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The section of the Barranco del Gredero (Caravaca, SE Spain): a crucial section for the Cretaceous/Tertiary boundary impact extinction hypothesis

La sección del Barranco del Gredero (Caravaca, sureste de España): una sección crucial para la hipótesis de la extinción por impacto en el límite Cretácico/Terciario

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Abstract

The Barranco del Gredero section is one of the most complete, expanded and well exposed Cretaceous Tertiary (K/T) boundary sections in the world. Therefore, the Gredero section has played a key role in the development and testing of the impact extinction hypothesis, and has a significant number of "first discoveries " to its name: The first discovered intact ejecta layer, microkrystites with K-spar pseudomorphs after clinopyroxene and Cr-rich spinels, abundant soot, carbonaceous chondritic ⁵³Cr/⁵²Cr ratios in the ejecta layer, the foraminiferal P0 Zone in the boundary clay, and the adaptive radiation of planktic foraminifers. Also, stable isotope, trace element analysis and the magneto- and cyclo stratigraphy, and the history of burrowing adds to the importance of the Gredero section. Recently urban and road-building development has threatened the excellent exposures, and the lower 100 meters of the upper Maastrichtian are already not longer accessible. The status of geological monument of the Region of Murcia would guarantee that the section will remain accessible for scientific investigation in the future.

Keywords: Caravaca, Spain, K/T boundary, extinction, impact.

Resumen

La sección del Barranco del Gredero es una de las secciones del límite Cretácico/Terciario (K/T) más completas, expandidas y bien expuestas en el mundo. Por tanto, la sección del Gredero ha jugado un papel clave en el desarrollo y la comprobación de la hipótesis de extinción por impacto, y tiene asociados a su nombre un número considerable de 'primeros descubrimientos': el primer lecho con ejecta intacto, con microkrystitas con seudomorfos en sanidina de clinopiroxeno y espinelas ricas en Cr, con abundante hollín, con proporciones de ⁵³Cr/⁵²Cr como los condritos carbonáceos en el nivel de ejecta, con la Zona P0 de los foraminíferos planctónicos en la arcilla del límite, y con el registro de la radiación adaptativa de los foraminíferos planctónicos. También aumentan la importancia de la sección del Gredero, el análisis de isótopos estables y de elementos traza, la magneto- y cicloestratigrafía, así como la historia de la bioturbación. El desarrollo reciente urbano y de carreteras ha puesto en peligro los excelentes afloramientos, de hecho los 100 m inferiores del Maastrichtiense superior no son ya accesibles. El estatus de monumento geológico de la Región de Murcia garantizaría que la sección permaneciera accesible a los investigadores en el futuro.

Palabras clave: Caravaca, España, límite K/T, extinción, impacto.

1. Introduction

The Barranco del Gredero section has attracted scientists since the 1950s (Fallot *et al.*, 1958; Paquet, 1961; Veen, 1969 and Hillebrandt, 1974) because of its exceptional thickness, completeness and richness of well-preserved foraminifers (Figs. 1, 2).

The section remains among the five most complete K/T sections, and is still the subject of detailed investigations, e.g. (Stoll and Schrag, 2000; Díaz *et al.*, 2002; Martínez *et al.*, 1997). The well-bedded Gredero section, displaying Milankovitch-style rhythmic bedding (Kate

and Sprenger, 1993), is part of the Loma de Solana tectonic unit. This unit is an almost undeformed, only gently folded block, bounded by thrust faults that are smeared and marked by Triassic gypsum. The Loma de Solana unit is usually placed in the allochtonous Subbetic zone, but the striking lithological similarities with the Agost, Relleu and Finestrat sections up to 150 km farther east, demonstrate that the Loma de Solana unit is rather part of the par-authochtonous Prebetic zone, deposited on the southern margin of the Iberian continent. The entire section in the Solana unit is continuous from the late Albian to the Eocene, and is more than 800m thick. It is entirely



Fig. 1.- Map of Europe, with the locations of the K/T sections mentioned in the text (after Smit, 1982). The thickness of the boundary clay (P0) is indicated (black interval)

Fig. 1.- Mapa de Europa con la situación de las secciones del límite K/T mencionadas en el texto (según Smit, 1982). La potencia de las arcillas del límite (P0) está indicada por el intervalo negro.



Fig. 2.- Map traced from enlarged aerial photographs of the Barranco del Gredero. Thick black line indicates outcrops of the K/T boundary. Fig. 2.- Mapa trazado sobre una fotografia aérea ampliada del Barranco del Gredero. La línea negra gruesa indica los afloramientos del límite K/T.

developed in a hemipelagic deep-water facies, characterized by high sedimentation rates (1.5cm/kyr) compared to open-ocean pelagic sequences. Turbidite-fan development is absent, isolated turbidites are only developed in limited intervals, mainly in the Jorquera Formation. (Figs. 3, 4)

The Jorquera Formation ranges in age from Early Maastrichtian to Early Eocene, is over 225m thick (Fig. 3; after van Veen, 1969) and developed in a bathyal, hemipelagic facies. In comparison, the same interval in the famous Gubbio section in Italy is only 10.5m thick. Analyses of meso-pelagic fish-teeth (Pat Doyle pers. comm.) suggest a depth of deposition of more than 1000m near the K/T boundary. Van Veen, (1969, p. 116) was one of the first to recognize that the K/T boundary interval was uniquely well exposed in the Barranco del Gredero.

Several sample sets have been collected from the Barranco del Gredero. The 1975 sample set of 150 samples was taken from the topmost 9m of the Maastrichtian and the basal 70m of the Paleocene. In 1979 the sample set was further extended to include the top 100m of the Upper Maastrichtian, up to just below the FAD of *Abathom*- *phalus mayaroensis*. This paper presents a synopsis of the major works that have been accomplished on the Gredero section, and their significance to the K/T boundary debate.

2. Paleomagnetism

The initial paleomagnetic analysis of the Gredero section was performed by G. Brunsmann (Univ Amsterdam) (Smit, 1982) (Fig. 4). The magnetostratigraphy of the uppermost 100m of the Maastrichtian and the basal 70m of the Paleocene showed magnetochrons C31 to C27, that correlate well with the magnetostratigraphy of the classic section at Bottaccione, Gubbio, (Alvarez and Lowrie, 1977) and the Agost section 100km farther east (Groot *et al.*, 1989). These paleomagnetic data were useful to calculate sedimentation rates for the Gredero section and established the chronostratigraphy of the K/T boundary events, using the reversal ages provided by Cande and Kent (1992). Assuming that the clay flux remained constant over the latest Maastrichtian and earliest Paleocene interval, the duration of the P0 Zone is here estimated at

COLUMNAR SECTION NORTHERN LOMA DE SOLANA UNIT





Fig. 3.- Columna litológica de la sección completa de la Loma de Solana (según van Veen, 1969). La barra a la izquierda son 50cm.

about 11 ky, and the P. eugubina Zone at 23 Ky. Those ages differ from the ages given by Olsson *et al.* (1999), but the definitions of the P α Zone of Olsson *et al.* (1999) differs from the definition of the P. eugubina Zone preferred here. The top of P α sensu Olsson *et al.* (1999) is at the LAD of *P. eugubina*, in the Gredero section 1.5m above K/T boundary, where we use the FAD of *P. pseudobulloides* at 60 cm as the top of the P. eugubina Zone.

3. Biostratigraphy

Two masters students of C. Hermes (University of Amsterdam, 1974, unpublished report), first measured the Gredero section in detail. Von Hillebrandt (1974) provided a planktic foraminiferal zonation of the Paleocene, and Abtahi (1975) recognized the presence of the Parvularugoglobigerina eugubina Zone, but analysed only three samples from the K/T interval. Hermes (pers. comm) and Abtahi (1975) mentioned a 10 cm clay-interval at the K/T boundary, but paid no further attention. Smit (1977) analysed the K/T interval in detail (Fig. 5): the K/T transitional interval, including the boundary clay (BCL) was sampled every cm. In 1977, (Smit (1977) found the 3 mm thick red lamina (sample sm 75-503), that most people now agree is the ejecta layer of the Chicxulub impact. Smit (1977, 1982) discovered a new biozone between the top of the Maastrichtian and the base of the G. eugubina Zone; the Guembelitria cretacea or the P0 Zone (Fig. 5). The type locality of P0 is therefore in the Gredero section, and the zone has now been widely recognized (Berggren et al., 1995).

4. Planktonic foraminifers

The Gredero section played a critical role in the development of the biostratigraphic zonation of the K/T boundary interval because the hemipelagic marls and limestone of the sequence are relatively easy to disaggregate in H_2O_2 , and to wash over a 40-micron nylon screen. The specimens are well preserved, although the chambers are invariably filled with secondary calcite.

A detailed pattern of extinction and radiation of the planktic foraminifers across the K/T boundary was first unravelled at Caravaca (Abtahi, 1975; Smit, 1977, 1982): This pattern reflects a five-stage (1 - 5) development (Smit and Romein, 1985).

4.1. Stage 1): Upper Maastrichtian.

Planktic foraminiferal faunas towards the close of the Cretaceous period are species-rich, tropical, and specialized. Specimens of Globotrucana stuarti and G. contusa reach sizes of just over one millimeter, a size that has not been reached again in planktonic foraminifera until the Pliocene. The topmost zone of the Maastrichtian, the Abathomphalus mayaroensis Zone, is about 100m thick in the Gredero section and has an unusually long duration of at least 3.25 million years (Berggren et al., 1995). (Fig. 6). Remarkably few changes occur in the composition of the planktic assemblages within that interval. Given that specialized foraminiferal faunas are sensitive indicators of paleoceanographic changes, such as temperature, salinity, water-mass and thermocline depth changes, the stability of the the A. mayaroensis Zone implies, therefore, unusually stable paleo-oceanographic conditions

during the entire late Maastrichtian. Therefore, the A. mayaroensis Zone was not further subdivided for a long time. It is worth noting, however, the disappearance of *G. gansseri*, and the first occurrence of a few new species (*H. hariaensis* and *P. hantkeninoides*) in the upper part of the zone. The latter data have been used to subdivide the A mayaroensis Zone into four subzones (Pardo *et al.*, 1996). Nonetheless, in the present study all species range up to the ejecta layer (sample sm75-503), or to the highest level of the Maastrichtian. Therefore, the presumed decline e.g. (Pardo *et al.*, 1996) in species abundance



Fig. 4.- Lithological column of the Jorquera Formation in the Gredero section, from 95m below to 85m above the K/T boundary. The magnetostratigraphy is from G. Brunsmann (after Smit, 1982). Important planktic foraminifers FADs and LADs are indicated. (~ = marl; -- = clay; stippled = sandstone; brick = limestone).

Fig. 4.- Columna litológica de la Fm. Jorquera en la sección del Gredero, desde los 95m bajo el límite K/T hasta los 85m por encima. La magnetoestratigrafía es de G. Brunsmann (según Smit, 1982). Se indican las FADs y LADs importantes de foraminíferos planctónicos. (~ = margas; -- = arcillas; punteado = areniscas; enladrillado = calizas).

just prior to the ejecta layer is here considered an artifact. This assertion is based on the fact that the top 10cm of the Maastrichtian is usually partially dissolved, and only a thorough search yields the rare "missing" species.

4.2. Stage 2): Mass-extinction.

The specimen abundance drops by more than one order of magnitude exactly at the ejecta layer, enriched in iridium and microkrystites. The ejecta layer itself is free of planktic specimens, as expected, and most species disappear at this level, possibly with the exception of a few non-specialized species found in stage 3 (see below).

4.3. Stage 3): "Strangelove ocean" conditions.

A thin, 8 cm-thick, clay layer directly overlies the ejecta layer. This clay layer has also been recognized elsewhere, but it is often much thinner (<1cm). The thickness appears to be related to local sedimentation rates, in particular the accumulation rate of clay. This clay layer contains a poor remnant of A. mayaroensis Zone faunas, non-specialized species such as *Guembelitria cretacea*, *Hedbergella holmdelensis, H. monmouthensis, Globigerinelloides messinae* and possibly *Heterohelix globulosa*. Only *Guembelitria cretacea* occurs in considerable numbers, and might be the only true survivor.

The clay layer can, therefore, be equated to the G. cretacea, or P0 Zone (Smit, 1977) and the question of survivorship is rhetorical. Indeed, the argument of a different stable isotopic signature for species present at either side of the K/T boundary (Barrera and Keller, 1990) has been effectively rejected (Kaiho and Lamolda, 1999)

4.4. Stage 4): Initial recovery.

The transition from the clay to foraminifer-rich marls is not preserved in the Gredero section because of shearing related to tectonism. However, in the almost identical undisturbed Agost section that transition is rapid, but gradual over about one cm. The first sample directly above the clay contains already an abundant fauna, that consists of at least five new, small species. By comparison, in the more expanded El Kef section, in Tunisia, these species appear in sequence: First *Globigerina minutula*, shortly thereafter followed by *P. fringa* and *P. eugubina*. It is likely that the initial evolution and radiation of these species took place elsewhere, and that they subsequently migrated into the Gredero region. The question of the ancestry to the Tertiary planktic foraminifers needs to be addressed, as several scenarios exist. Smit (1982) suggested



Fig. 5.- Detailed lithological column of the K/T interval (after Smit, 1977). Bar on the left is 5cm.

Fig. 5.- Columna litológica detallada del intervalo K/T (según Smit, 1977). La barra a la izquierda corresponde a 5cm.

that the clear survivor species *G. cretacea* is the only ancestral species to modern planktic faunas. On the other hand, Liu and Olsson (1992) indicated that three species (*G. cretacea*, *H. holmdelensis* and *H. monmouthensis*) are the ancestral forms to the early Paleocene stock. These taxa soon diversified to cancellate-spinose and non-spinose premuricate lineages. However, the wall-structure between these species and earliest Paleocene cancellate species differs considerably, thus such a change would have required some morphological jumps that have not yet been observed among the planktic faunas of the latest Maastrichtian or the earliest Paleocene.

4.5. Stage 5): Adaptive radiation.

The short G. eugubina Zone not only shows a rapid (within one cm) appearance of new species, but these

species are also successively dominant (Smit, 1982) (Fig. 7). These acmes appear to be different in different locations (cf. Shatsky rise, Pacific ocean, Gerstel et al., 1986) , and probably show the effects of local environments and adaptive radiations of the newly developing planktic faunas. The upper part of the G. eugubina Zone includes a 40cm thick limestone bed that occurs about 0.5 m above the K/T boundary. This bed is characterized by an abundance of calcareous dinoflagellates, Thoracosphaera operculata, and can be traced over hundreds of kilometers in SE Spain (Finestrat). Such a bloom of Thoracosphaera as well as Braarudosphaera occurs in the basal Paleocene (Romein, 1977) (Fig. 7), and these species were therefore considered survivor species. These acmes further testify to unstable paleo-oceanographic conditions at the onset of the Paleocene, and are an important argument in support of a sudden, catastrophic, extinction event at the K/T boundary, as such radiations presumably take place only in a vacant, largely empty, ecospace.

Later studies (Canudo *et al.*, 1991; Arenillas and Molina, 1997; Kaiho and Lamolda, 1999) confirmed this extinction-radiation pattern, and differ only in minor details. A cursory review of the recent literature, reveals that the basalmost Paleocene may contain over 23 species. In the authors opinion, the uncertainty in the number of species is certainly due to oversplitting, in particular in the genera *Eoglobigerina* and *Parvularugoglobigerina*.

The extremely short extinction interval <0.5 cm), is compatible with a catastrophic extinction because very few changes occurred in planktic foraminiferal assemblages in the preceding 100 m thick interval . The only extinction recorded is *G. gansseri* which disappeared about 10 m below the K/T boundary (Fig. 7). The strong adaptive radiation of foraminifers within the first 50 cm above the boundary clay, further strengthens the catastrophic postulate, which is also corroborated by the iridium anomaly, the geochemical signature of a large impact event.

5. Benthic foraminifers

Benthic foraminiferal assemblages were studied in the Gredero section by Coccioni and Galeotti (1994) who demonstrated a sudden collapse of benthic ecosystems directly above the K/T boundary, with only a few taxa blooming under low-oxygen conditions. Many benthic taxa have temporarily migrated elsewhere (Smit, 1982), because the majority returned within the P. eugubina Zone (between 10 and 35 kyr) to the Gredero seafloor when oxygenation improved.

6. Trace element and isotopic analysis

A subset of one hundred samples was analysed from the top of the Maastrichtian and the base of the Paleocene by instrumental neutron activation (INAA) in 1977, at Delft Technical University. The results (Table 1, Fig 8) show a strongly anomalous content of Cr, Co, Ni, As, Sb, Zn in the ejecta layer (sample Sm75-503), which is 15-250 times enriched relative to background values (Smit, 1979). The iridium anomaly was not initially discovered in this series of INAA analyses. However, elements such as Ni already pointed to an extraterrestrial origin for the geochemical anomaly, because nickel is often associated with Ni-iron meteorites, and Ni concentrations of 1990 ppm are rare anywhere on earth. Although the high Ni and Cr concentrations were a firm indication of a substantial extraterrestrial contribution in sample 75-503, these are not unequivocally extraterrestrial, since terrestrial sources for these elements are available in many places on earth.

Around the same time, Alvarez *et al.* (1979) published the discovery of anomalous iridium concentrations in the Bottaccione section, Italy. They used a similar, but more sensitive radiochemical neutron activation analysis (RNAA) method. Jan Hertogen of Gent University also used RNAA in 1979 to demonstrate the presence of anomalous Ir in the Gredero section, particularly in sample 75-503 (Smit and Hertogen, 1980). The magnetic residues of sample 75-503, consist primarily of chromite and magnesioferrite, which are highly enriched in Ir, Ni and Cr (Table 1, cf. Fig. 8). This demonstrates a common source for these siderophile elements.

Another important discovery made at the Gredero section, is the chondritic abundance ratios of all the platinum group elements (PGE) (Kyte *et al.*, 1985). Such ratios meant that the source of the PGEs must have been unfractionated, strongly indicating that the Ir anomaly was not from a terrestrial (e.g. a volcanic) source, as suggested by some.



Fig. 6.- Chronostratigraphy of the K/T interval (after Berggren *et al.*, 1995). Fig. 6.- Cronoestratigrafia del intervalo K/T (según Berggren *et al.*, 1995).





Fig. 7.- Acmés de los foraminíferos planctónicos y nanofósiles en la parte basal del Paleoceno de la sección del Barranco del Gredero (según Smit, 1982 y Romein, 1977). El Maastrichtiense y el Paleoceno están representados a diferentes escalas.

Furthermore, Shukolyukov and Lugmair (1998) demonstrated anomalous ${}^{53}Cr/{}^{52}Cr$ isotope ratios in sample 75-503. These ${}^{53}Cr/{}^{52}Cr$ isotope ratios are an important clue to the composition of the impacting bolide, because asteroids, comets and Mars all have different ${}^{53}Cr/{}^{52}Cr$ -isotope ratios and those are all different from the terrestrial ratios. Global data compilations of K/T sites where both Cr and Ir were measured, show that the concentration profiles of both elements are almost identical, invari-

ably with the highest peaks in the ejecta layer (Fig. 8). Sm75-503 holds the K/T boundary 'record' in terms of Cr concentration. The conclusion, therefore, is that the source of the iridium is also the source for the excess Cr. The earth's 53 Cr/ 52 Cr ratio is everywhere the same, for the mantle and crust (epsilon 53 Cr of the earth is therefore by definition set at zero). Ordinary chondrites, achondrites, and martian meteorites have a positive epsilon 53 Cr, carbonaceous chondrites a negative epsilon 53 Cr.



Fig. 8.- Concentration profiles of the siderophile elements Cr, Ni and Ir (INAA see text) in the Gredero section. Anomalous values of all three elements in the same (K/T boundary) level indicate a common source.

Fig. 8.- Variaciones en la concentración de los elementos siderófilos Cr, Ni e Ir (INAA, ver texto) en la sección del Barranco del Gredero. Las anomalías de los tres elementos en el mismo nivel (límite K/T) indican una fuente común.

The ejecta layer (sample75-503) yielded a strong negative epsilon ⁵³Cr ratio, identical to carbonaceous chondrites and unlike ordinary chondrites and asteroids which have a positive epsilon ⁵³Cr. This discovery effectively excludes a terrestrial origin of both Cr and Ir at the K/T boundary.

In contrast to the reliability of the Cr ratios, Os isotope ratios are more susceptible to misinterpretations because Os isotope ratios between the earth's mantle and meteorites are practically indistinguishable (187 Os/ 186 Os =1), whereas this ratio is 10 for the crust (Luck and Turekian, 1983)

7. Microkrystites

The Gredero section remained a key player in the investigations that followed the launch of the impact-extinction theory after the finding of the iridium anomaly.

Smit and Klaver (1981) discovered tiny (50-500 μ m) spherules, initially thought to be composed of "sanidine", in sm75-503. The 'sanidine' spherules were first interpreted as altered microtektites, but, later became known as microkrystites, which are now best explained as condensation droplets from the hot impact vapour cloud.

Smit (1977) initially regarded the spherules as "gypsum nodules", because gypsum is abundant in these pelagic sediments. Gypsum, unfortunately, has the same index of refraction as sanidine, so their importance went unnoticed for several years. Gerard Klaver (NITG/TNO) recognized a quench crystalline texture within the 'sanidine' spherules, because he had observed similar textures in the chilled crust of basaltic pillow-lavas on the island of Bonaire (Klaver, 1987). Nonetheless, the occurrence of sanidine presented a problem: K-spar is characteristic of K-rich, very viscous igneous rocks, not the ideal environment for producing quench crystals. Studies at Furlo and Petriccio (Italy) identified identical 'sanidine' spherules in the Ir-rich layer. At these localities the spherules were associated with dark, clay-rich spherules full of quench crystals of magnesioferrite spinel, and enriched in iridium opposite the Ir concentration of the K/T boundary clay itself (33 and 2 ppb, respectively). The spherules were much more mafic, in composition consistent with the quench crystallinity, but hard to reconcile with Kspar spherules, assuming that both came from the same source. The Cr-rich magnesioferrite and chromite quench crystals also occur in great abundance in 75-503 (Fig. 9), but are seemingly floating in the clay matrix, as if they were formed directly by condensation. Close inspection of sample 75-503, however, shows that the spinels occur only in flat, round clusters, of the same size as the Furlo



Fig. 9.- SEM graph of skeletal Ni-Cr-rich spinels from sample 75-503, Gredero section.

Fig. 9.- Fotomicrografía SEM de espinelas ricas en Ni-Cr de la muestra 75-503, sección del Gredero.

element	average upper Maastrichtian (n=31)	ejecta layer 503 a	ejecta layer 503b	503 high magnetic (<0.2 Amp.)	503 low magnetic (0.2>2 Amp.)	503<10μ (Actlabs)	average dark boundary clay (n=5)	average Lower Paleocene(n=30)
Na	730	1400	1/30	101 1	241	550	1287	407
INA K	139	13000	1430	3940	241 670	559	1207	3071
Ca	318353	<100	<100	5740	070	25000	126440	323567
Sc	5 80	9.46	9.06	10.65	94	10.9	12 94	5 20
Cr	58.0	801.0	769.0	2348	740	640	162.8	68.4
Fe	14096	52200	50700	251400	188900	38900	34860	12708
Со	9.08	537	471	1840	920	138	33.56	5.17
Ni	9.14	1990	1930	8600	9786	690	133.4	45.27
As	1.24	456	431	2288	795.2	190	5.166	1.14
Br	0.48	2.23	4.3		3.4	1.2	2.482	1.37
Rb	32.53					33	61.9	20.93
Sr	797.17					800	597.25	691.40
Sb	0.24	13.7	12.4	51.64	19.56	4.9	0.8054	0.22
Cs	2.24					1	3.806	1.42
Ba	223					51	144	211
La	17.37	3.78	3.65	8.71	8.02	9.8	34.26	20.20
Ce	33.88	9.19	8.46	20.42	17.74	17	67.38	32.40
Sm	2.959	0.735	0.662	2.172	2.28	1.35	7.508	3.65
Eu	0.623	0.204	0.184	0.61	0.755	0.37	0.997	0.64
Tb	0.257					0.2	0.854	0.40
Yb	1.054	0.481	0.557	2.24	0.62	0.6	1.560	1.236
Lu	0.089					0.1	0.233	0.17
Hf	1.32	4.66	4.54	4.84	4.21	3.5	3.256	1.10
Та	0.18					1.6	0.95175	0.44
Ir	< 0.2	24.4	26.3	121.3	63.0	34.0	8.5	< 0.2
Th	3.73	8.59	8.29	16.62	23.72	7.5	8.536	3.20
U	1.01	11.7	11.1	15.14	12.55	6.5	1.702	1.08
CaCO ₃	72.53	2	2			41	28.48	74.70

Table 1.- Instrumental Neutron Activation Analysis of the K/T interval of the Gredero section. Values in ppm (μ g/g), except for Ir and Au in ppb (ng/g). Analyses performed at IRI, Delft University, and Actlabs, Toronto (column '503<10 μ '). n=number of analyses.

Tabla 1.- Análisis instrumental por activación neutrónica del intervalo K/T de la sección del Gredero. Valores en ppm (µg/g), excepto para el Ir y Au en ppb (ng/g). Análisis realizados en el IRI, Universidad Delft, y Actlabs, Toronto (columna '503<10µ'). n=número de análisis.

spherules. Apparently, the matrix between the spinel crystals has been altered to a soft clay that is easily lost in the extraction techniques applied. Textures as in the 'sanidine' spherules were also found in spherules of pure smectite (Fonte d'Olio, Italy; Bidart, France), in arsenopyrite spherules from Zumaya (Spain), and goethite from New Zealand and Tetri-Tskaro, Georgia. Thus it became clear that the K-spar quench crystals were pseudomorph alteration products of another precursor, preferably a mafic mineral. The high $\delta^{18}O$ (+25‰) of the sanidine (Epstein, 1982) also confirmed their low temperature origin. Finally, the precursor mineral, which consists of Ca-rich clinopyroxene was discovered at DSDP site 577, Shatsky Rise, in the Pacific; (Smit *et al.*, 1992) (Fig. 10).

8. Soot

Wolbach *et al.* (1985) determined an anomalous amount of soot in sample 75-503, indicative of large wildfires just after the impact. It is worth noting, however, that at the "twin" site Agost not a trace of soot has been discovered, whereas all other characteristics (lithology, biotic changes, geochemistry) are almost identical.

9. Stable isotopes

Stable isotope analyses have played a major role in establishing the magnitude of the K/T mass-extinctions. Romein (Romein and Smit, 1981) analysed stable isotopes in detail across the K/T boundary in the Gredero



Fig. 10.- SEM graphs of skeletal Ca-rich clinopyroxene from DSDP site 577, Shatsky Rise Pacific (left). Small crystals of K-spar (sanidine) from Caravaca (sm75-503). The identical texture suggests these are pseudomorphs after clinopyroxene (right)

Fig. 10.- Fotomicrografías SEM de clinopiroxeno rico en Ca del site 577 DSDP, Shatsky Rise en el Pacífico (a la izquierda), y de pequeños cristales de sanidina de Caravaca (sm75-503). La textura idéntica sugiere que estos últimos (a la derecha) son seudomorfos de clinopiroxeno.

section. He was the first to find the short-term strongly negative (2.5% δ^{13} C) anomaly, which later became the fingerprint of the "Strangelove ocean" condition (Hsu and McKenzie, 1985). In fact, all major mass-extinctions are characterized by such negative $\delta^{13}C$ shifts. In these conditions the vertical $\delta^{13}C$ gradient in the oceans temporarily disappeared during the deposition of the boundary clay. The δ^{18} O profile of Caravaca (Smit, 1990) suggests that sea-surface temperatures rose considerably at the base of the boundary clay. Kaiho and Lamolda (1999) confirmed these anomalies in detail, as they showed that the vast majority of Cretaceous species above the K/T boundary are reworked specimens. These authors avoided the problem of the calcite infilling of foraminifers by analysing the crushed shells only. Their results invalidate earlier conclusions of survivorship of Cretaceous species above the K/T boundary, based on the analyses by Barrera and Keller (1990), of the calcite infilled foraminifers of Brazos river.

10. Burrowing

The 3 mm thin ejecta layers in the sections at Agost, Relleu, Finestrat and Gredero are almost completely intact, without apparent bioturbation. This demonstrates that burrowing organisms also temporarily disappeared from the region, presumably for the same temporary lack of oxygen on the sea floor that reduced the benthic foraminiferal faunas (Coccioni and Galeotti, 1994). The top 10 cm of the Maastrichtian often contains dark grey burrows, of the same composition and colour as the P0 boundary clay (e.g. *Zoophycos, Chondrites, Thalassinoides*). Those burrows contrast strongly with the light colour of the greenish marls. Kotake (1989) has shown that this type of burrowers, especially *Zoophycos*, scavenge the seafloor, and transport debris from the seafloor surface down into their burrows. In the Gredero section the dark burrows are filled with dark boundary clay only, but never with ejecta layer debris, such as spherules. This implies that these burrows were made after the ejecta layer was covered by a sufficient amount of clay that the *Zoophycos* burrower could not scavenge the ejecta layer anymore. Although these burrows have penetrated the ejecta layer, they leave the ejecta layer itself intact.

In contrast, similar burrows in the topmost Maastrichtian elsewhere, e.g. from Italy (Furlo, Petriccio) and Bidart (France), often contain the debris of ejecta (spherules, iridium). At these locations the ejecta layer is also bioturbated, indicating either less anaerobic conditions on the sea floor after the K/T mass-extinction event, or low sedimentation rates, allowing the ejecta layer to be scavenged and bioturbated.

11. Conclusions

The Gredero section has provided numerous discoveries of the K/T boundary event that demonstrate the intimate relationship between the biotic events across the K/T boundary and the impact event at Chicxulub. The section is still well accessible, but increasing urban and industrial developments threaten to cover and destroy this unique section.

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13. References

- Abtahi, M. (1975): Stratigraphische und micropaleontologische Untersuchung der Kreide/Alttertiair Grenze im Baranco del Gredero (Caravaca, Prov. Murcia SE-Spanien). 174p. Unpublished PhD thesis, Technische Universitat Berlin.
- Alvarez, W., Alvarez, L. W., Asaro, F., Michel, H. (1979): Experimental evidence in support of an extra-terrestrial trigger for the Cretaceous-Tertiary extinctions. *Eos*, 60: 734.
- Alvarez, L. W., Alvarez, W., Asaro, F., Michel, H. V. (1980): Extraterrestrial cause for the Cretaceous-Tertiary extinction. *Science*, 208: 1095-1108.
- Alvarez, W., Lowrie, W. (1977): Upper Cretaceous-Paleocene magnetic stratigraphy at Gubbio, Italy, III. Upper Cretaceous magnetic stratigraphy. *Bulletin of the Geological Society of America*, 88: 374-377.
- Arenillas, I., Molina, E. (1997): Analisis cuantitativo de los foraminiferos planctonicos del Paleoceno de Caravaca (Cordillera Betica); bioestratigrafia y evolucion de las asociaciones. *Revista Española de Paleontologia*, 12: 207-232.
- Barrera, E., Keller, G. (1990): Stable isotope evidence for gradual environmental changes and species survivorship across the Cretaceous/Tertiary boundary. *Paleoceanography*, 5: 867-890.
- Berggren, W. A., Kent, D. V., III, C. C. S., Aubry, M.-P. (1995). A Revised Cenozoic Geochronology and Chronostratigraphy *Geochronology, time scales and global stratigraphic correlation.* SEPM Special Publication 54: 129-212
- Cande, S. V., Kent, D. V. (1992): A new Geomagnetic Polarity timescale for the Late Cretaceous and Cenozoic. *Journal of Geophysical Research*, 97: 13917-13951.
- Canudo, J. I., Keller, G., Molina, E. (1991): Cretaceous/ Tertiary boundary extinction pattern and faunal turnover at Agost and Caravaca, S.E. Spain. *Marine Micropaleontology*, 17: 319-341.
- Coccioni, R., Galeotti, S. (1994): K-T boundary extinction: Geologically instantaneous or gradual event? Evidence from deep-sea benthic foraminifera. *Geology*, 22: 779-782.
- Diaz, M. E., Sanz, R. E., Martinez, F. J. (2002). Sedimentary record of impact events in Spain. In: Koeberl, C. MacLeod, K. (Eds.) *Catastrophic events and mass extinctions; impacts and beyond*. Geological Society of America. Special Paper 356; 551-562.

- Epstein, S. (1982): The δ^{18} O of the sanidine spherules at the Cretaceous -Tertiary boundary. *Lunar and Planetary Science XIII*, 13: p. 123.
- Fallot, P., Delga, M. D., Busnardo, R., Sigal, J. (1958): El Cretacico Superior del Sur de Caravaca (Provincia de Murcia). *Notas y Comunicaciones del Instituto Geológico y minero de Espana*, 50: 283-299.
- Groot, J. J., de Jonge, R. B. G., Langereis, C. G., ten Kate, W. G. H. Z., Smit, J. (1989): Magnetostratigraphy of the Cretaceous-Tertiary boundary at Agost (Spain). *Earth and Planetary Science Letters*, 94: 385-397.
- Hillebrandt, A. v. (1974): Bioestratigrafia del Paleogeno en el Sureste de Espana (Prov. de Murcia y Alicante). *Cuadernos de Geología*, 5: 135-153.
- Hsu, K. J., McKenzie, J. (1985). A "Strangelove" ocean in the earliest Tertiary. In: E. T. Sundquist, W. S. Broecker (Eds.): *The Carbon cycle and Atmospheric CO2: Natural variations from Archean to the present*. American Geophysical Union, monograph 32: 487-492..
- Kaiho, K., Lamolda, M. A. (1999): Catastrophic extinction of planktonic Foraminifera at the Cretaceous-Tertiary boundary evidenced by stable isotopes and foraminiferal abundance at Caravaca, Spain. *Geology*, 27: 355-358.
- Kate, W. G. T., Sprenger, A. (1993): Orbital cyclicities above and below the Cretaceous/Paleogene boundary at Zumaya (N Spain), Agost and Relleu. *Sedimentary Geology*, 87: 69-101.
- Klaver, G. T. (1987): The Curacao Lava Formation: an ophiolitic analogue of the anomalous thick layer 2B of the Mid-Cretaceous oceanic plateaus in the western Pacific and central Caribbean. *GUA papers of Geology*, 27: 169.
- Kotake, N. (1989): Paleoecology of the Zoophycos producers. *Lethaia*, 22: 327-341.
- Kyte, F. T., Smit, J., Wasson, J. T. (1985): Siderophile interelement variations in the Cretaceous Tertiary boundary sediments from Caravaca, Spain. *Earth and Planetary Science Letters*, 73: 183-195.
- Liu, C., Olsson, R. K. (1992): Evolutionary Radiation of Microperforate Planktonic Foraminifera Following the K/T Mass Extinction Event. *Journal of Foraminiferal Research*, 22: 328-346.
- Luck, J. M., Turekian, K. K. (1983): Osmium-187/Osmium-186 in manganese nodules and the Cretaceous-Tertiary boundary. *Science*, 222: 613-615.
- Martinez, R. F., Ortega, H. M., Palomo, I., Acquafredda, P. (1997): Quench textures in altered spherules from the Cretaceous-Tertiary boundary layer at Agost and Caravaca, SE Spain. *Sedimentary Geology*, 113: 137-147.
- Olsson, R. K., Hemleben, C., Berggren, W. A., Huber, B. T. (1999): *Atlas of Paleogene Planktonic Foraminifera*. 252 p. Smithsonian Contributions to Paleobiology, Washington.
- Paquet, J. (1961): Donnees nouvelles sur le Crétacé subbetique au sud-est de Caravaca (prov. de Murcie, Espagne). *Bulletin de la Societé Géologique de France*, N.S. 3: 74-76.
- Pardo, A., Ortiz, N., Keller, G. (1996). Latest Maastrichtian and Cretaceous-Tertiary Bundary foraminiferal turnover and environmental changes at Agost, Spain. In: N. Macleod, G. Keller (Eds.): *Cretaceous-Tertiary Mass Extintions*: 139-172. W. W. Norton, New York.

- Romein, A. J. T. (1977): Calcareous nannofossils from the Cretaceous/Tertiary boundary interval in the Barranco del Gredero (Caravaca, Prov. Murcia, S.E. Spain). *Proc. Koninklijke Nederlandse Akademie van Wetenschappen*, 80: 256-279.
- Romein, A. J. T., Smit, J. (1981): The Cretaceous-Tertiary boundary: calcareous nannofossils and stable isotopes. *Proc. Koninklijke Nederlandse Akademie van Wetenschappen*, 84: 295-314.
- Shukolyukov, A., Lugmair, G. W. (1998): Isotopic evidence for the Cretaceous-Tertiary impactor and its type. *Scienc,e* 282: 927-929.
- Smit, J. (1977): Discovery of a planktonic foraminiferal association between the Abathomphalus mayaroensis zone and the "Globigerina" eugubina zone at the Cretaceous/Tertiary boundary in the Barranco del Gredero (Caravaca, SE Spain): a preliminary report. *Proc. Koninklijke Nederlandse Akademie van Wetenschappen*, 80: 280-301.
- Smit, J. (1979). The Cretaceous/Tertiary transition in the Barranco del Gredero, Spain. In: W. K. Christensen, T. Birkelund (Eds.): Cretaceous-Tertiary Boundary Events Symposium; II. Proceedings:156-163. Copenhagen.
- Smit, J. (1982): Extinction and evolution of planktonic foraminifera after a major impact at the Cretaceous/Tertiary boundary. *Geological Society of America Special Paper*, 190: 329-352.

- Smit, J. (1990): Meteorite impact, extinctions and the Cretaceous-Tertiary boundary. *Geologie en Mijnbouw*, 69: 187-204.
- Smit, J., Alvarez, W., Montanari, A., Swinburne, N., Kempen, T. M. v., Klaver, G. T., Lustenhouwer, W. J. (1992): "Tektites" and microkrystites at the Cretaceous Tertiary boundary: Two strewnfields, one crater? *Proc. Lunar and Planetary Science conference*, 22: 87-100.
- Smit, J., Hertogen, J. (1980): An extraterrestrial event at the Cretaceous-Tertiary boundary. *Nature*, 285: 198-200.
- Smit, J., Klaver, G. (1981): Sanidine spherules at the Cretaceous-Tertiary boundary indicate a large impact event. *Nature*, 292: 47-49.
- Smit, J., Romein, A. J. T. (1985): A sequence of events across the Cretaceous-Tertiary boundary. *Earth and Planetary Science Letters*, 74: 155-170.
- Stoll, H. M., Schrag, D. P. (2000): High-resolution stable isotope records from the Upper Cretaceous rocks of Italy and Spain; glacial episodes in a greenhouse planet? *Geological Society of America Bulletin*, 112: 308-319.
- Veen, G. W. v. (1969): *Geological investigations in the region west of Caravaca, south-eastern Spain.* 143p. Amsterdam, University dissertation.
- Wolbach, W. S., Lewis, R. S., Anders, E. (1985): Cretaceous extinctions: evidence for wildfires and search for meteoritic material. *Science*, 230: 167-170.