THE PRISTINE CHICXULUB EJECTA SEQUENCE AT ODP Leg 207: A MICRO-CHEMICAL STUDY.

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Introduction: The discovery of high concentrations of platinum group elements (PGEs) in the uppermost clay-rich sediments of the Cretaceous (K) was the key to link the mass extinction at the Cretaceous-Paleogene ("K/T") boundary to the impact of a large extraterrestrial projectile, now known to have formed the Chicxulub crater [1]. The true nature of this "Iridium anomaly" as well as of other striking features (e.g., presence of unusual carbonate clasts, various geochemical anomalies) at the K/T boundary [2] is still not understood in detail. This is in part due to the lack of high-resolution studies across "pristine" K/T sections. Here we report first results of a micro-chemical study of the exceptionally well preserved K/T boundary in Site 1259C from ODP Leg 207 (Fig. 1; Demerara Rise, ~4500 km off the Chicxulub crater center [2, 3]).

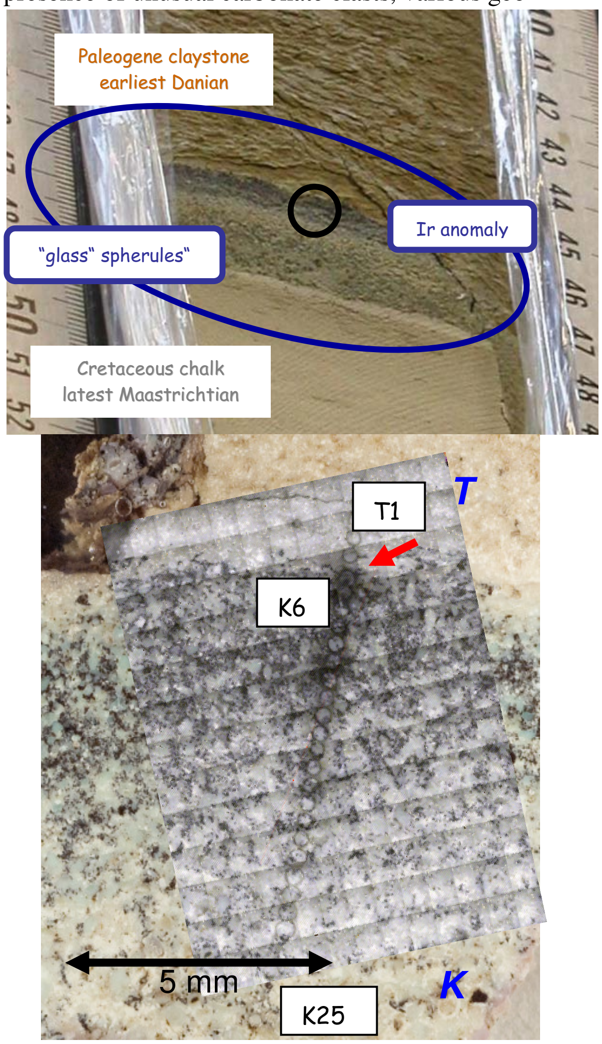

Fig. 1. (Upper) The ~2-cm-thick, slightly graded, apparently complete K/T ejecta deposit in Site1259C, ODP 207, core R8, totally lacks bioturbation – faults/slips at the rim of the core are drilling artifacts; (Lower) Enlarged micrograph of the polished upper part of the K/T section (black circle in the upper picture) displaying the traces of one La-ICP-MS profile. The dark part is the upper "spherule layer" consisting of glass spherules altered to smectite, carbonate clasts, and rare shocked quartz grains (cf. [2, 3]). Red arrow corresponds to "K-T boundary" in Figs. 2 and 4. T1, K6, and K25 are ablation spots mentioned in Fig. 3.

Analytical techniques: Major and minor elements were analyzed along five profiles across the K/T section of core 1259C, with the JEOL JXA 8900 Superprobe (15 kV acceleration voltage, 5 nA sample current, 50 µm spot Ø), and trace elements with the Element 2 La-ICP-MS (235 µm spot Ø) at the Inst. f. Mineralogie, WWU Münster. SiO_2 concentrations determined by electron microprobe were used as internal standard (^{29}Si) for quantification of the trace element data determined by La-ICP-MS. NIST 612 glass was used as standard for rare earth elements [REE], high field strength elements [HFSE] and PGEs except for Ir, which was measured using a yet not certified laboratory standard with 12 ppm Ir. Standard materials BIR1-G and BHVO-2G were used as monitors for precision and accuracy during La-ICP-MS analysis.

Results: The five profiles yielded similar and reproducible results indicating that the K/T boundary in Site 1259C is indeed undisturbed. Values reported below are all from one profile.

PGEs. The Pt concentrations in the lowermost Danian (0 – 1200 µm in Fig. 2) range from 0.0034 to 0.01 ppm, followed by a sharp increase to a maximum value of ~0.1 ppm in the uppermost spherule layer, and a smooth decrease to ~0.0073 ppm ~6 mm below. We interpret slight variations in the $^{195}Pt/^{194}Pt$ ratio (Fig. 2) to reflect the very small size of the PGE-carrying particles. The Ir concentrations also increase towards the top, reaching there a maximum of 0.04 ppm Ir.

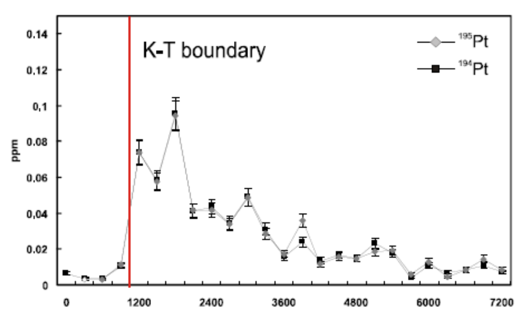

Fig. 2. Platinum concentrations over the K/T profile Site 1259C calculated from counts measured for ^{195}Pt and ^{194}Pt.

Nickel - Chromium. Ni/Cr ratios range in the Danian from 2.97 to 3.52 (mean ± 1σ is 3.24 ± 0.22; N = 5, one profile), and in the spherule layer from 2.31 to 2.84 (mean 2.64 ± 0.14; N = 20).

REE (Fig. 3). The REE concentrations differ by a factor of 3 to 5, with generally lower amounts in the spherule layer. The La_{CN}/Yb_{CN} ratio in the lowermost Danian ranges from 13.3 to 9.5 (mean 11.6 ± 1.5); again a sharp drop occurs at the topmost spherule layer to 6.2. In the spherule bed La_{CN}/Yb_{CN} varies from 6.05 to 11 (8.96 ± 1.7), with the lower values dominating in upper part.

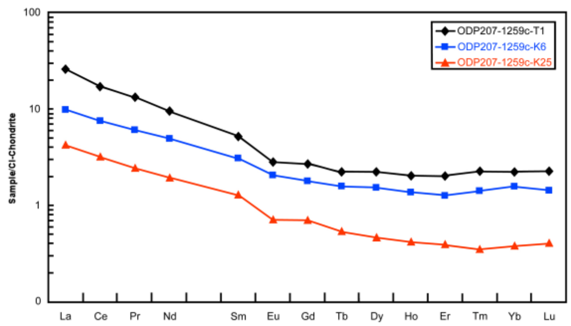

Fig. 3. CI chondrite-normalized REE distribution patterns for three spot analyses in the K/T boundary profile Site 1259C. T1 and K25 (cf. Fig. 1) display a minor negative Eu anomaly, typical for upper crustal rocks. This anomaly is absent in the uppermost spherule layer (spot K6)

HFSE. Already during documentation of the spherule layer with the scanning electron microscope we have noticed the presence of Ti-rich phases, some occurring as infilling of foraminifera shells [2]. The spherule bed has the following concentrations (in ppm): Ti >4000, Zr 44 - 67, Nb 0.90 - 10.6, Hf 2.36 - 3.26, and Ta 0.23 - 0.70. A Cretaceous reference sample collected 10 to 12 cm below the spherule bed contains: Zr 75 - 117, Nb 7.51 - 11.0, Hf 2.26 - 3.10, and Ta 0.57 - 0.78, and the Danian reference sample from 40 cm above the boundary: Zr 83 – 105, Nb 10.5 – 13.8, Hf 2.10 – 2.61, Ta 0.63 – 0.94.

The *Nb/Ta ratio* drops in the lowermost Danian in five consecutive spots from 13.9 to 7.03, and is exceptionally low in the spherule layer (5.43 ± 0.81; Fig. 4). Three analyses of the Danian reference sample resulted in a "normal crustal value" of 15.4 ± 1.1 (N = 3); similar to the value for the Cretaceous reference sample (15.0 ± 2.4, N = 3). The *Zr/Hf ratio* drops also in the five consecutive spots from 26 to 20.4, and remains fairly constant in the spherule layer at a very low value of 20.5 ± 0.95. The Danian reference sample yielded a "normal crustal value" of 39.2 ± 1.4; similar to the value for the Cretaceous reference sample (35.5 ± 2.3). The Nb/Ta and Zr/Hf ratios for the standards BIR1-G and BHVO-2G measured in the course of this study correspond within errors to published values.

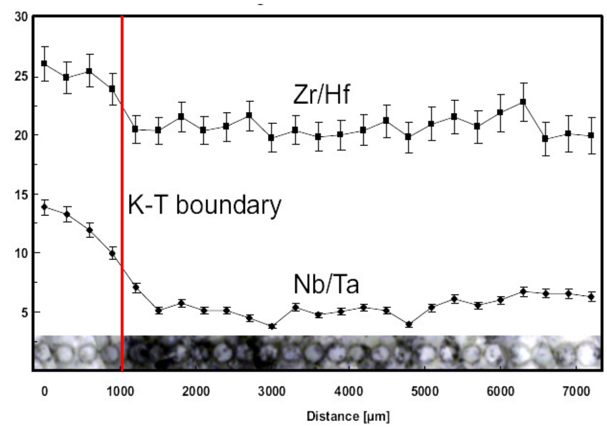

Fig. 4. Variation in Zr/Hf and Nb/Ta ratios across the K/T profile Site 1259C. Chondritic values are 34.3 for Zr/Hf, and 19.9 for Nb/Ta [4]. The reference samples yielded Zr/Hf of 39.2, and Nb/Ta of 15.4 for the Danian, and Zr/Hf of 35.5, and Nb/Ta of 15.0 for the Cretaceous.

Compilation: This high-resolution micro-chemical study clearly shows that various components contributed to the uppermost 5 mm of the K/T boundary at site 1259C. (i) *Projectile matter* is only documented by the increase of PGE concentrations in the topmost mm; this material probably settled out as nm-sized particles stuck to larger ejecta material or glass spherules. The low Ni/Cr ratios are in contrast to what was expected, namely a contribution from the projectile, supposed to be a type CM2 chondrite [5] with a Ni/Cr ratio of 4.053 [6]. Ni/Cr ratios but also the rather flat REE_{CN} patterns point to (ii) *mafic precursor materials* – probably forming *part of the ejecta*; this view is supported by EMP data for individual spherules. Given the very short residence times of HFSE in the ocean, the strongly negative $\varepsilon_{Nd}^{T=65Ma}$ (-17 [2]) and the very exotic Zr/Hf and Nb/Ta ratios point to some "flush" of material from the nearby Guayana craton – the (iii) *local component*, whereas the quite radiogenic Sr [2] obviously stem from (iv) the *contemporaneous seawater*. It is yet not constrained, to which proportions components (ii) to (iv) have contributed to the geochemistry of the uppermost spherule layer in Site 1259C.

Outlook: We consider the spherule bed 1259C to be a key for understanding the mode of deposition and preservation of the various components that now compose the remarkable K/T boundary.

References: [1] Smit J. (1999) *Ann. Rev. Earth Planet. Sci. 27*, 75-113. [2] Schulte P. et al. (2009) *LPSC 40*, this volume. Schulte P. et al. (2009) *GCA in press*. [3] MacLeod K.G. et al. (2007) *GSA Bull. 119,* 101-115. [4] Münker C. et al. (2003) *Science 301*, 84–87. [5] Trinquier A. et al. (2006) *EPSL 241*, 780-788. [6] Tagle R. and Berlin J. (2008) *MAPS 43*, 541-559.

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