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Rare earth element composition as evidence of the precursor material of Cretaceous–Tertiary boundary sediments at distal sections

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Abstract

The Chicxulub impact event led to a worldwide deposition of impact materials originated from target rocks and the vaporized bolide. Relative contributions of both types of material to the K/T ejecta deposits vary with distance to the crater site. At distal sites (e.g., Agost and Caravaca in the SE of Spain) a major contribution of extraterrestrial material is indicated by different impact signatures, such as Os and Cr isotope composition, abundant microkrystites, platinum group elements and other siderophile elements that are typical of extraterrestrial components. Closer settings to the Chicxulub crater, for example the Blake Nose Plateau in the North American margin, display major continental crustal rock contributions in the ejecta layer. REE compositions provide additional evidence for terrestrial vs. extraterrestrial rock contributions. Previous research has not focused specifically on REE concentrations and corresponding C1- and NASC-normalized patterns. However, normalized REE patterns are already generating supplementary insights into the nature of the original material of the K/T boundary layer. Thus, Blake Nose ejecta C1-normalized patterns indicate a derivation from continental crustal target rocks. In more distal sections REE compositions point to a probable mafic precursor and confirm that extraterrestrial materials represent a major contribution the ejecta layer.

Keywords: K/T boundary; Chicxulub; Spherules; Rare earth elements

1. Introduction

The Chicxulub crater was excavated in the Yucatan Peninsula 65 million years ago. Although its size and morphology have been subjected to some debate (e.g., Hildebrand et al., 1991; Sharpton et al., 1993; Hildebrand et al., 1995; Morgan et al., 1997, 2000), recent results have offered greater insight into structural characteristics of this crater (e.g., Vermeesch and Morgan, 2004; Morgan et al., 2005). It has been demonstrated that the impact affected materials down to the base of the crust and that a large portion of that crust was ejected (e.g., Christeson et al., 2001; Kring and Durda, 2002; Vermeesch and Morgan, 2004; Morgan et al.,

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2005). Thus, the Chicxulub impact produced a wide range of ejecta materials derived from the target and the vaporized bolide. Although the angle of impact is significantly influential, the contribution of various types of impact debris to the world-wide distributed ejecta depends largely on the distance relative to the crater site. At increasing distances from Chicxulub, target rock input decreases, and extraterrestrial material is the most significant contribution to the ejecta layer (e.g., Smit, 1999; Claeys et al., 2002). Previous research has already documented preimpact stratigraphy (e.g., López Ramos, 1975; Hildebrand et al., 1991; Sharpton et al., 1996; Urrutia-Fucugauchi et al., 1996; Claeys et al., 2003). It is well known that the Yucatan Peninsula at the end of the Cretaceous was a shallow water platform overlying a crystalline basement (e.g., Kring, 2005 and references herein). U–Pb ages of shocked zircons suggest that this basement dates to the pan-African age (Krogh et al., 1993). Recent drilling by the International Continental Drilling Program (ICDP) has also shed light on the composition of the target rocks and impact-generated materials (e.g., Urrutia-Fucugauchi et al., 2004; Tuchscherer et al., 2005). Kettrup and Deutsch (2003) have reported, on the basis of core sample analyses (Yaxcopoil-1 borehole, ICDP), a heterogeneous crystalline target. They suggested that Gondwanan and Laurentian crust may be present since amphibolite, granite and gneiss are fragments from the basement. The heterogeneity of the Yucatan target is also clearly indicated by the composition of the suevite breccia. Claeys et al. (2003) distinguished three subunits in this suevite, the composition of the upper members being dominated by the sedimentary cover of the Yucatan target, while the proportion of evaporite, silicate melt and basement clast increases with depth. These authors also showed that different melt compositions can still be identified at thin section scale, suggesting incomplete homogenization of the melt. Outside the crater, varieties of impact glass compositions in Gulf of Mexico sections (e.g., Sigurdsson et al., 1991; Koeberl and Sigurdsson, 1992; Koeberl, 1993) reflect the mixing of the target lithologies. The same has been inferred from the compositions of altered spherules at the Blake Nose section (ODP Leg 171B, Hole 1049), which is located at a greater distance from Chicxulub (Martínez-Ruiz et al., 2001a, 2002). Finally, at more distal K/T boundary sections (e.g., Italy or El Kef or SE Spain), the lower contributions of target rocks led to relative elevated concentrations of extraterrestrial material (e.g., Smit, 1999). Geochemical data, such as Cr and Os isotope composition and trace element anomalies (e.g., Platinum Group Element-PGE-enrichments), support the presence of these high concentrations of extraterrestrial materials (e.g., Alvarez et al., 1980; Smit, 1990; Robin et al., 1991; Martínez-Ruiz et al., 1997; Shukolyukov and Lugmair, 1998; Smit, 1999; Martínez-Ruiz et al., 1999; Wdowiak et al., 2001; Frei and Frei, 2002.).

Differences in the precursor materials are additionally indicated by characteristics of the K/ boundary spherules. These impact generated materials are represented by a diversity of glass compositions in the Gulf of Mexico and surrounding locations (e.g., Koeberl and Sigurdsson, 1992; Smit, 1999; Claeys et al., 2003). In contrast, microkrystites have been found at the most distal section (Smit et al., 1992; Bohor and Glass, 1995). Both impact glasses and microkrystites commonly altered to diverse mineral phases, e.g., clays, K-feldspar, Fe oxides, etc. (e.g., Smit, 1990; Montanari, 1991; Martínez-Ruiz et al., 1997; Smit, 1999). Thus, most of the elements in original phases may be partially mobilized, enhanced, depleted or removed during diagenetic alteration. Therefore, the assessment of the nature of precursor materials based on altered material may be difficult. However, findings of unaltered microkrystites in the Pacific that are composed of clinopyroxene support a mafic composition as the precursor of microkrystites (Smit et al., 1992). Kyte and Bohor (1995) also showed Ni-rich magnesiowüstite within magnesioferrite spinels recovered from K/T boundary sediments in the Pacific that indicate crystallization from ultramafic liquids. Furthermore, the Cr isotope composition (Shukolyukov and Lugmair, 1998) and the finding of a piece of the projectile in the North Pacific Ocean (Kyte, 1998) indicate that the impactor was a carbonaceous chondrite. The presence of C-rich cores in microkrystites (Martínez-Ruiz et al., 1997) may also further support the idea that this composition was the precursor since this carbon is probably a relict of the extraterrestrial material. In addition, even though postdepositional alteration may have affected materials from the ejecta layer, extraterrestrial geochemical signatures are generally preserved and, despite diagenesis, some elements traditionally considered mobile can retain valuable information, as is the case of Rare Earth Element (REE).

Consequently, the present paper focuses on the REE composition of K/T boundary sediments and spherules at distal sections. Most of the research to date has neglected this geochemical characteristic of the Chicxulub impact generated materials. However, REE C1-normalized patterns may represent an additional proxy, which would further support the nature of the precursor melt. Ejecta deposits from well-known representative distal sections, such as Agost and Caravaca (SE Spain), and from the Blake Nose section (closer to Chicxulub), have been analyzed (Fig. 1) in order to validate this proxy.

1.1. K/T boundary stratigraphy

The Agost and Caravaca sections are located in the Betic Cordillera (SE Spain), which is part of the peri-Mediterranean Alpine orogenic belt. The K/T boundary is marked by a 2–3 mm thick layer consisting mainly of smectite at both sections and abundant spherules. These spherules are diagenetically altered to K-feldspar at Caravaca. At Agost, in addition to K-feldspar, Fe-oxides are also present (Fig. 2). The boundary layer is intensely rust-colored at Caravaca and mainly dark-green with rusty patches at Agost. A sharp contact with Cretaceous light-green marly limestones underlies the layer, while it is overlain by marly clays with Early Danian microfossils. Impact signatures at these sections suggest that it represents the altered fireball layer in which considerable extraterrestrial contamination has been observed (e.g., Kyte et al., 1985; Smit and Romein, 1985; Bohor et al., 1986; Smit, 1990; Robin et al., 1991; Martínez-Ruiz et al., 1997, 1999; Ebel and Grossman, 2005).

The Blake Nose boundary layer sharply overlies the uppermost Cretaceous foraminiferal-nannofossil ooze and is overlain by a clay rich ooze with foraminiferal assemblages indicative of the Early Danian (Norris et al., 1998; Klaus et al., 2000). A poorly sorted and cemented layer (9 to 17 cm) marks the boundary and is composed of round and oval spherules altered to smectite (Martínez-Ruiz et al., 2001a). This spherule bed is capped by a 3 mm rusty layer, initially interpreted as the fireball layer (Norris et al., 1998). However, the scarcity of Ir (under 1 ppb; Smit et al., 1997; Martínez-Ruiz et al., 2001b), as well as the absence of significant enrichment in Ni, Co and other typical extraterrestrial elements, would suggest that it originated from the diagenetic remobilization of Fe (Martínez-Ruiz et al., 2001b). Ir concentrations are highest (1.3 pp) above the spherule bed, whereas within this bed such concentrations are lower (0.2–0.9 ppb) (Smit et al., 1997; Martínez-Ruiz et al., 2001b). The variable thickness of this bed as well as the presence of Cretaceous foraminifera and clast of Cretaceous sediments indicate reworking of the spherule bed material (Klaus et al., 2000). However, despite the lack of preservation of the original thickness, the paleodistance from Chicxulub, ~2000 km, would suggest it could have been considerable due to the higher contribution of target rock materials. Increasing contribution of target rock material resulted in turn in significant dilution of the extraterrestrial input.

2. Samples and methods

After careful cleaning of the altered surface, Cretaceous sediments from the Caravaca and Agost sections were sampled continuously at intervals of 2 cm. Tertiary sediments from these sections were sampled at intervals of 1 cm. The boundary layer was carefully separated to avoid contamination from Tertiary and Cretaceous sediments. Hundreds of spherules were hand-picked after sieving and further cleaned ultrasonically. Bulk sediments, K-feldspar and Fe-oxide spherules were ground

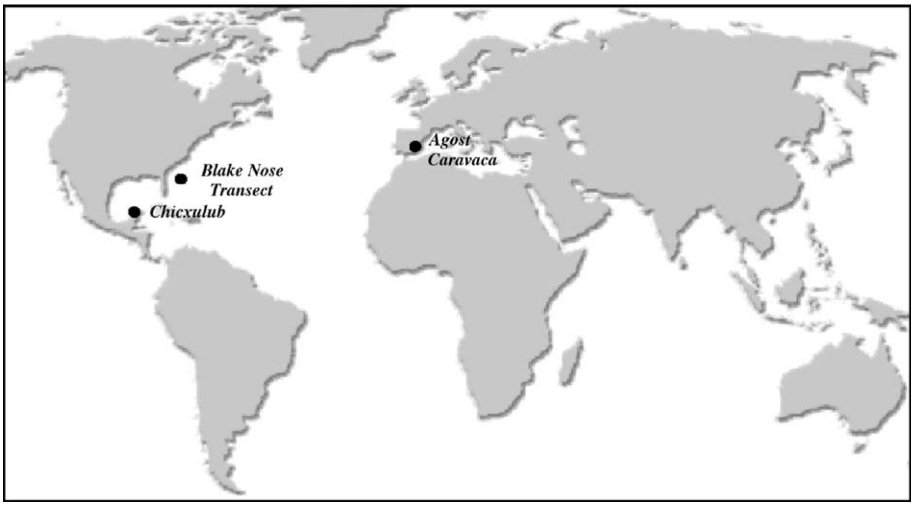

Fig. 1. Location map showing the studied sections and the Chicxulub crater.

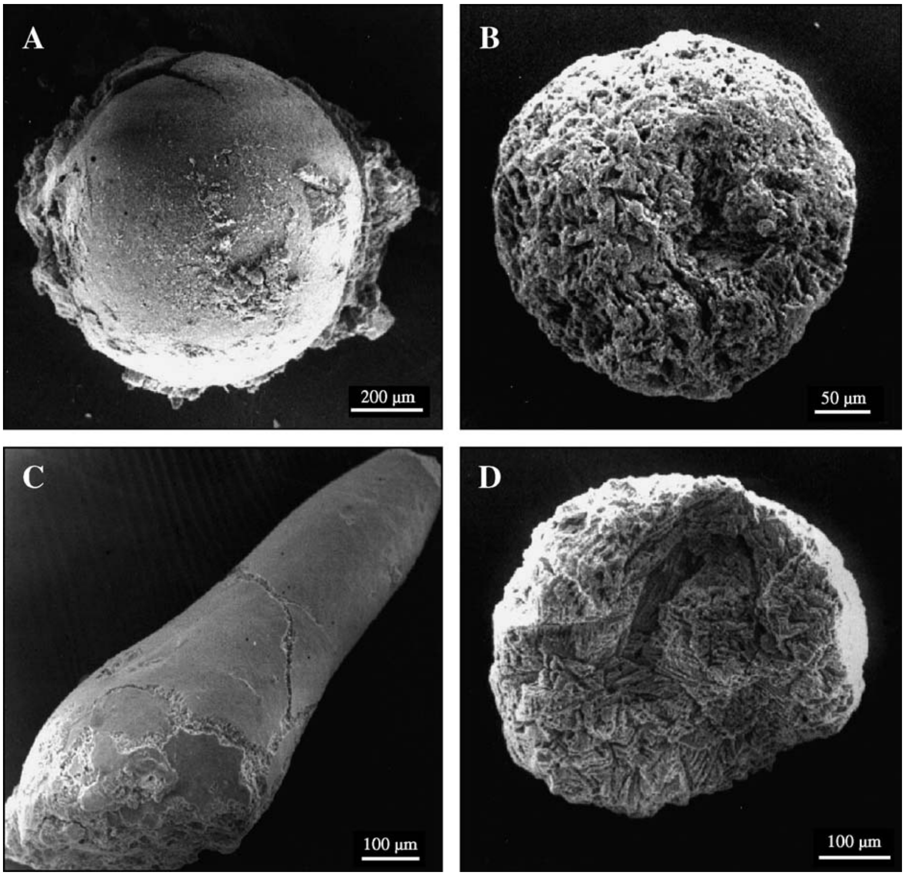

Fig. 2. Scanning electron microscopy photographs: (A) smectite spherule from Blake Nose at Site 1049; (B) K-feldspar spherule from Agost; (C) Fe-oxides spherule from Agost; (D) K-feldspar spherule from Caravaca.

and homogenized in an agate mortar. Representative powder portions were used for chemical analyses. The Blake Nose K/T boundary interval was recovered at Site 1049 in Holes A, B, and C. Samples were taken at 2 cm intervals in sections 1049A-17X-2 and 1049B-8H-2 and cretaceous clasts were eliminated. Sediments above and below the boundary were also sampled at 2 cm, and then ground and homogenized.

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was used to obtain Rare Earth element composition. ICP-MS analyses were performed following sample digestion with HNO_3+HF. Sample powders (0.100 g) including those of spherules were attacked in a teflon-lined vessel at high temperature and pressure, and then evaporated to dryness. Subsequently, residues were dissolved in 100 ml of 4% vol. HNO_3. Instrument measurements were carried out in triplicate using a Perkin Elmer Sciex Elan-5000 spectrometer and Rh as internal standard. Laboratory and international standards (MAG-1, UB-N, AGV-N, DR-N, GS-N, GA, GH y BR-N) were used to check analysis quality. Precision was better than ±2% and ±5% rel. for analyte concentrations of 50 and 5 ppm, respectively.

3. Results

Mineral and chemical composition of K/T boundary sediments from the studied sections have been reported in previous works (e.g., Smit and ten Kate, 1982; Kyte et al., 1985; Smit and Romein, 1985; Ortega-Huertas et al., 1995; Martínez-Ruiz et al., 1997; Ortega-Huertas et al., 1998; Martínez-Ruiz et al., 2001a,b). The Agost and Caravaca K/T boundary layer is composed of smectite and abundant spherules. Major mineral components of Cretaceous sediments are calcite, quartz and clays. Clay mineral assemblages are predominantly detrital mica, smectites and kaolinite. The lowermost Danian clay layer is also composed of calcite, quartz and clays. Calcite content gradually rose with productivity recovery to proportions similar to those of Cretaceous sediments. Clay assemblages are also detrital mica, smectites and kaolinite (Martínez-Ruiz et al., 1992;

Ortega-Huertas et al., 1995; Martínez-Ruiz et al., 1997; Ortega-Huertas et al., 1998).

At Blake Nose, Cretaceous and Tertiary sediments are mainly composed of calcite and minor amounts of clays; quartz and dolomite are also present, but always below 5% wt. The spherule layer is composed of clays. Spherules altered diagenetically to smectite (Martínez-Ruiz et al., 2001a), as previously mentioned. Many papers have described the chemical composition of Cretaceous and Tertiary sediments at Caravaca (e.g., Smit and ten Kate, 1982; Kyte et al., 1985; Smit and Romein, 1985; Martínez-Ruiz et al., 1999). Although the Agost section has not been the focus of as much research as that of Caravaca, the geochemical composition of its K/T boundary interval has also been studied (e.g., Smit, 1990; Martínez-Ruiz et al., 1992, 1999). Chemical compositions of Cretaceous and Tertiary sediments are similar to those of average shales. In contrast, the boundary layer is characterized by significant geochemical anomalies. At Blake Nose a typical crustal sediment composition is also reported throughout the entire K/T boundary interval (Martínez-Ruiz et al., 2001b). As is the case for most of the well known K/T boundary sections, the REE composition of Cretaceous, K/T and Tertiary sediments has not yet been described in detail.

In order to present the REE background concentrations for these sediments (Fig. 3, Table 1), representative Cretaceous and Tertiary data have been selected from the intervals above and below the boundary layer. K/T boundary sediments and individual spherules concentrations are also presented. C1- and NASC-normalized patterns can be seen in Fig. 3. In all three sections Cretaceous and Tertiary sediments show typical C1-normalized patterns for sedimentary rocks. These

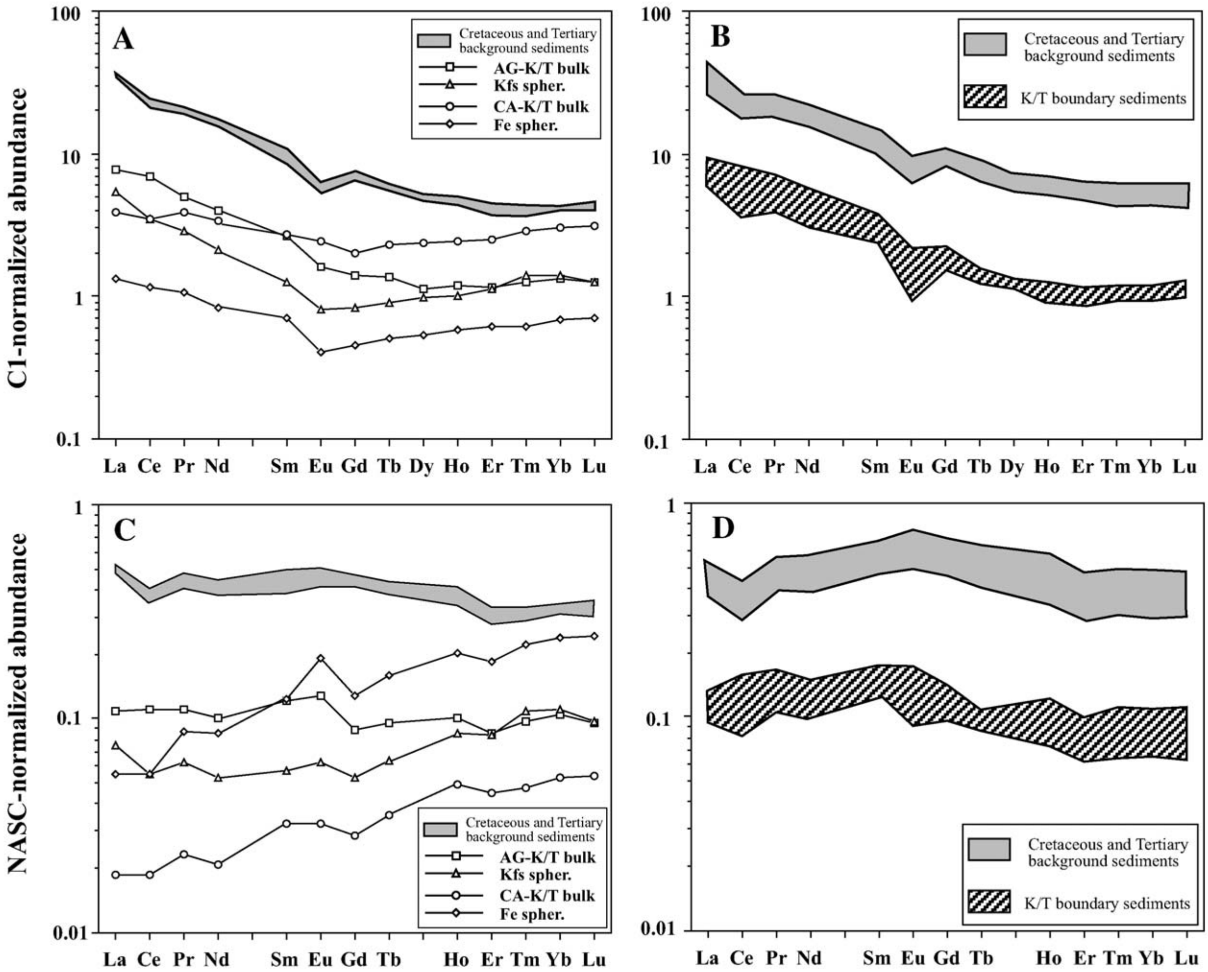

Fig. 3. REE abundances (normalized to the C1 chondrite values of Anders and Ebihara, 1982; and NASC values of Haskin et al., 1968): (A) and (C) Agost and Caravaca sections, (B) and (D) Blake Nose (Hole 1049A, ODP Leg 171 B).

Table 1
REE concentrations at Agost (AG), Caravaca (CA) and Blake Nose (ODP Leg 171B, Hole 1049A) sections

Samples	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	La/Yb	Eu/Eu*
CA-Cretaceous	15.3	26.0	3.47	13.5	2.54	0.57	2.24	0.34	1.91	0.38	0.94	0.15	0.97	0.15	15.8	0.7
CA-Tertiary	16.7	29.5	3.77	14.8	2.81	0.63	2.47	0.38	2.05	0.43	1.13	0.17	1.06	0.17	15.7	0.7
AG-Cretaceous	15.0	24.3	3.23	12.4	2.21	0.52	2.06	0.31	1.81	0.36	0.96	0.14	0.97	0.14	15.5	0.7
CA-Kfs spherules	0.60	1.36	0.19	0.69	0.18	0.04	0.15	0.03	0.22	0.05	0.15	0.02	0.17	0.03	3.6	0.7
CA-K/T	2.41	4.02	0.50	1.75	0.34	0.08	0.28	0.05	0.39	0.09	0.29	0.05	0.35	0.05	7.0	0.8
AG-Fe spherules	1.75	3.99	0.68	2.84	0.70	0.24	0.67	0.14	0.94	0.21	0.63	0.11	0.74	0.12	2.4	1.1
AG-K/T	3.47	8.1	0.87	3.35	0.70	0.16	0.46	0.08	0.45	0.11	0.29	0.05	0.32	0.05	10.7	0.8
171B1049A-																
17 × 02 028–030	15.4	20.7	3.51	13.8	2.72	0.61	2.67	0.38	2.15	0.44	1.20	0.18	1.07	0.16	14.4	0.7
17 × 02 040–042	14.8	20.8	3.42	13.7	2.75	0.64	2.72	0.40	2.20	0.45	1.16	0.18	1.03	0.16	14.4	0.7
17 × 02 042–044	15.1	21.8	3.52	14.3	2.87	0.66	2.87	0.43	2.45	0.47	1.24	0.17	1.04	0.16	14.5	0.7
17 × 02 044–046	15.5	22.4	3.67	14.9	2.95	0.69	3.04	0.45	2.36	0.48	1.21	0.16	1.03	0.16	15.1	0.7
17 × 02 050–052	13.6	21.0	3.31	12.9	2.68	0.65	2.75	0.40	2.20	0.48	1.23	0.19	1.13	0.17	12.0	0.7
17 × 02 052–054	13.8	22.4	3.36	13.4	2.87	0.67	2.81	0.42	2.32	0.45	1.28	0.20	1.23	0.20	11.2	0.7
17 × 02 054–056	15.6	28.7	3.96	16.5	3.62	0.81	3.27	0.49	2.79	0.55	1.46	0.22	1.44	0.22	10.9	0.7
17 × 02 056–058	16.5	31.1	4.41	18.1	3.77	0.93	3.52	0.54	2.94	0.60	1.60	0.25	1.53	0.23	10.8	0.8
17 × 02 062–064	3.14	4.91	0.82	2.88	0.70	0.12	0.55	0.08	0.46	0.10	0.27	0.04	0.28	0.04	11.2	0.6
17 × 02 064–066	4.24	9.4	1.23	4.62	1.00	0.21	0.74	0.09	0.52	0.11	0.29	0.05	0.29	0.05	14.6	0.6
17 × 02 068–070	3.54	8.9	1.09	4.11	0.83	0.19	0.59	0.08	0.45	0.08	0.23	0.04	0.23	0.04	15.7	0.8
17 × 02 072–074	2.48	6.5	0.83	3.33	0.73	0.11	0.50	0.07	0.46	0.08	0.21	0.04	0.23	0.04	10.7	0.6
17 × 02 074–076	2.99	6.0	0.83	3.18	0.78	0.13	0.57	0.09	0.58	0.13	0.34	0.06	0.34	0.05	8.8	0.6
17 × 02 076–078	11.6	20.9	3.15	12.5	2.62	0.61	2.35	0.34	1.75	0.35	0.97	0.15	0.90	0.14	12.9	0.8

The shaded area corresponds to individual spherules and K/T boundary sediments from Caravaca, Agost and Blake Nose, others shown as representative of Cretaceous and Tertiary REE backgrounds.

sediments thus display negative Ce and Eu anomalies and LREE enrichments relative to HREE. At Blake Nose, the REE content found in K/T boundary sediments was lower than in those of the Cretaceous and Tertiary sediments; however, the C1-normalized patterns are similar to those of Cretaceous and Tertiary sediments and, consequently, to "average shales" (Fig. 3). At the Agost and Caravaca sections, the C1-normalized patterns from the boundary layer and K/T boundary spherules are quite different from those of Cretaceous and Tertiary sediments and thus from "average shales." Distinctive almost flat patterns are also displayed by spherules (Fig. 3). NASC-normalized patterns are also clearly different when comparing Blake Nose with the most distal locations (Agost and Caravaca).

3.1. Nature of the impact generated material

The chemical composition and the nature of the K/T boundary bed at Blake Nose indicates that this bed derives from Chicxulub melted target rocks. Previous data clearly show that the contents of Ir (0.2–0.9 ppb) and of other typical extraterrestrial elements are low (Smit et al., 1997; Martínez-Ruiz et al., 2001b). The terrestrial origin for Blake Nose boundary materials agree with the absence of Ir anomalies in tektites and impact-generated materials derived from crustal rocks (e.g., Koeberl, 1990). Such an origin is also supported by the spherule composition (Martínez-Ruiz et al., 2001a). Smectite composition varies from highly Si-enriched smectites to Ca-rich smectites. This fits with the composition of the original material, which is considered to be variable since time was insufficient for the composition to be homogenized (e.g., Alvarez et al., 1992; Claeys et al., 2003). In addition, Blake Nose spherules are far different from microkrystites (Smit et al., 1992). Blake Nose morphologies also correspond to spheres and oval spherules (Martínez-Ruiz et al., 2001a). Crystalline textures have not been observed and glass relicts are present. The composition of such relicts corresponds to Ca-rich and Si-rich (Martínez-Ruiz et al., 2002), which is also in agreement with that of the impact glasses found in the Gulf of Mexico area (Koeberl and Sigurdsson, 1992). Blake Nose spherules are also similar to those of different locations in the Northamerican Atlantic margin, e.g., Bass River (Miller et al., 1998) and DSDP 603B (Klaver et al., 1987), and thus represent the same Chicxulub impact ejecta.

At increasing distances from Chicxulub, such as the Agost and Caravaca sections (SE Spain), both the chemical composition of the ejecta layer and the nature of the spherules evidence significant extraterrestrial contamination (Smit et al., 1992). This layer is composed of pure smectite and abundant microkrystites according to the term proposed by Glass and Burns (1987). Despite alteration, quench-crystal textures have been observed (Smit, 1990; Smit et al., 1992; Martínez-Ruiz et al., 1997). Other than enrichments in typical extraterrestrial elements, such as Ir, Cr, Co and Ni, the isotopic Cr composition has also been interpreted as extraterrestrial at Caravaca and it has been proposed that the impactor was a carbonaceous chondrite (Shukolyukov and Lugmair, 1998). Furthermore, K-feldspar spherules from this section contain C-rich cores that are enriched in PGE and Ni, thus evidencing an important extraterrestrial contribution. Such cores represent an unusual phase composed of variable percentages of carbon, as well as other elements, including elevated sulphur concentrations. The concentrations of these additional elements largely coincide with mafic compositions. These core compositions indicate that the precursor is likely to have been a mixture of carbon, sulphide and silicate phases (Martínez-Ruiz et al., 1997). All of the above-mentioned data evidence that these spherules originated in the higher energy environment in which rapid crystallization led to quench crystalline textures (Smit et al., 1992; Martínez-Ruiz et al., 1997). Such an origin is proposed by Melosh and Vickery (1991), whose model estimates the droplet size of spherules originated during an impact similar to that of Chicxulub. These sizes are consistent with those found at Agost and Caravaca. This supports the hypothesis that materials deposited at such distances with respect to Chicxulub would derive mainly from the higher-energy part of the ejecta plume where extraterrestrial contributions were more significant. In contrast, the ejecta layer at closer locations to Chicxulub mostly comprises target material (e.g., Smit et al., 1992; Smit, 1999; Claeys et al., 2002) which is consistent with the chemical and mineral composition reported at Blake Nose.

REE composition provides further evidence regarding the nature of ejecta materials relative to their distance from Chicxulub. REE C1- or NASC-normalized patterns of boundary materials cannot be accounted for exclusively on the basis of the process of alteration, since they are also a consequence of the characteristics of the impact-generated material. Although diagenetic alteration led to REE depletion, the REE composition reported at the studied sites shows that normalized patterns are still informative. The shape of these patterns suggests that they remain similar to those of the precursor materials. Thus, despite depletion, it is likely that the normalized patterns of K/T boundary materials do in fact reflect the original shape of precursor normalized patterns.

Until recently, REE compositions of K/T boundary sediments from distal sections have been reported at few locations. Kastner et al. (1984) showed REE patterns at DSDP Hole 465A with a typical seawater negative cerium anomaly, indicating an open water–rock diagenetic system. These authors also showed REE patterns from Stevns Klint and suggested that the absence of a negative cerium anomaly indicates smectite formation in a low water–rock diagenetic system. Thus, the smectite composition would reflect that of the precursor glass. Frei and Frei (2002) also showed Stevns Klint REE-patterns with cerium anomalies, which suggests that different samples may have evolved in slightly different diagenetic regimes. Furthermore, the patterns are typically LREE-enriched and resemble those of the continental crust. This may suggest that a more local derived input contributed to the analyzed samples from the Fish Clay layer, in addition to extraterrestrial material. Frei and Frei (2002) have proposed the same on the basis of lithophile elements such as Pb, Nd and Sm whose abundance and isotopic composition was probably affected by enhanced erosion. Ebihara and Miura (1996) reported REE abundances at the Gubbio K/T boundary interval and concluded that most of the REE in the boundary samples were contributed mainly by seawater on the basis of negative cerium anomalies.

At closer distances to Chicxulub, Izett (1991) reported the REE concentrations in tektites from the Haiti section and suggested that their progenitor material was sedimentary deposits with a bulk composition of andesite. However, comparisons between amounts of REE in tektite glass and in smectites supported that REE were severely depleted during diagenetic alteration. The REE patterns of the smectite were found to be similar to those of seawater with a pronounced negative cerium anomaly and therefore different from the precursor glass. Koeberl and Sigurdsson (1992) also showed the REE compositions of smectites deriving from Haitian impact glasses and found that normalized patterns are almost flat as a result of alteration. Izett (1991) reported REE concentrations from Raton basin and Montana section also stating that REE were leached from the glass during alteration.

In contrast, the absence of negative cerium anomalies in the analyzed K/T boundary sediments from Blake Nose, Agost and Caravaca support a significantly low water–rock diagenetic system and thus similar patterns to those of the precursor material. Separation of cerium from the other REE is also a common weathering process effect on meteorite materials (Crozaz et al., 2003). In addition, at Agost and Caravaca the excellent preservation of the fireball layer allows for sampling, which precludes the contamination of materials from the boundary clay deposited above this layer (Ortega-Huertas et al., 2002). This also minimizes the effect of local derived input. At Blake Nose, the absence of negative cerium anomalies also indicates that seawater did not contribute to REE patterns which, despite depletion, still resemble those of the precursor glass.

The C1-normalized patterns of Cretaceous and Tertiary materials from Blake Nose, Agost and Caravaca are all similar to those of "average shales" and display the composition of the sediments supplied by the North American and the Iberian margin, respectively. However, notable differences are observed when comparing the K/T boundary materials of these sites. Blake Nose patterns are also similar to those of "average shales" (McLennan, 1989). This suggests that spherules derive from crustal material melted during the Chicxulub impact as also established in settings close to Chicxulub (e.g., Smit et al., 1992; Bohor and Glass, 1995). The impact glasses and tektites originated during the impact were subsequently altered to smectite. Similar REE behaviors during leaching resulted in normalized patterns, which have not been substantially modified. Consequently, at Blake Nose REE patterns, which are similar to those of "average shales" cannot be explained only by alteration processes. NASC normalized patterns indicate a preferential loss of HREE, although the general shape is quite similar to that of Cretaceous and Tertiary sediments. As mentioned above, the absence of significant cerium anomalies indicate low water/rock interaction during diagenetic alteration.

At the Agost and Caravaca sections, C1-normalized patterns from the K/T boundary layer are highly different from those of sediments above and below this layer, and subsequently from those corresponding to "average shales." Studies of the normalized patterns from the fireball layer and also from individual spherules show that fireball layer patterns are more similar to shale patterns than those from individual spherules. As microkrystites at these sections derive from the more energetic part of the vaporized cloud generated by the Chicxulub impact, the REE composition of individual spherules would reflect the composition of such materials, in which a high bolide contribution is evidenced by different impact signatures such as PGE content and Cr isotopes as mentioned above. These patterns may reveal the original shapes of precursor material patterns, thus evidencing a non-continental crust-derived material. The absence of Ce anomalies also points to a low water/rock interaction during alteration (Kastner et al., 1984). Furthermore, Gd to Lu enrichments have been observed in both K-feldspar and Fe-oxide spherules. Such enrichments cannot be accounted for by HREE uptake, since uptake in seawater would enhance that of lower ionic radius LREE. Thus, considering the significant extraterrestrial contribution at these more distal locations, as well as the possible precursor of the crystalline K/T boundary spherules (Smit et al., 1992; Martínez-Ruiz et al., 1997), we propose that these patterns at least partially reflect the original composition. Such patterns display typical increases in HREE, which also point to an extraterrestrial mafic precursor. REE data thus further support more significant bolide contributions at the most distal locations from Chicxulub, as previous work has shown on the basis of PGE, Cr isotope composition, Os isotopes and other impact signatures (e.g. Smit et al., 1992; Kyte and Bohor, 1995; Shukolyukov and Lugmair, 1998; Smit, 1999; Frei and Frei, 2002).

4. Conclusions

The distinct compositions of the Chicxulub impact-generated materials enable a more detailed understanding of the nature of the precursors. Precursor characteristics vary according to site distance from the Chicxulub crater (Smit, 1999). The most distal sections display high concentrations of Platinum group elements, as well as other typical extraterrestrial trace elements. However, relative terrestrial contributions are observed as distances with respect to Chicxulub become smaller. Such differences in the nature of the impact derived material can be inferred from the REE composition of the Chicxulub ejecta. Despite the fact that REE concentrations were depleted during diagenetic alteration, the absence of Ce anomalies points to low water/rock interaction. Thus, the C1-normalized patterns of K/T boundary materials still reflect those of the original precursors. Since Blake Nose C1-normalized patterns are similar to Cretaceous and Tertiary sediments, and thus to those of "average shales," it can also be inferred from REE compositions that the main contribution to the ejecta layer derived from continental crust. In contrast, at Agost and Caravaca C1-normalized patterns of microkrystites and bulk fireball layer are far different from those of Cretaceous and Tertiary sediments. The flat-like C1-normalized patterns found at these sites suggest that the precursor was composed of mafic materials. This further strengthens the hypothesis that extraterrestrial materials represent the greatest contribution to the ejecta layer at the most distal locations.

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