

Geochemistry of the Cretaceous-Tertiary transition boundary at Blake Nose (N.W. Atlantic): Cosmogenic Ni

PAVLE I. PREMOVIĆ^{1,*}, NIKOLA D. NIKOLIĆ¹, MIRJANA S. PAVLOVIĆ² and KATJA I. PANOVIĆ¹

¹Laboratory for Geochemistry, Cosmochemistry & Astrochemistry, University of Niš, P. O. Box 91, 18000 Niš and ²Vinča Institute of Nuclear Sciences, P. O. Box 522, 11001 Belgrade, Serbia and Montenegro (e-mail: asteroid_2000_2000@yahoo.com)

(Received 17 October 2003)

Abstract: The Cretaceous-Tertiary (KT) boundary transition at the Blake Nose Plateau recovered by ODP Leg 171B (site 1049, hole A, core 17X, section 2) contains an ejecta bed (thickness *ca.* 17 cm) marking a late Cretaceous asteroid impact. The nature and geochemical composition of this bed imply that it originated mainly from the target rocks of the Chicxulub impact site (Yucatan Peninsula, Mexico), the site of the presumed asteroid impact. The ejecta bed of hole 1049A contains relatively high concentrations of Ni (up to 165 ppm) within the carbonate fraction. It is reasoned that this enhancement represents a sudden and rapid airfall of high cosmogenic Ni into the Blake Nose Basin. The source of the metal was the Chicxulub impacting (carbonaceous) chondrite. It is suggested that many calcareous planktons in the KT ocean surface water of the Blake Nose Plateau were probably vulnerable to the high influx of superacid rainfall and associated toxic metals (*e.g.*, Ni) created by the impact.

Keywords: nickel, Cretaceous-Tertiary boundary, ODP, Blake Nose Plateau.

INTRODUCTION

Alvarez *et al.*¹ reported an anomalously high Ir concentration in the KT boundary transition (BT) deposits from Italy, Denmark and New Zealand. According to these authors, this enhanced Ir concentration was produced by an asteroid impact. It has been suggested that the impactor was a (carbonaceous) chondrite-type body.² Apart from the well-known "Ir anomaly", the KT–BT deposits show a "cosmogenic Ni anomaly".³ The KT–BT beds of site 1049 from the Blake Nose Plateau provide excellent samples to examine this anomaly.

Very recently, Keller *et al.*⁴ proposed that the KT–BT was a time of multiple impacts (cometary shower?) during the last 5×10^5 y of the late Maastrichtian and continuing into the early Danian. They identified a sequence of three impact events

* Corresponding author. Fax: +381-18-533-014.

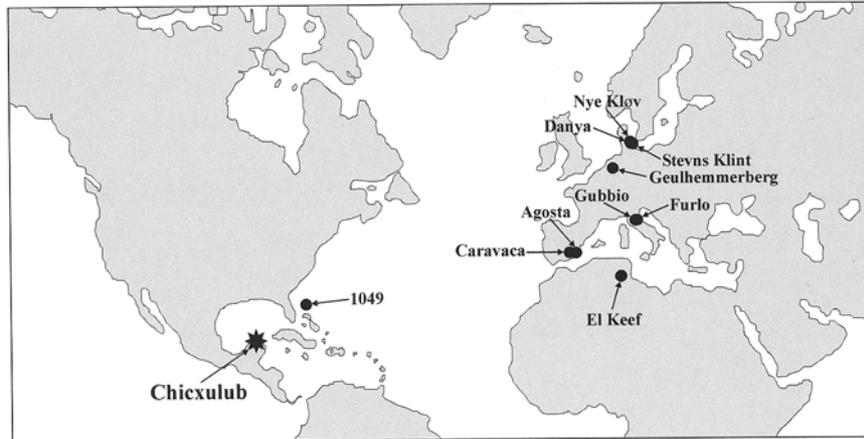


Fig. 1. Location map showing the (ODP) 1049 KT–BT site in relation to other KT–BT sites world-wide.

in the Gulf of Mexico and adjacent areas. The first impact (related to the Chicxulub crater) occurred in the late Maastrichtian at about 65.3 Ma. The second impact is the well-known KT boundary event (65 Ma ago) and the third impact event occurred in the early Danian at *ca.* 64.9 Ma.

The sequence of the Chicxulub impact ejecta is composed of two macroscopic beds in (and adjacent to) N. America.⁵ The lower bed is derived from a low-energy ejecta deposited from an ejecta curtain. The upper bed is derived from higher energy ejecta carried in the fireball plume and dispersed globally by the winds of the upper atmosphere.^{5,6} This bed is usually termed the fireball or impact layer.

Site 1049 is located on a proximal paleorange of *ca.* 2000 km from the Chicxulub impact site (Fig. 1) and at a present depth of 2671 m below sea level. Paleodepth estimates based on benthic foraminifers revealed a bathyal depth (1000–2000 m) at this site throughout the latest Cretaceous and Paleogene.⁷

We studied Ni in the KT–BT deposit of hole 1049A (hereinafter, ODP–BT) (Fig. 2). Keller *et al.*⁴ recognize two distinct beds that comprise ODP–BT (Fig. 2). A central part of ODP–BT is represented by the *ca.* 17 cm thick (coarse/poorly graded and reworked) ejecta bed. This bed is predominantly composed of mostly dark-green smectitic spherules (commonly 0.1–1 mm) with (reworked) late Cretaceous planktic foraminifera. According to Martinez-Ruiz *et al.*,⁸ these spherules are derived mainly from the Chicxulub (andesitic) target rocks with a minute contribution of the impacting asteroid. Also occurring in the ejecta bed are lithic fragments, the chalk clasts and shocked quartz grains. These materials also originated from the Chicxulub crater, indicating that a relatively large amount of (low-energy) ejecta reached the Blake Nose Plateau.⁸ The ejecta bed forms a sharp contact with the underlying soft (late Maastrichtian) sediment (ooze) that was deposited before the impact event and where the latest Maastrichtian is missing.⁴ The upper (*ca.* 2

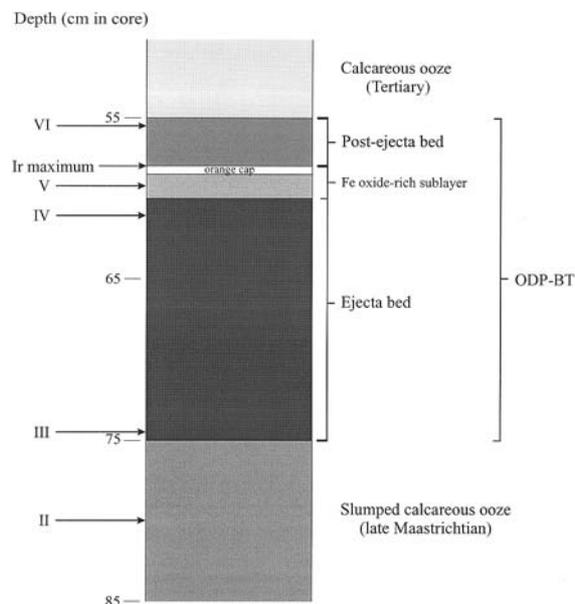


Fig. 2. Schematic illustration of the internal layering in a stratigraphic section from ODP leg 171B (site 1049, hole A core 17X, Section 2) recovered from the US Atlantic continental slope east of Florida (the Blake Nose Plateau).

cm thick) sublayer of the ejecta bed is enriched with Fe-oxides (mostly goethite) and is capped by a *ca.* 3 mm orange cap. Martinez-Ruiz *et al.*⁸ found that the geochemical composition (except for high Fe) of this cap is similar to the rest of the ejecta bed. The ejecta layer is overlain sharply by a dark clay (*ca.* 3 cm thick) (hereinafter, the post-ejecta bed) of the earliest Danian with (early) Danian planktic species. The final bed in the sequence is Tertiary biogenic ooze.

Various KT–BT deposits are enriched with cosmogenic Ni but most attention has been focused on the presence of this metal in the whole-rock sample. Much less regard has been paid to the trace Ni associated with the various fractions of a particular KT–BT bed. As carbonate minerals (mainly biogenic calcite) constitute an essential component of KT–BT samples, variations in trace metal abundances between such samples are often governed by variations in the distribution of these minerals. In this study we principally focused our attention on Ni in the carbonate fractions of ODP–BT samples.

EXPERIMENTAL

Eight ODP samples from the KT–BT interval studied were analyzed. The correlation of these samples to the 1049A sequence is noted in Table I/ Fig. 2.

The ODP–BT samples were dried in an oven and carefully ground in an agate mortar. The powdered rock (0.5 g) was completely dissolved in a HF (22 M)/HCl (12 M) mixture at 80 °C. This solution was analyzed for Ni representing the total (whole-rock) metal in the sample. The powdered rock (0.5 g) was also treated (12 h) with 0.5 M acetic acid to remove most of calcite (and other carbonates except dolomite and ankerite).⁹ The soluble portion constitutes the carbonate fraction analyzed for Ni. Carbonate removal (up to 0.5 % of the whole ODP sample) was checked by the X-ray diffraction (XRD) and Fourier transform infrared (FTIR) analyses. The Ni contents in the carbonate-free fractions of the samples III/IV were obtained by a simple chemical calculation.

TABLE I. The distributions of total/carbonate Ni (± 5 ppm) in the 1049A beds. (See Fig. 2 for location of samples)

Layer	Interval (cm)	Comment	Carbonate fraction of total rock (± 5 wt%)	Total Ni	Carbonate Ni	Carbonate-free (clay) Ni	Fraction ^a (± 5 wt%)
VIII	–	Tertiary bed: <i>ca.</i> 1.20 m above the ejecta bed	68	–	10	–	–
VII	–	The Tertiary ooze bed <i>ca.</i> 0.8 m above VI	85	–	15	–	–
VI	55–55.5	The post-ejecta bed	87	10	10	10	< 10
V	59–59.5	The Fe-oxide rich sublayer	39	90	< 20	< 130	< 6
IV	61–62	Upper part of the ejecta bed	29	260	165	300	22
III	74–74.5	Lower part of the ejecta bed	19	80	105	75	25
II	80–80.5	Late Maastrichtian ooze bed (just below the ejecta bed)	45	75	80	70	48
I	–	Cretaceous ooze bed: <i>ca.</i> 1 m below the ejecta bed	79	–	< 15	–	–

^aFraction of total Ni as carbonate Ni

Mineralogical analyses reveal that the carbonate-free fraction of the ejecta bed is mainly (> 95 %) composed of (cheto-type) dioctahedral smectite typical of weathered impact glasses.⁴ The Fe-rich sublayer contains also some goethite. In the layers below and above the ejecta bed, the predominant clays are smectite, illite and kaolinite (Martinez-Ruiz *et al.*⁸; this work).

Ni in the whole-rock samples and their carbonate fractions was analyzed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) in the Laboratory for Physical Chemistry, Vinča Institute of Nuclear Sciences (Belgrade, Serbia). A Spectroflame ICP-OES instrument was employed and Ar was used as the plasma gas.

RESULTS

Very recently, Martinez-Ruiz *et al.*⁸ reported atomic absorption spectrometry (AAS) data for Ni (on a whole-rock basis) in more-closely-spaced samples across hole 1049A. The distribution of total Ni within the 1049A interval is presented in Fig. 3. The zero level of this Figure corresponds to the impact event, which is defined as the interface between the late Maastrichtian sediment below and the ejecta bed immediately above. The Ni values reach a profound peak concentration of 293 ppm at the top of the ejecta bed (about two centimeters below IV). Upward from this level the concentration of Ni decreases sharply in the overlying post-ejecta/Tertiary beds to background values of < 15 ppm.

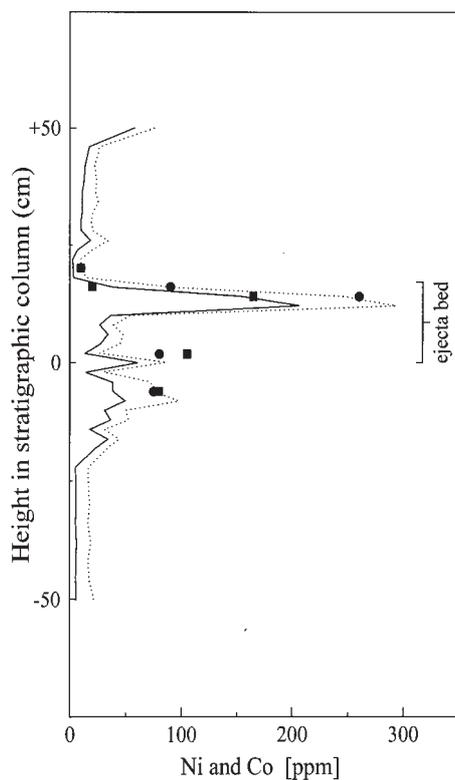


Fig. 3. The distributions of total Ni (---) and Co (—) (determined by AAS: Martinez-Ruiz *et al.*⁸) across the 1049A interval. The concentrations of the carbonate (■) and total (●) Ni determined by ICP-OES. Zero on the vertical scale corresponds to the base of the ejecta bed; the late Maastrichtian is below.

For comparison, the cosmogenic Co distribution in the above interval is also illustrated in Fig. 3. (This metal was chosen because it shows a similar geochemical behavior to Ni in natural waters/sedimentary environments). As Ni, the Co values reach a profound peak (207 ppm) at the top of the ejecta bed (about two centimeters below IV).

The Ni contents in the carbonate fractions of eight samples are given in Table I/ Fig. 3. The highest carbonate Ni was in the segment IV (165 ppm) of the ejecta bed. The carbonate fractions of the segments I/V–VIII contain normal background concentrations of Ni (< 20 ppm). Additionally, the distributions of Ni between these fractions and carbonate-free fractions of the segments II–VI are given in Table I.

DISCUSSION AND CONCLUSIONS

Sedimentation rate of ODP–BT

Noris *et al.*⁷ calculated the sedimentation rates of the 1049 build up based on stratigraphic age determinations from calcareous nannofossils/planktonic foraminifers. According to these authors, sedimentation during the late Maastrichtian/Paleocene was steady at a rate of *ca.* 0.36 cm per 1000 y. Cyclostratigraphy constrains, however, the sedimentation rate before (Maastrichtian) and after (Paleocene) KT–BT, but cannot be applied to the ODP–BT beds.

The materials (including spherules) in the ejecta curtain of the Chicxulub impact fell back to the Earth's surface within hours or days, forming ejecta deposits of the proximal sites.^{5,10} The deposition of ejecta on the ocean floor of site 1049 had, therefore, to take place in ≤ 1 week. Martinez-Ruiz *et al.*⁸ suggest that the sharp contact between the ejecta (spherule) bed and the underlying (late Maastrichtian) and overlying (post-ejecta) beds indicates a very rapid deposition of ejecta (*i.e.*, spherules). This was an event that just preceded the deposition of the post-ejecta bed. Certainly, the bulk of the post-ejecta bed was deposited over a much longer time period.

Impact-derived spherules

It is widely accepted that glass spherules of the lower-energy ejecta are the precursor of the clays in the KT–BT (marine and continental) sediments.¹¹ These spherules have been identified as microtektites or microcrystites. Smit¹¹ suggested that microtektites predominate in the proximal ejecta sites within 2500 km of Chicxulub, whereas microcrystites dominate in the more distal sites. According to Keller *et al.*,⁴ altered microtektites and microcrystites occur together in the proximal ODP ejecta beds.

Martinez-Ruiz *et al.*⁸ suggested that the glass precursor(s) of smectite within the ejecta bed of ODP–BT could have been compositionally similar to the impact glasses (microtektites) reported for the Haitian KT–BT sites. Two types of glasses have been recognized at these locations: predominant dark and minor yellow

glasses (*ca.* 2 % of total material).¹² Very recently, Keller *et al.*⁴ and Stinnesbeck *et al.*,¹³ stated that the Haiti spherule beds may not be of the KT age at all. According to these authors, it is not clear whether these beds represent a reworked KT or latest Maastrichtian (pre-KT) deposit, or even a Danian (post-KT) accumulation.

Apparently, the high input of impact glass spherules into the oceanic water had to occur within hours or days, *i.e.*, during the ejecta deposition on the ocean floor of Blake Nose. In contrary, the (low-temperature) geochemical process that led to the alteration (devitrification, hydration, *etc.*) of the impact glass spherules and subsequently to the formation of smectitic spherules took place over a long period of time (likely more than 10^5 y).

What is enigmatic regarding the spherules within the ejecta bed is that they disintegrate completely on contact with H₂O (Martinez-Ruiz *et al.*⁸; this work). Undoubtedly, the original smectitic spherules (formed in the oceanic water from the impact glass spherules through diagenesis) were stable to contact with H₂O. This could suggest that these spherules were later subjected to some kind of geochemical process (dehydration?) during their 65 million years of geologic history which made them susceptible towards H₂O. We have, at this moment, no definite clue as to the nature of this process.

Martinez-Ruiz *et al.*⁸ propose that the clay mineral assemblages of the late Maastrichtian, post-ejecta and Tertiary beds were derived from nearby continental soils. Microscopic examination of ODP–BT reveals that the relatively high content of smectitic spherules begins abruptly with the ejecta bed. Upward the amount of spherules is considerably reduced in the Fe oxide-rich cap and stops to exist at all in the overlying post-ejecta bed.⁸ This suggests that a substantial part of the clay fraction of the post-ejecta bed was probably a local (continental) provenance. Considering this, it seems very likely that the formation of the post-ejecta bed was due to a post-impact process that is not related to an asteroid impact. This means that the ejecta bed is the sole representative of the original Chicxulub ejecta.

Al, Mg and Fe

Cheto-type smectite is characterized by high concentrations of Al and Mg;^{4,12} indeed, high concentrations of Al (> 6 %) and Mg (*ca.* 2 %) occur throughout the ejecta bed, Fig. 4. The Al and Mg concentrations are roughly proportional to the amount of smectite present in this bed, *i.e.*, to the amount of impact glasses in the initial ejecta deposit.

The distribution of Fe (on a whole-rock basis) across the KT–BT interval is presented in Fig. 4. The Fe values reach a prominent peak concentration of *ca.* 4.7 % in the Fe-rich sublayer of the ejecta bed. Upward from this sublayer, the Fe concentrations decrease sharply within the post-ejecta bed to background levels (< 1 %). Like Al, Fe is highly concentrated (*ca.* 3.5 %) in the dark Haiti impact glasses¹² and the excess of Fe in the ejecta bed is most likely derived from the impact glasses.

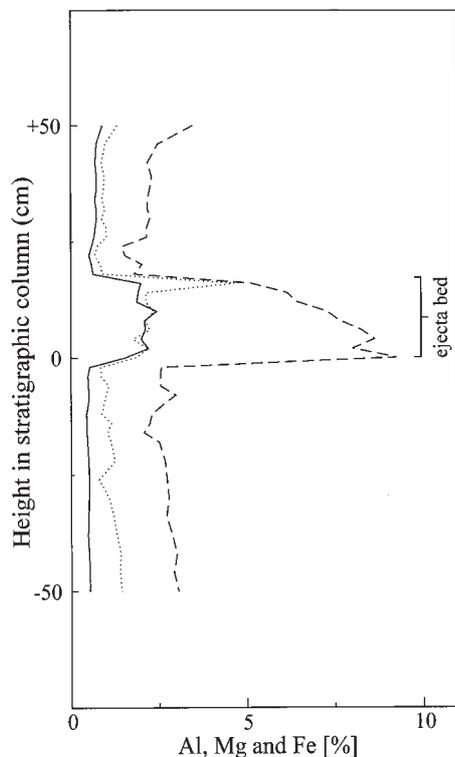


Fig. 4. The distributions of Al (---), Mg (—) and Fe (···) (determined by AAS: Martinez-Ruiz *et al.*⁸) across the 1049A interval.

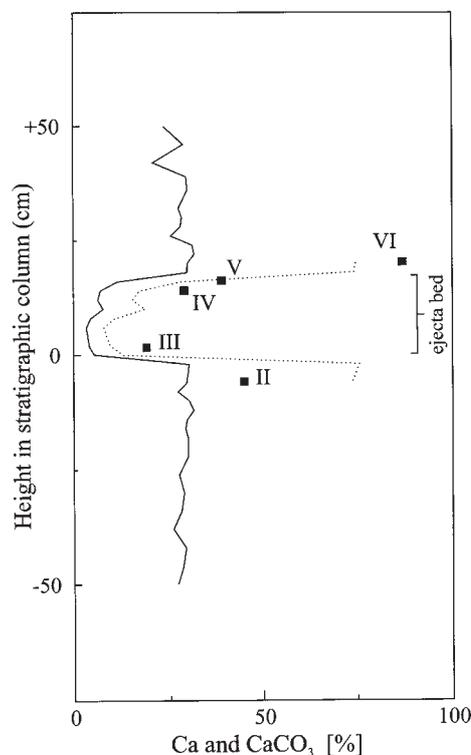


Fig. 5. The distributions of Ca (—) and carbonates (■) (determined by AAS: Martinez-Ruiz *et al.*⁸) across the 1049A interval. The carbonate contents of the II – VI samples were determined by simple chemical leaching (see the Experimental section). The calculated CaCO_3 (···) is discussed in the text.

Finally, the distribution patterns of Al, Mg, Fe and Ca (Figs. 4/5) are constant (within $\pm 10\%$), indicating that the bulk of these beds contains comparable amounts of similar carbonate and clay materials.

The KT superacid rainfall and biogenic calcite

The carbonate fractions of the ODP–BT samples contain predominantly authigenic calcite formed from biogenic calcite recrystallization. Microscopic inspection of thin sections of the samples indicated that biogenic calcite is derived exclusively from calcareous photosynthetic planktons (foraminifera) ($> 90\%$). (Note that these organisms live in the upper 100–200 m of temperate to tropical/subtropical oceans). The distribution of Ca (on a whole-rock basis) across the 1049 interval is presented in Fig. 5. The Ca values are much lower in the ejecta bed compared to the values in the underlying and overlying layers. The distribution pattern of Ca is

roughly invariable across the ejecta bed, indicating that most of the Ca is associated with biogenic calcite within this unit. Such a distribution also infers a steady influx of this calcite during the formation of the ejecta bed. Additionally, the calcite contents across the 1049A interval (Fig. 5) was calculated assuming that the whole-rock Ca is only in this mineral. On the whole, the actual carbonate distribution approximately correlates with the distributions of both the total Ca and the calculated calcite (CaCO_3).

The fireball vapor cloud would expand, reaching site 1049 within hours of days after the Chicxulub impact.¹⁴ At this location, the cloud would generate superacid rainfall.^{15,16} This rain would rapidly reduce the alkalinity of the top *ca.* 100 m of the ocean water of Blake Nose Plateau so much so that many calcareous photosynthetic planktons would be almost instantaneously annihilated (Prinn and Fegley,¹⁷ Davenport *et al.*,¹⁸ Brett¹⁹ and references therein). Indeed, D'Hondt *et al.*²⁰ estimated that the Chicxulub impact would have reduced globally the pH of the upper 100 m marine column to below 7. Lyons and Ahrens²¹ estimated that the impact-induced acid rainfalls delivered about 2×10^{17} equivalents of acids to the late Maastrichtian seas, enough to acidify their surface water.

Considering this, it appears very likely that the ejecta bed was produced by both a temporary loss of biogenic calcite (*i.e.*, the calcareous shells of annihilated photosynthetic planktons) and a high influx of the impact glasses. Hence, an upward decline of biogenic calcite from its relatively high values in both the underlying (late Maastrichtian) and overlying post-ejecta beds to its minimum in the ejecta bed (Table I/ Fig. 5) is simply a reflection of the increased proportion of the impact glasses relative to the decreasing contribution of biogenic calcite (Table I/ Fig. 5); accordingly, the Al and Mg distributions of the ejecta bed (Fig. 4) show a negative correlation with both the total carbonate and Ca distributions displayed in Fig. 5.

We propose that the sudden and sharp decline of biogenic calcite within the ejecta bed (Table I/ Fig. 5) to be related, at least partly, to an abrupt rise in the acidity of the ocean surface waters of the Blake Nose Plateau, which halted the formation of biogenic calcite which resulted from a sudden advance of the superacid rainfall pulse. However, a variety of other impact-induced atmospheric/hydrospheric factors (including a sudden and drastic drop of temperature/decrease of solar daylight, *etc.*) may also have contributed synergistically to this halt.

The profiles of immobile Zr and Hf

High concentrations of Zr (103–168 ppm) and Hf (*ca.* 4 ppm) occur throughout the ejecta bed (Fig. 6) compared with background levels (Zr: < 20 ppm and Hf: < 0.5 ppm). (Note that, for sake of clarity, the Hf concentrations in Fig. 6 have been multiplied by a factor 10). The high Zr and Hf concentration in the ejecta bed can be interpreted by an input of these metals on the ocean floor of the Blake Nose attained through a high external supply. These metals are rather immobile in sedi-

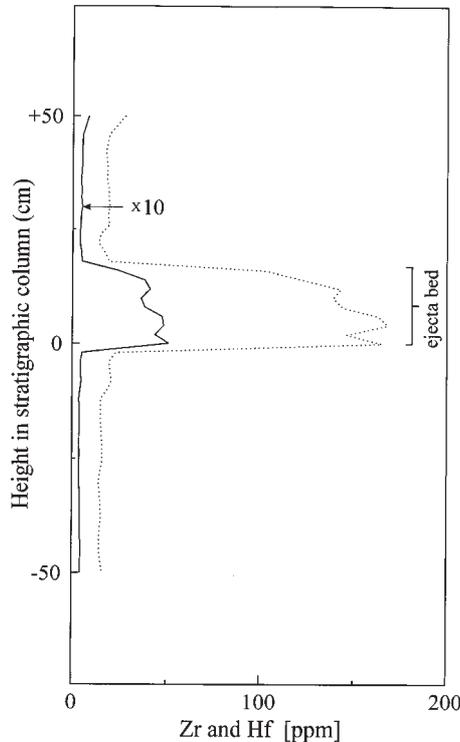


Fig. 6. The distributions of total Zr (····) and Hf (—) (determined by AAS: Martinez-Ruiz *et al.*⁸) across the 1049A interval. The concentrations of Hf is multiplied by a factor 10.

mentary environments and, as could be expected, the distribution profiles of Zr and Hf are almost identical across the 1049A interval, Fig. 6.

The mean concentrations of Zr (*ca.* < 4 ppm) and Hf (*ca.* < 105 ppb) are rather low in (carbonaceous) chondrites²² and their excesses in the ejecta bed are, therefore, most likely derived from the Chicxulub target rocks. Indeed, there is a rough positive correlation of Zr and Hf (Fig. 6) of the ODP-BT with Al and Mg (*i.e.*, with the amount of smectite) (Fig. 4), indicating that these metals were probably associated with the impact glasses. The fact that the dark Haiti impact glasses contain relatively high amounts of Zr (100–360 ppm) and Hf (3.6–14.1 ppm)¹² supports such a view.

The Zr and Hf distributions within the ejecta bed are approximately constant to within $\pm 10\%$. This distribution pattern indicates a steady influx of ejecta during the formation of the ejecta bed. The fact that the distribution patterns of Zr and Hf are almost straight lines across the underlying (late Maastrichtian) and overlying (post-ejecta/Tertiary) beds lends additional support to the notion that these layers are compositionally indistinct.

Ir and Cr

An Ir concentration of about 50 ppt represents the background value for marine carbonates.²³ The mean concentration of Ir within the ejecta bed is *ca.* 0.55 ppb. The concentrations of cosmogenic Ir are relatively high (≥ 0.2 ppb) in the

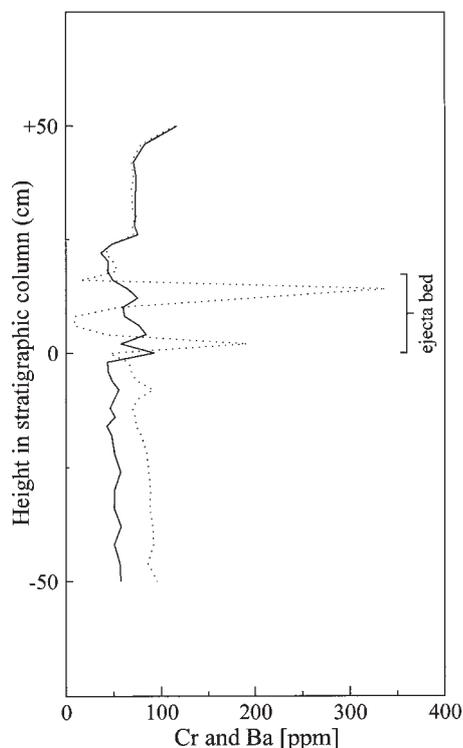


Fig. 7. The distributions of total Cr (—) and Ba (····) (determined by AAS: Martinez-Ruiz *et al.*⁸) across the 1049A interval.

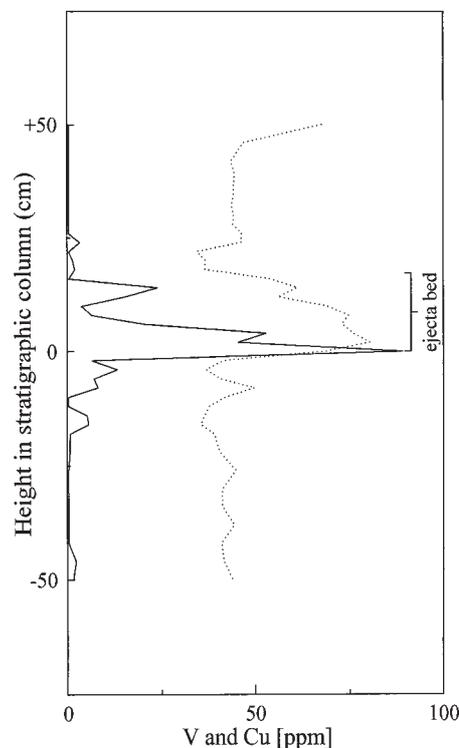


Fig. 8. The distributions of V (····) and Cu (—) (determined by AAS: Martinez-Ruiz *et al.*⁸) across the 1049A interval.

lower part of the ejecta bed and start to increase gradually, reaching a maximum (*ca.* 1.2–1.3 ppb) in the very top of the ejecta bed, (Martinez-Ruiz *et al.*⁸; Fig. 2). We reason that the increase of the Ir up-section across the ejecta bed indicates a single and sudden input of cosmogenic Ir to the ocean floor of the Blake Nose Plateau. Upward from this level, the Ir concentrations decrease sharply so that in the post-ejecta bed the bulk-sample Ir concentrations reach lower levels (*ca.* 0.2 ppb). Ir has relatively high abundances (< 1 ppb to < 10 ppb) in the dark Haiti impact glasses,¹² indicating that similar glasses are the most likely source of this metal within the ejecta bed.

Cr represents an enigma in the ejecta bed geochemistry. Namely, Cr is one of the metals that is invariably enriched in KT–BT clays together with Ir. Consequently, Cr should be one of the most important indicators of cosmogenic material in the ejecta bed. The average Cr concentrations in (carbonaceous) chondrites are usually several thousands ppm,^{2,24} whereas in marine clays and limestones they are 90 ppm and 11 ppm,²⁵ respectively. The mean abundance of Cr in the ejecta bed is *ca.* 69 ppm. Cr is low (23.3–93.4 ppm) in the ejecta bed and its abundance shows only a slight variation across this bed (Fig. 7).

The dark Haiti impact glasses are characterized by rather low Cr contents (< 30 ppm).¹² This means that most of the Cr in the ejecta bed is probably derived from a local (continental) source. The high Cr concentrations (up to 165 ppm) in the ODP segments about 5 m above the ejecta bed⁸ give support for this conclusion.

A still unresolved problem is a geochemical process to account for the depletion of Cr within the ejecta bed. Our data give no definite clue as what may have caused this depletion. It is likely that most of the cosmogenic Cr diffused out of this bed. Indeed, geochemical studies suggest that hexavalent Cr (as highly mobile HCrO_4^- and/or CrO_4^{2-} ions depending of the pH) is the major stable form of this metal in (oxygenated) oceanic water with pH 7–8.²⁶ (Note that Martinez-Ruiz *et al.*⁸ suggest that the presence of authigenic palygorskite and zeolites in the ejecta bed implies that diagenesis had occurred in the mildly alkaline medium of pH > 7). These studies also suggest that the uptake of these anionic complexes by the (negatively charged) clay particles would be minimal at these pH values. Very little of the asteroidal Cr in the oceanic water of the Blake Nose Plateau would, therefore, be incorporated into the structures of the smectitic spherules of the ejecta bed.

V, Cu and Ba

The distributions of V and Cu (on a whole-rock basis) across the 1049A interval are presented in Fig. 8. The V and Cu values reach peak concentrations of *ca.* 80 ppm and 89 ppm, respectively, in the lower parts of the ejecta bed. The mean concentrations of V and Cu within the ejecta bed are 68 ppm and 29 ppm, respectively. These metals have rather low abundances in (carbonaceous) chondrites < 100 ppm (V) and 124 ppm (Cu).^{22,24,27,28} The concentrations of V and Cu in the dark Haiti impact glasses are 104 ppm and 24 ppm, respectively.²⁹ The above data imply that V and Cu were probably associated at the outset with the impact glasses. Note that V (Fig. 8) positively correlates with Al and Mg (Fig. 4).

The ejecta bed is characterized by a high mean Ba content (> 100 ppm). The peak Ba concentrations (> 190 ppm) occur near the basal and top units of the ejecta bed (Fig. 7). The average Ba abundance in (carbonaceous) chondrites is several ppm.²² The Ba concentrations (310–1270 ppm) are very high in the dark Haiti impact glasses;¹² consequently, it seems that the impact glasses can account for the Ba enrichments in the ejecta bed.

Ni and Co

As one would expect, the Ni and Co profiles are almost identical across the ejecta bed (Fig. 3), indicating a common origin and similar geochemical behavior during diagenesis. The mean concentration of Ni within the ejecta bed is *ca.* 104 ppm. The peak Ni concentration (> 245 ppm) in the top of the ejecta bed (Table I/Fig. 3) is comparable with the average Ni concentrations found in marine clays (225 ppm).²⁵ The Ni concentrations in (carbonaceous) chondrites are very high ($>$

12500 ppm).²⁴ Ni is rather low (15–50 ppm) in the dark Haiti impact glasses (except in one of the samples that contains 260 ppm of Ni).¹²

The main concentration of Co within the ejecta bed is *ca.* 70 ppm. The concentrations of Co in the top of the ejecta bed are as high (> 200 ppm) (Fig. 3) and much higher than the average concentrations of Co in marine clays and limestones: 74 ppm and 0.1 ppm, respectively. The average Co contents are relatively high (> 600 ppm) in (carbonaceous) chondrites.²⁴ The Co contents of the dark Haiti impact glasses are also rather low (12.4–20.4 ppm).¹²

Relatively high levels of Ir,⁸ Ni (Table I) and Co (Fig. 3) in the ejecta bed (especially near its top) indicate that this bed is probably the true KT boundary (or, at least, is a part of it). On the other hand, the low levels of Ir,⁸ Ni (Table I) and Co (Fig. 3) in the post-ejecta bed imply that this bed is not part of the KT boundary. In contrast to the post-ejecta bed, the ejecta bed also contains relatively high Ni in the carbonate fraction (Table I/Fig. 3). This fact gives additional support to the notion that the ejecta bed is probably the true KT boundary.

Very recently, Griscom and Beltran-Lopez³⁰ found that the ratio [SO³⁻/Mn²⁺] is a useful geochemical marker of the KT boundary. As indicated by these authors, there is a high-resolution peak in this ratio within the ejecta layer which strongly highlights its boundary origin.

The excesses of Ir, Ni and Co in the ejecta bed are most likely derived from a component of the Chicxulub impactor associated with ejecta, but not from the impact glasses. This scenario suggests that the original KT ejecta deposit contained an additional impact component enriched with significant concentrations of these metals. Indeed, (cheto-type) smectite comprises a minimum of 70 % of the ejecta bed⁸ (Table I), but the original impact glasses may have constituted approximately 90 % of the original ejecta bed if smectite is their alteration product.³¹ If this is accepted as a reasonable hypothesis, it follows that the ejecta component enriched with Ni and Co comprised *ca.* 10 % of the bulk ejecta, a simple calculation then reveals that the average abundances of these cosmogenic metals in this component would be 1040 ppm (Ni) and 700 ppm (Co). These results are only harmonious if the ejecta bed is of a KT origin.

The carbonate Ni concentration of the segment IV (165 ppm) (Table I/Fig. 3), when compared with the average concentration (7 ppm) found in marine calcareous rocks,²⁵ is distinctly anomalous. This implies that the KT ocean water of the Blake Nose may have been strongly enriched in Ni. It is quite likely that the location of the carbonate Ni is in the biogenic calcite of the ejecta bed. Indeed, Ni²⁺ ions may substitute Ca²⁺ ions in the calcite matrix since Ni²⁺ (0.70 Å) has a similar ionic radius and the same charge as Ca²⁺ (1.00 Å). Under the sedimentation conditions of site 1049, the bulk of Ni in normal (midly alkaline with pH *ca.* 8) or acidic (pH < 7) ocean surface water should be present as Ni²⁺.³² This indicates that Ni was present in the KT ocean surface water of the Blake Nose mostly in ionic (Ni²⁺)

form. Obviously, the abrupt rise of the carbonate Ni in the ejecta bed (Fig. 3) is only consistent with a sudden and rapid introduction of cosmogenic Ni into the oceanic surface water of the Blake Nose Plateau through the Chicxulub ejecta. Evidently, calcareous planktons would be particularly vulnerable to this injection of high Ni (and other toxic metals, such as Co) into this water.^{17,18}

The background levels of total/carbonate Ni of both the Fe-rich sublayer and the post-ejecta bed (Table I/Fig. 3) suggest that during the deposition of these layers the influx of cosmogenic Ni probably ceased to exist at all. This implies that the high input of Ni into the oceanic water of the Blake Nose Plateau was also of extremely short duration (only hours or days) during the deposition of ejecta onto the ocean floor. Indeed, assuming that the Ir, Ni and Co anomalies and spherules in the ejecta bed are derived from the Chicxulub impactor, the above input cannot have lasted more than a few days.

Our analysis also shows that more than 75 % of the total Ni resides in the carbonate-free fractions (> 95 % of smectite) of the segments III/IV (Table I/Fig. 3). Thus, it is reasonable to suggest that smectite is the dominant carrier phase of Ni in the ejecta bed. Experimental and theoretical studies clearly show that Ni²⁺ ions are weakly incorporated into calcite (Rimstidt *et al.*³³ and references therein). Contrary to calcite, smectites are characterized by a large surface area ($6-8 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$)³⁴ and by a relatively high cation exchange capacity (1000 meq kg⁻¹).³⁵ It is, therefore, quite likely that metal ions the size of Ni²⁺ ions could reside in the available exchangeable interlayer sites of smectite contained in the ejecta bed. These sites are excellent coordinating sites within the smectite structures which would be very rapidly filled with Ni²⁺ ions (through uptake from the overlying oceanic water) during smectite genesis. Consequently, most (if not all) Ni²⁺ present in the water overlying the KT ocean floor at site 1049 would have been taken up by the developing smectitic spherules. The incorporation of Ni²⁺ ions into calcite had, therefore, to occur even before the formation of the smectitic spherules (from the impact glass spherules) began. For this reason, it is proposed that the high Ni in the carbonate phase of the ejecta bed represents biological Ni, *i.e.*, Ni²⁺ ions directly incorporated into the calcite (CaCO₃) skeletons of the marine planktons. This process had to take place during their metabolic uptake of KT ocean surface water already enriched with these ions.

The carbonate fraction of the ejecta bed could contain a minor amount of recondensed carbonates as accretionary lapilli (Griscom and Beltran-Lopez³⁰ and references therein). It seems, however, implausible that the Ni-rich calcite particles could have evolved during recondensation of the vaporized carbonate rocks of the Chicxulub impact site.

It is also possible to argue that a transmetallation reaction between biogenic calcite and the Ni-rich smectite on the post-KT ocean floor of the Blake Nose Plateau could have been responsible for the high amounts of carbonate Ni in the ejecta bed. However, the fact that, for example, the smectite content of IV is approxi-

mately more than 5 times higher than the carbonate fraction (Table I) excludes such a possibility.

V/Cr and Ni/Co ratios

The V/Cr and Ni/Co ratios have been used as paleoenvironmental indicators of sediment deposition (Jones and Manning³⁶ and references therein). Values of $V/Cr \geq 24$ are thought to represent suboxic/anoxic depositional conditions. Values ≤ 4 are indicative of slightly oxidizing (dysoxic) conditions, with values ≤ 2 suggesting oxic conditions within the sediment. The V/Cr ratios of the 1049A interval are lower than 2 (0.6–1.4), Fig. 9. These values indicate that all beds (including the ejecta bed) of this interval were deposited in an oxidizing (or normal) marine environment. The presence of authigenic Fe-oxide minerals in these beds lends support to this notion. For comparison, the Ni/Co ratios of the 1049A are also presented in Fig. 9. Across this interval the Ni/Co ratios are < 4 , *i.e.*, also consistent with an oxic depositional milieu.

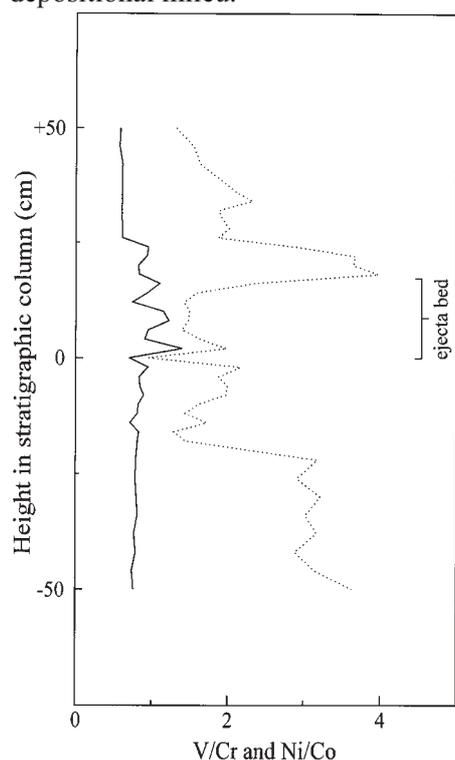


Fig. 9. Variations of the V/Cr (—) and Ni/Co (····) ratios across the 1049A interval.

Comparison with other ejecta beds of site 1049

Martinez-Ruiz *et al.*⁸ also analyzed samples from the KT–BT intervals at holes 1049B, 1050C and 1052E for trace metals. The mean concentrations of Ni and Co in the ejecta bed (*ca.* 9 cm thick) of the hole 1049B deposit are *ca.* 226 ppm and 169

ppm, respectively. High concentrations of cosmogenic Ni (115–433 ppm) and Co (75–287 ppm) were detected across this bed. The mean Ir content of the 1049B ejecta bed is 0.65 ppb. The Ir concentrations gradually increase in this bed, reaching peak values of 1.15–1.32 ppb in the top of the ejecta bed. Upward from this level, the Ir concentrations decrease sharply to background values of *ca.* 0.05 ppb. For these reasons, it can be concluded that the ejecta bed of hole 1049B also represents the true KT boundary (like the ejecta bed of hole 1049A). (Note that the mean Cr concentration is *ca.* 86 ppm in the 1049B ejecta bed. This low value indicates diffusion of Cr out of this bed had also occurred).

At holes 1050C and 1052W, the ejecta (spherule) bed is not, however, well preserved, although hole 1052 burrows contain spherules.⁸

Comparison with distal marine BT boundaries

Premović *et al.*^{37,38} reported high levels (275–300 ppm, Table II) of Ni within the biogenic calcite of the grey-to-dark KT–BT marl (Fiskeler) at a distal location (Stevns Klint, Denmark) at a paleorange of *ca.* 9700 km (Table II/Fig. 1). These results were interpreted by the authors to reflect an enormous influx of cosmogenic Ni into the Fiskeler seawater induced by the Chicxulub asteroid impactor. As discussed above, our preferred hypothesis is that a global (impact-induced) superacid rainfall and associated toxic metals (including Ni) decimated calcareous photosynthetic planktons in the surface seawater at this distal site.

TABLE II. The carbonate fractions (± 5 wt.%) and their Ni (± 5 ppm) of the KT–BT rocks at various distal localities. (See Fig. 1 for location of the KT–BT rocks)

Sample	Paleorange (± 300 km) ^a	Carbonate fraction	Ni
Caravaca	9750	32	70
Agosta	9750	70	10
El Keef	11000	50	15
Geulhemmerberg	11500	60	< 5
Furlo	11750	40	< 10
Gubio	11750	42	15
Nye Kløv	12000	53	15 ^b – 25 ^c
Danya	12000	70	10 ^b – 30 ^c
Stevns Klint	12000	56	275 – 300 ^b

^aApproximate distance from the Chicxulub impact site. ^bPremović *et al.*^{37,38} ^cThis work

According to Premović *et al.*,^{37,38} Schmitz,³⁹ Schmitz *et al.*⁴⁰ and Bauluz *et al.*,⁴¹ the abundant (cheto-type) smectite, pyrite (FeS₂) and kerogen of Fiskeler were produced in early diagenesis under anoxic conditions. These components are the major carriers of Ni in Fiskeler. Ni concentrations in the smectite concentrate of the ejecta

bed samples, however, are very small (Table I) compared with the Ni concentration (1315 ppm) measured in the corresponding part of the anoxic Fiskeler.³⁷ There is, however, no indication in the form of abundant pyrite (FeS₂) and kerogen that anoxic conditions existed during the deposition of the ejecta bed. Instead, oxic conditions may have prevailed (see earlier section concerning V/Cr and Ni/Cr ratios).

We also analyzed Ni in the carbonate fractions of other distal marine KT–BT deposits: Caravaca/Agosta (Spain), El Keer (Tunisia), Geulhemmerberg (Holland), Furlo/Gubio (Italy) and Nye Kløv/Dania (Denmark) (Fig. 1). The data are presented in Table II. These results indicate that the carbonate fractions of all these deposits contain normal background Ni (< 30 ppm) except the Caravaca sample (70 ppm). Thus, high biogenic calcite enriched with Ni is not a world-wide phenomenon, because only one (Fiskeler) of the distal marine KT–BT sites points, for certain, to this enrichment. It is reasonable to assume that local variables (*e.g.*, distributions and abundances of living calcareous photosynthetic planktons) may have affected the process of concentrating Ni in the biogenic calcite of the other distal KT–BT sediments.

Acknowledgments: We thank our colleagues of the Laboratoire de Mineralogie et Cristallographie de Paris (LMCP) without whose help this paper would not have appeared. Funding support from le Ministère français de l'Éducation Nationale, de l'Enseignement Supérieur et de la Recherche to P. I. P. for his stay at LMCP, Université Pierre et Marie Curie (Paris), is gratefully acknowledged. This work was supported in part by the Ministry of Science, Technology and Development (Serbia), Project 1235. Our thanks go to Dr. David L. Griscom who generously supplied the ODP samples and provided bibliographic material essential for the writing of this report.

ИЗВОД

ГЕОХЕМИЈА ГРАНИЧНОГ СЛОЈА КРЕДЕ-ТЕРЦИЈАРА СА ПЛАТОА ВЛАКЕ NOSE (СЕВЕРОЗАПАДНИ АТЛАНТИК): КОСМОГЕНСКИ Ni

ПАВЛЕ И. ПРЕМОВИЋ¹, НИКОЛА Д. НИКОЛИЋ¹, МИРЈАНА С. ПАВЛОВИЋ² и КАТЈА И. ПАНОВ¹

¹Лабораторија за геохемију, космохемију и астирохемију, Природно-математички факултет, Универзитет у Нишу, б. бр. 91, 18000 Ниш и ²Институт за нуклеарне науке Винча, б. бр. 522, 11000 Београд

Гранични слој прелаза креде-терцијара (КТ) са платоа Blake Nose откривен на ODP налазишту 171Б (локалитет 1049, бушотина А, језгро 17Х, секција 2) садржи (17 cm дебео) пре-КТ "ејекта" слој, који означава астероидни удар у периоду касне креде. Природа и геохемијски састав овог слоја указују да он потиче углавном од стена са места удара Chicxulub (полуострво Јукатан, Мексико), места претпостављеног астероидног удара. "Ејекта" слој 1049А садржи релативно високе концентрације Ni (до 165 ppm) у карбонатној фракцији. Мишљења смо да је ово обогаћење узроковано наглим и брзим приливом атмосферске падавине са високим садржајем космогенског Ni у басен Blake Nose. Извор метала био је хондрит Chicxulub удара. Сматрамо да је високи прилив суперкиселих киша и пратећих токсичних метала (нпр. Ni) насталих ударом, вероватно био веома погубан за многе карбонатне планктонске организме у пре-КТ океанској површинској води Blake Nose-а.

(Примљено 17. октобра 2003)

REFERENCES

1. L. W. Alvarez, W. Alvarez, F. Asaro, H. V. Michel, *Science* **208** (1980) 1095
2. A. Shukolyukov, G. W. Lugmair, *Science* **282** (1998) 927
3. I. Gilmour, E. Anders, *Geochim. Cosmochim. Acta* **53** (1989) 503
4. G. Keller, W. Stinnesbeck, T. Adatte, D. Stuben, *Earth-Sci. Rev.* **1283** (2002) 1
5. W. Alvarez, P. Claeys, S. W. Kieffer, *Science* **269** (1995) 930
6. K. O. Pope, *Geology* **30** (2002) 99
7. R. D. Norris, D. Kroon, A. Klaus, in *Proceedings of the Ocean Drilling Program, Initial Reports*. Ocean Drilling Program, College Station, TX. 3. Site 1049, Shipboard 171B (1998) 47
8. F. Martinez-Ruiz, M. Ortega Huertas, D. Kroon, J. Smit, I. Palomo, R. Rocchia, *Western North Atlantic Paleogene and Cretaceous Paleooceanography*, Geological Society, Special Publications **183** (2001) 131
9. C. Barber, *Chem. Geol.* **14** (1974) 273
10. R. K. Olsson, K. G. Miller, J. V. Browning, D. Habib, P. J. Sugarman, *Geology* **25** (1997) 759
11. J. Smit, *Ann. Rev. Earth Planet. Sci.* **27** (1999) 75
12. C. Koeberl, H. Sugerdsen, *Geochim. Cosmochim. Acta* **56** (1992) 2113
13. W. Stinnesbeck, G. Keller, T. Adatte, D. Stüben, U. Kramer, Z. Berner, C. Desreux, E. Moliere, *Terra Nova* **11** (2000) 303
14. H. J. Melosh, *Impact Cratering: A Geologic Process*, Oxford University Press, New York, 1989, p. 245
15. S. K. Croft, *Geol. Soc. Am. Spec. Pap.* **190** (1982) 143
16. K. O. Pope, K. H. Baines, A. C. Ocampo, B. A. Ivanov, *Earth Planet. Sci. Lett.* **128** (1994) 719
17. R. G. Prinn, B. Fegley, *Earth Planet. Sci. Lett.* **83** (1987) 1
18. S. A. Davenport, T. J. Wdowiak, D. D. Jones, P. Wdowiak, *Geol. Soc. Am. Spec. Pap.* **247** (1990) 71
19. R. Brett, *Geochim. Cosmochim. Acta* **56** (1992) 3603
20. S. D'Hondt, H. Sigurdson, A. Hanson, S. Carey, M. Pilson, in *New Developments Regarding the K/T event and Other Catastrophes in Earth History*, LPI Contrib. Houston, 1994, p. 29
21. L. R. Lyons, T. J. Ahrens, Personal communication, 2001
22. E. Andres, N. Grevesse, *Geochim. Cosmochim. Acta* **53** (1989) 197
23. U. Kramar, D. Stuben, Z. Berner, W. Stinnesbeck, H. Philipp, G. Keller, *Planet. Space Sci.* **49** (2001) 831
24. G. W. Kallemeyn, J. T. Wasson, *Geochim. Cosmochim. Acta* **45** (1981) 1217
25. H. J. M. Bowen, *Environmental Chemistry of the Elements.*, Academic Press Inc., London, 1979, p. 133
26. F. C. Richard, A. C. M. Bourg, *Water Res.* **25** (1991) 807
27. A. E. Ringwood, *Geochim. Cosmochim. Acta* **24** (1961) 159
28. G. W. Kallemeyn, A. E. Rubin, D. Wang, J. T. Wasson, *Geochim. Cosmochim. Acta* **53** (1989) 2747
29. N. Oskarsson, O. Helgason, H. Sigurdsson, *Geol. Soc. Am. Spec. Pap.* **307** (1996) 445
30. D. L. Griscom, V. Beltran-Lopez, *Adv. ESR Appl.* **18** (2002) 123
31. H. Sigurdsson, S. D'Hondt, M. A. Arthur, T. J. Bralower, J. C. Zachos, M. van Fossen, J. E. T. Channell, *Nature* **349** (1991) 482
32. D. G. Brookins, *Eh-pH Diagrams for Geochemistry*, Springer-Verlag, Berlin, 1988
33. J. D. Rimstidt, A. Balog, J. Webb, *Geochim. Cosmochim. Acta* **62** (1998) 1851
34. R. E. Grim, *Clay Mineralogy*, McGraw-Hill, New York, 1968, p. 569
35. H. van Olphen, J. Fripiat, *Data Handbook for Clay Materials and other Non-metallic Minerals*, Pergamon Press, New York, 1979, p. 346
36. B. Jones, D. A. C. Manning, *Chem. Geol.* **111** (1994) 111
37. P. I. Premović, N. Z. Pavlović, M. S. Pavlović, N. D. Nikolić, *Geochim. Cosmochim. Acta* **57** (1993) 1433
38. P. I. Premović, N. D. Nikolić, M. S. Pavlović, B. Ž. Todorović, D. M. Đorđević, R. S. Nikolić, L. Lopez, S. Lo Monaco, *J. Serb. Chem. Soc.* **66** (2001) 647

39. B. Schmitz, *Geology* **16** (1988) 1068
40. B. Schmitz, P. Andersson, J. Dahl, *Geochim. Cosmochim. Acta* **52** (1988) 229
41. B. Bauluz, D. R. Peacor, C. Elliot, *Earth Planet. Sci. Lett* **182** (2000) 127.

