20	0.39	0.48	0.03	2.10	0.21	0.00	0.16	0.37
	3.56	0.44	1.04	0.48	0.48	0.00	2.00	0.06	0.11	0.48	0.65
	3.76	0.24	1.24	0.40	0.40	0.01	2.05	0.05	0.05	0.13	0.23

Note: Smectite formulae normalized to $O_{10}(OH)_2$. a.f.u. = atoms per formulae unit.

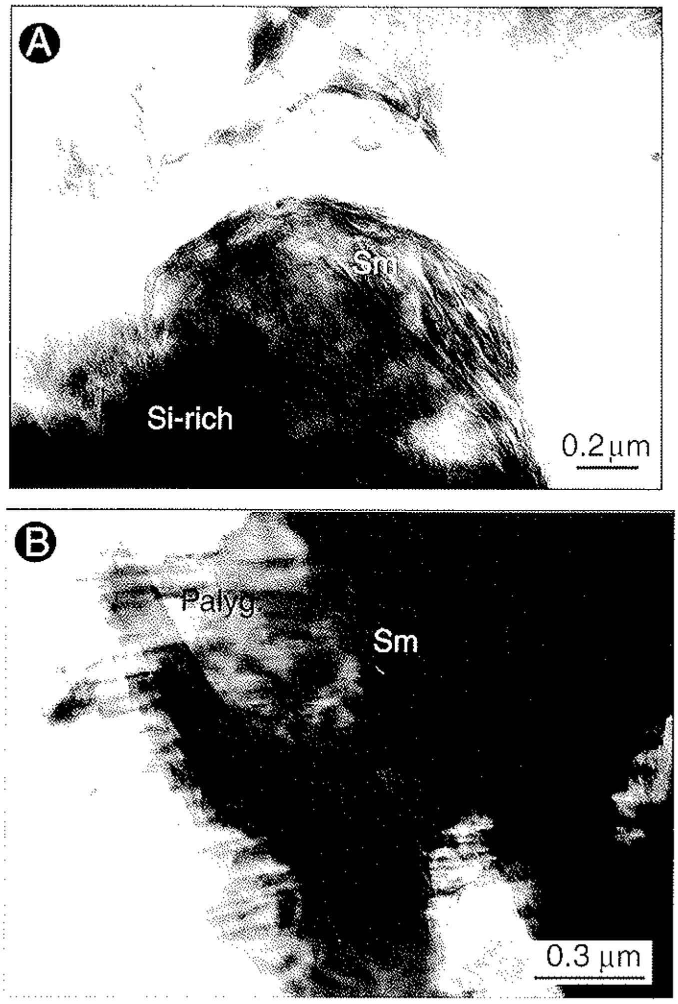

Figure 5. Transmission electron microscopy micrographs of smectites from dark green spherules (Site 1049). A: Smectites formed from high-silica material, probably altering glass. B: Higher resolution micrograph showing authigenic palygorskite fibers.

to be a morphological and chemical gradation from glass material to smectites (Fig. 5A).

During the smectite-forming diagenetic alteration of the Blake Nose spherules, zeolites and palygorskite were also formed, requiring a Si-rich source and alkaline conditions. In general, Si-rich environments favor the precipitation of chain-structure silicates (Beck and Weaver, 1978). Smectites can be a precursor of fibrous clays (Singer, 1979). Just like the low-temperature alteration of basalts (Velde, 1985), the diagenetic alteration of the precursor glass involved the expulsion of fibrous clay and zeolite-forming elements. In the present case, when the original Si-rich glass was altered to smectite, the latter did not incorporate all the available silica, thereby producing the Si-rich environments required for the formation of zeolites and palygorskite. In addition, some calcite may also have been derived from diagenetic reactions leading to clay authigenesis, such as reactions including the formation of palygorskite from smectite and dolomite (Jones and Galán, 1988). This suggestion is supported by TEM observations that reveal that the palygorskite formed from a smectite precursor (Martínez-Ruiz et al., 2001b) (Fig. 5B) and that dolomite might have been abundant in the ejecta material, as it is in other K-T ejecta deposits such as those from Albion Island, Belize (Ocampo et al., 1996; Pope et al., 1999). Furthermore, XRD and SEM data also show the presence of dolomite in the spherule bed. Thus, except for the calcite, which could be derived from either Cretaceous material or authigenic reactions, dolomite and calcite could be partially derived as original phases from carbonate target rocks. Carbonate material present in other K-T ejecta deposits supports this proposal (Smit et al., 1992a). The existence of Ca-rich and Si-rich phases is consistent with the preimpact target stratigraphy (Swisher et al., 1992; Blum et al., 1993; Koeberl, 1993; Hough et al., 1998). All this evidence suggests that the K-T boundary material from Blake Nose spherule layer was derived from Chicxulub target rocks.

The spherules from Blake Nose are comparable to spherules from other locations on the North America Atlantic margin, such as Bass River (Olsson et al., 1997) and Deep Sea Drilling Project Sites 390b and 603B (Klaver et al., 1987), and therefore they probably all represent the same diagenetically altered impact ejecta from the Chicxulub crater. Spherules from numerous sections in eastern Mexico, such as El Mibral and La Lajilla, are also similar, but moreover contain a preserved impact glass core (e.g., Smit et al., 1992b).

Chemical composition

Element concentration within the spherule bed (Fig. 3) is mainly affected by two factors: (1) a difference in composition, in particular an increase in Al and a decrease in Ca and K contents, compared with overlying and underlying sediments, and (2) diagenetic alteration under reducing conditions (Martínez-Ruiz et al., 2001a) favoring the remobilization of Fe and Mn, which diffused upward and reprecipitated upon encountering oxygenated pore waters. Differences in the Eh stability field of these elements made them uncouple during diagenetic alteration. Fe was reprecipitated, forming the limonitic layer capping the spherule bed, and Mn was diffused further upward and reprecipitated in the burrow-mottled ooze.

The REE concentrations significantly decrease in the spherule bed relative to overlying and underlying sediments. Originally, some assumed that REEs are relatively immobile during diagenetic alteration, and explained the low REE concentration in K-T boundary sediments as resulting from an impact in oceanic crust (e.g., Smit and ten Kate, 1982; Hildebrand and Boynton, 1987). However, REE mobilization during diagenesis has been demonstrated (e.g., Nesbitt, 1979; Taylor and McLennan, 1988), and therefore diagenetic remobilization could explain the low REE abundances in the K-T boundary sediments, as demonstrated by Izett (1990), who compared the REE composition of impact glass cores with the smectite rims.

Although it has also been suggested that REEs may not reflect the nature of the progenitor material (Izett, 1990), we suggest that at Blake Nose the K-T boundary sediments show C1-normalized REE patterns that can be considered informative. In certain diagenetic environment REE are leached during alteration (e.g., Zelinski, 1982) but C1-normalized patterns remain similar to the parent glass. The latter seems to be the case for the Blake Nose spherule bed material because its REE patterns are similar to those of upper crustal rocks (McLennan, 1989) and to Cretaceous and Tertiary sediments (Fig. 6), and Haitian glass cores (Izett, 1990). Koeberl and Sigurdsson (1992) reported the REE C1-normalized patterns of smectites, derived from Haitian impact glasses, being almost flat. At Blake Nose the C1-normalized patterns are not flat, and cannot be attributed solely to alteration, but instead suggest inheritance from upper crustal rocks.

Regarding extraterrestrial elements, Cr, Co, Ni, and Ir appear in low concentrations in the spherule bed at Blake Nose. A slight Ir enrichment was only reported above the spherule bed (Smit et al., 1997). Although Co and Ni concentrations (Martínez-Ruiz et al., 2001a) are not as high as in some more distal sections (e.g., Caravaca and Agost sections, Smit and ten Kate, 1982; Martínez-Ruiz et al., 1999), both elements are enriched in the upper part of the spherule bed, suggesting possible extraterrestrial contamination. However, little evidence for significant extraterrestrial contribution is observed at Blake Nose (absence of Ir enrichment and Ni-rich spinels), suggesting that the spherule-bed material mainly originated from the alteration of target-rock-derived material, as also suggested by the REE composition.

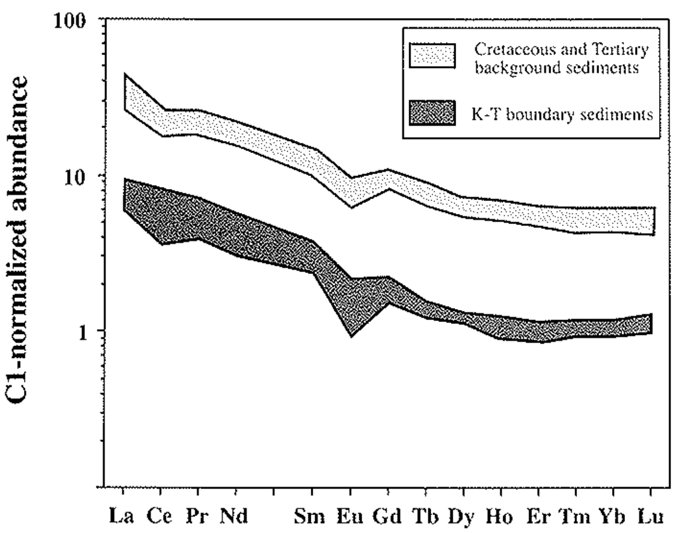

Figure 6. Rare earth element abundances normalized to C1 (Anders and Ebihara, 1982) from Blake Nose sediments (Hole 1049A). Analyzed samples are listed in Table 1.

CONCLUSIONS

The biostratigraphic K-T boundary at Blake Nose is marked by a coarse, poorly cemented bed composed mostly of spherules. These spherules are morphologically and compositionally similar to spherules from different locations on the North American Atlantic margin, and the Gulf of Mexico and the Caribbean, and all of them represent the same diagenetically altered impact ejecta. Mineralogical and geochemical analyses of the Blake Nose spherule bed reveal that this bed is mainly composed of smectite (derived from the alteration of the original precursors), minor proportions of calcite and dolomite, and other trace components such as quartz, rutile, zeolites, and lithic fragments. Different types of spherules were observed in the Blake Nose spherule bed: dark green, pale yellow, and light green spherules, which can be related to different precursors. TEM observations showed that smectite directly replaced the original material and that dark green spherules originated from a Si-rich precursor, whereas pale yellow spherules originated from a Ca-rich precursor. This result is in agreement with the variation of impact glass compositions reported in other K-T boundary sections around the Gulf of Mexico. Prior to smectite formation the precursor of the Blake Nose spherules was probably compositionally similar to the impact glasses reported at Haitian sections. Other mineral phases that originated during alteration, such as palygorskite and zeolites, also indicate a very Si-rich environment. In addition, the occurrence of palygorskite suggests the presence of dolomite in the original precursor material. Some dolomite and calcite within the spherule bed may represent original phases. The chemical composition of the spherule-bed material at Blake Nose does not show a significant extraterrestrial contribution, suggesting that the spherule-bed material mainly originated from the alteration of target-rock-derived material. Major chemical changes accompanied the diagenetic alteration of glass to smectite, the REE concentrations being significantly depleted during this alteration. Low Eh conditions also led to trace element remobilization. Fe and Mn were the most significantly mobilized elements, diffusing upward and reprecipitating upon encountering oxygenated pore waters. Diagenetic alteration is therefore the main control of the geochemical profiles across the K-T boundary at Blake Nose. However, REE C1-normalized patterns suggest that this material was derived from upper crustal rocks.

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