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The Cretaceous–Tertiary (K/T) boundary transition at Coxquihui, state of Veracruz, Mexico: evidence for an early Danian impact event?

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Abstract

The Cretaceous–Tertiary (K/T) transition at Coxquihui, State of Veracruz, Mexico, differs from all other Mexican sections by the presence of two spherule-rich layers interbedded with pelagic marls, but lacking the characteristic siliciclastic deposit. A 1-cm-thick spherule layer is located at or near the K/T boundary and contains a small Ir enrichment of 0.2 ng/g (background values <0.1 ng/g). The precise stratigraphic position of this spherule layer with respect to the K/T boundary is uncertain due to a hiatus that spans from to the lower *Parvularugoglobigerina eugubina* Zone (Pla) to the upper part of the latest Maastrichtian *Plummerita hantkeninoides* Zone. A 20-cm-thick marl layer separates the first spherule layer from a 60-cm-thick second spherule layer, which is also within Zone Pla. An Ir enrichment of 0.5 ng/g is present in the overlying 10-cm-thick marl layer. The stratigraphic positions of these two spherule layers and Ir enrichments are strikingly similar to those found at two other localities, Beloc in Haiti and Caribe in Guatemala, and suggest the possibility of an early Danian impact event.

Keywords: Cretaceous–Tertiary boundary; Spherule-rich deposits; Early Danian impact event

1. Introduction

Glass spherules in Cretaceous–Tertiary (K/T) boundary sections around the Gulf of Mexico and the Caribbean are generally interpreted as impact-generated melt droplets of target rocks dispersed by the Chicxulub impact on Yucatan, Mexico. Spherule-rich deposits (SRDs) have been documented from numerous localities (Fig. 1), including Beloc, Haiti (Izett et al., 1990; Izett, 1991; Maurasse and Sen, 1991; Sigurdsson et al., 1991; Jéhanno et al., 1992; Leroux et al., 1995; Stinnesbeck et al., 2000; Keller et al., 2001), over 40 localities in northeastern and east central Mexico (Smit et al., 1992, 1996; Stinnesbeck et al., 1993, 2001; Smit, 1999; Keller et al., 1997, 2002a,b), Guatemala (Stinnesbeck et al., 1997; Fourcade et al., 1998, 1999; Keller and Stinnesbeck, 2000), Belize (Sigurdsson, 1998; Smit, 1999), Alabama (Pitakpaivan et al., 1994), Texas (Yancey, 1996), the Gulf of Mexico (Alvarez et al., 1992; Bralower et al., 1998) and the Western Atlantic (Olsson et al., 1997; Norris et al., 1999, 2000; Martínez-Ruiz et al., 2000). Many of these authors interpret the spherule layers as K/T boundary marker based on the yet unproved assumption that the Chicxulub impact event is of precisely K/T boundary age. Others have questioned this assumption, particularly when conventional biostratigraphic K/T boundary markers (e.g. extinction of tropical and subtropical planktic foraminifera, first appearance of Danian species) do not coincide with the spherule deposits. In this study we review the stratigraphy of the spherule layers and Ir anomaly within the context of recent new discoveries in three critical areas (Haiti, NE Mexico, Guatemala), and provide detailed biostratigraphic analysis of a section at Coxquihui in east central Mexico.

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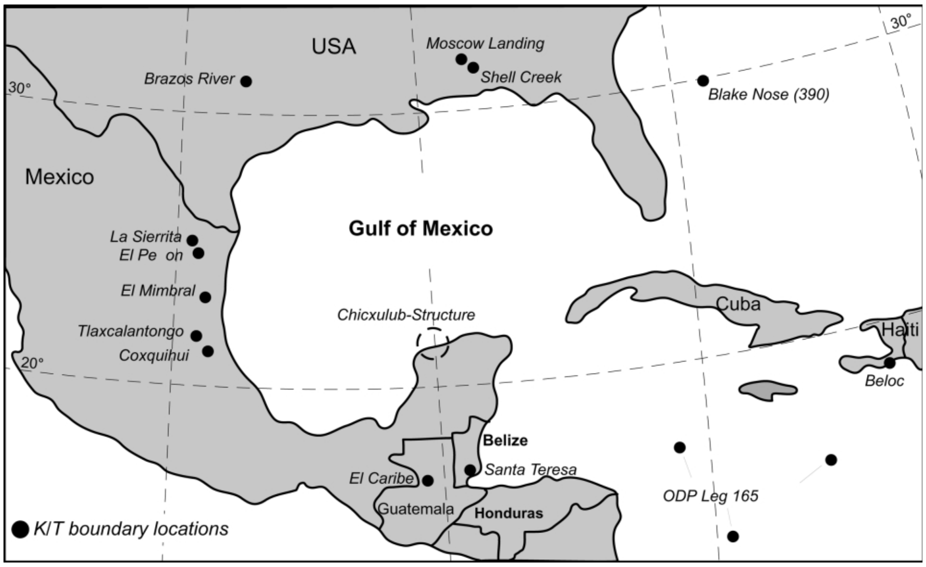

Fig. 1. Location map of K/T boundary sections with spherule-rich deposits (SRDs) around the Gulf of Mexico and the Caribbean.

2. Age of spherule deposits revisited

Recently, high-resolution biostratigraphic analyses of new sections in Haiti, Guatemala and northeastern and central Mexico revealed that multiple spherule layers are frequently present and that their stratigraphic positions are variable. For example, in sections at Beloc 3, Haiti, rare early Danian *Parvularugoglobigerina eugubina* Zone (Pla) assemblages are present in the lower part of the spherule layer along with reworked late Cretaceous species (Fig. 2).

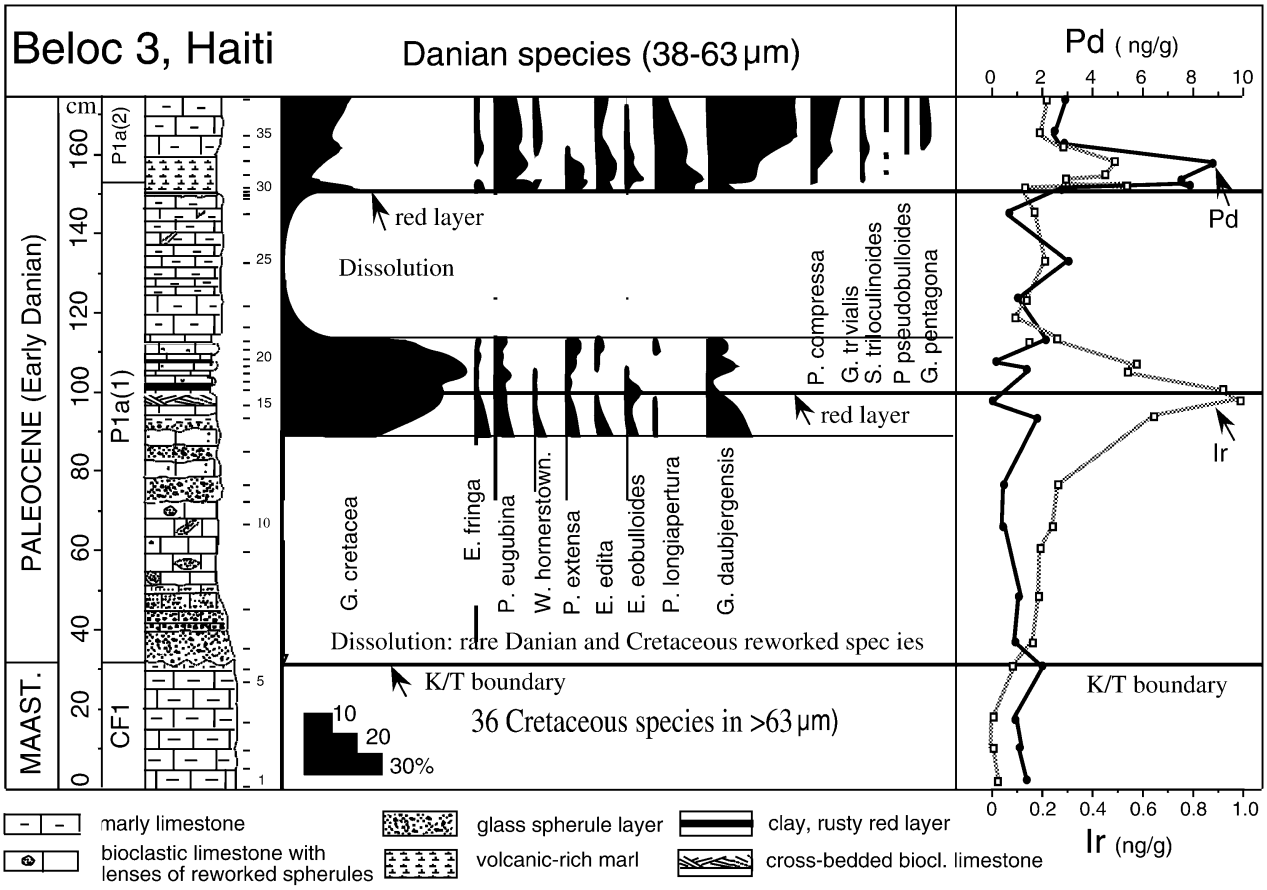

Fig. 2. Spherule deposits, Pd and Ir anomalies and relative abundances of planktic foraminifera in the early Danian at Beloc, Haiti. Note that the first abundant early Danian assemblage and Ir anomaly above the spherule deposit is stratigraphically coeval with that at Coxquihui in Fig. 6.

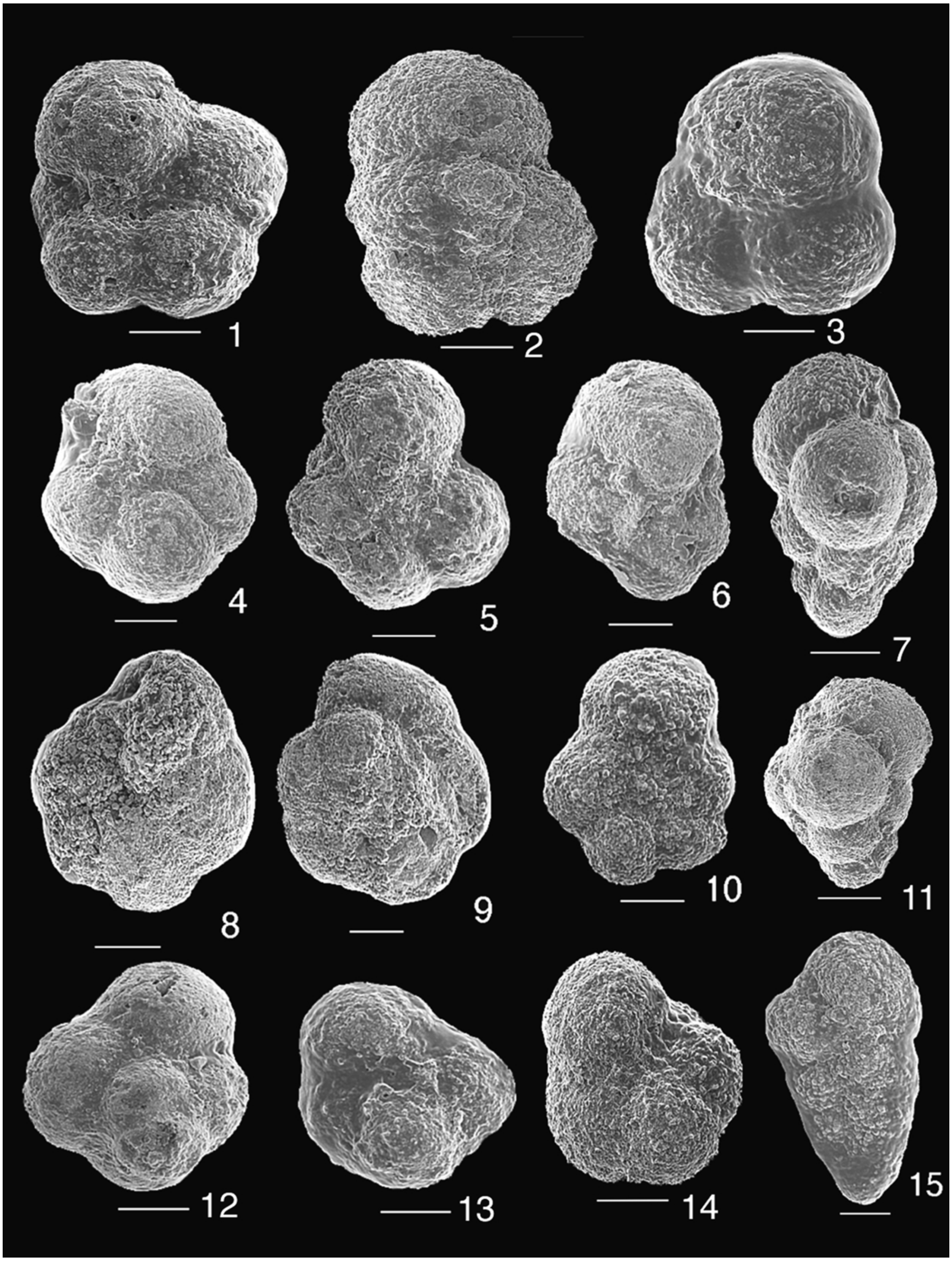

Plate 1. Tiny early Danian species from the lower *P. eugubina* Zone Pla(l) at Beloc, Haiti. Compare these small species with those shown for the same stratigraphic interval at Coxquihui in Plate 2. All specimens are within the 38–63 μm size fraction (scale bar = 20 μm) and were taken from the interval below the Ir and PGE anomalies (for details see Keller et al., 2001). (1) *Eoglobigerina edita*, (2, 3) *Eoglobigerina eobulloides*, (4, 5) *Eoglobigerina fringa*, (7, 11) *Guembelitria cretacea*, (8, 9) *Parvularugoglobigerina longiapertura*, (10) *P. eugubina*, (12, 13) *P. extensa* (= *G. conusa*), (14) *Globoconusa daubjergensis*, (15) *Woodringina hornerstownensis*.

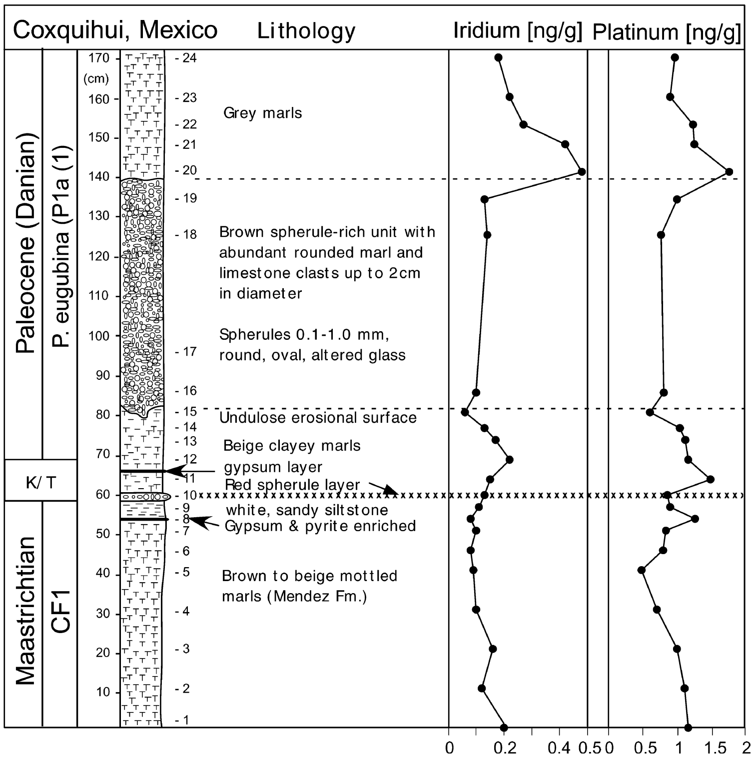

Fig. 3. Lithology, and distribution of iridium and platinum across the K/T transition at Coxquihui, State of Vera Cruz, Mexico.

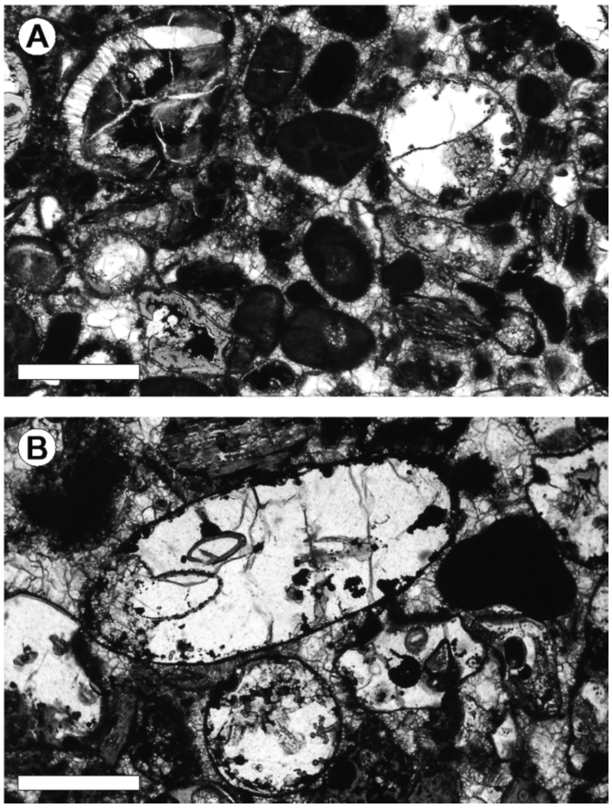

Fig. 4. (A and B) Microphotographs of thin sections showing characteristics of the early Danian (Zone Pla) spherule-rich deposit at Coxquihui. Note the abundance of rounded marl and carbonate clasts and shell fragments that suggest reworking. Terrigenous detritus is rare. Scale bar: 0.5 mm.

In the upper part of the spherule layer early Danian species are abundant, including *P. eugubina* and *P. longiapertura*, followed by an Ir anomaly above the spherule layer. The presence of the spherule layer in the early Danian zone Pla has been interpreted as likely reworked based on the presence of common Cretaceous species mixed with the early Danian assemblage (Fig. 2, Stinnesbeck et al., 2000; Keller et al., 2001). Previous studies of the Beloc sections failed to detect these early Danian species (shown in Plate 1), because they are within the small size fraction (38–63 μ) that is not generally examined in routine biostratigraphic analyses, and because less complete outcrops along the roadside were examined. Very small Danian species are commonly present in high-stress early Danian environments (e.g. Haiti, Guatemala, El Kef, Keller et al., 1995, 2001; Keller and Stinnesbeck, 2000), and their analysis permits more precise biostratigraphic dating and correlations with sections in Mexico and elsewhere. If these small-sized early Danian species are ignored, the stratigraphic placement of the K/T boundary may be erroneously placed based on the presence of spherules and overlying Ir anomaly.

The common assumption that any iridium enrichment at or near the K/T boundary is the result of the Chicxulub impact also deserves re-examination (Sawlowicz, 1993). For example, the early Danian (Pla) SRDs in Haiti underlie pelagic limestones that contain an Ir anomaly of chondritic type compatible with an impact event, but with a slight enrichment of Pt and Pd due to an overprint with the normal sedimentary PGE pattern (1.0 ng/g Ir, 2.1 ng/g Pt, 0.14 ng/g Rh and 2.51 ng/g Pd; Kramar et al., 2001; Stüben et al.,

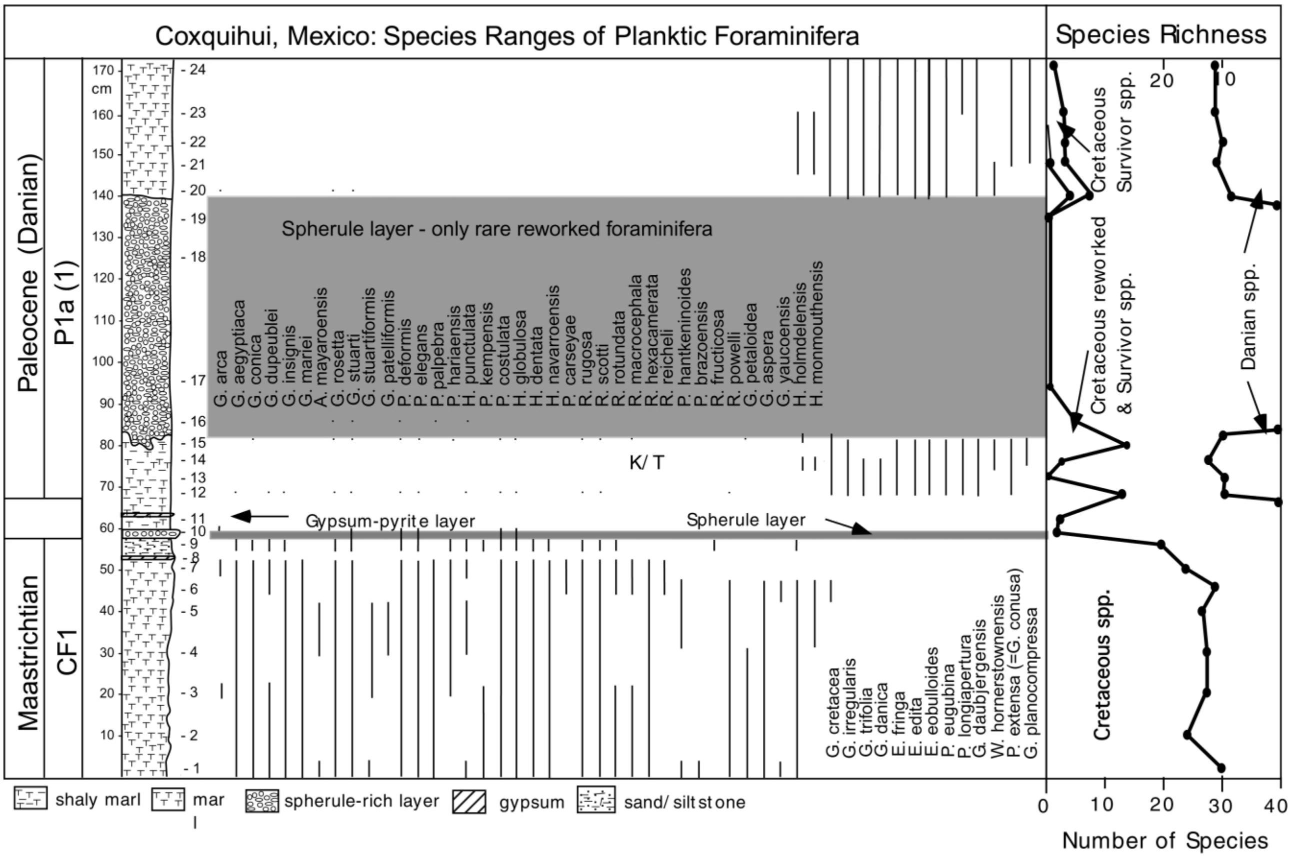

Fig. 5. Planktic foraminiferal species ranges and richness across the K/T boundary at Coxquihui, State of Veracruz, Mexico. Note that the thin spherule layer 1 is located at or close to the K/T boundary. Spherule layer 2 is within the lower part of the *P. eugubina* Zone, or Pla(l). The early Danian species are very small and can only be recovered in the 38–63 μm size fraction.

2002)(Fig. 2). The position of this Ir anomaly, however, is above the presumably reworked spherules in the early Danian Zone Pla. A K/T boundary age for this Ir anomaly can only be inferred, if the iridium is transported and redeposited in a characteristic anomaly pattern, a process that is difficult to explain by reworking (Sawlowicz, 1993). An alternate hypothesis is an early Danian source (impact or volcanism). In Guatemala (Caribe section) a similar pattern is observed. There, the spherule-rich deposit is also within the early Danian *P. eugubina* Zone, as indicated by abundant tiny early Danian planktic foraminifera, followed by a small (0.4 ng/g) iridium anomaly (Fourcade et al., 1998, 1999; Keller and Stinnesbeck, 2000).

In constrast, SRDs in northeastern Mexico are at the K/T boundary or in the latest Maastrichtian sediments below the boundary. These SRDs were originally discovered at the base of a prominent siliciclastic unit that separates late Maastrichtian and early Danian sediments and hence were interpreted as K/T boundary age by Smit et al. (1992), and pre-K/T boundary age by Stinnesbeck et al. (1993). The recent discovery of two to three additional spherule layers in the 10 m of late Maastrichtian marls below the siliciclastic unit in numerous sections in the La Sierrita and Peñón areas (Fig. 1) indicate a late Maasrichtian age for deposition of the lowermost spherule layer (Stinnesbeck et al., 2001; Keller et al., 2002a). Alternatively, based on small-scale slumps in one area Arz et al. (2001a,b) interpreted any additional spherule layers in late Maastrichtian sediments as the result of widespread margin collapse due to the Chicxulub impact. Although small slumps are present, they are isolated, intraformational and restricted to folding of the spherule layer (Keller et al., 2002b). In general, the spherule layers are interbedded with hemipelagic marls of the latest Maastrichtian *Plummerita hantkeninoides* Zone (CF1) which spans the last 300 ky of the Maastrichtian (Pardo et al., 1996). There is no evidence for significant reworking in these marls, or within the lowermost spherule layer, though reworked marl clasts are commonly present in the succeeding spherule layers (Keller et al., 2002a). These recent discoveries suggest that deposition of spherules around the Gulf of Mexico was not necessarily linked to the K/T boundary event.

The K/T boundary sections in east-central Mexico have not received much attention to date, although they are much closer to Chicxulub than the famous localities in the northeast. However, K/T boundary sections at Coxquihui, La Ceiba, and Tlaxcalantongo have been reported by various researchers (e.g. Smit et al., 1996; Cedillo-Pardo and Grajales-Nishimura, 1997; Lopez-Oliva et al., 1998; Smit, 1999; Arz et al., 2001a,b), who indicate spherule

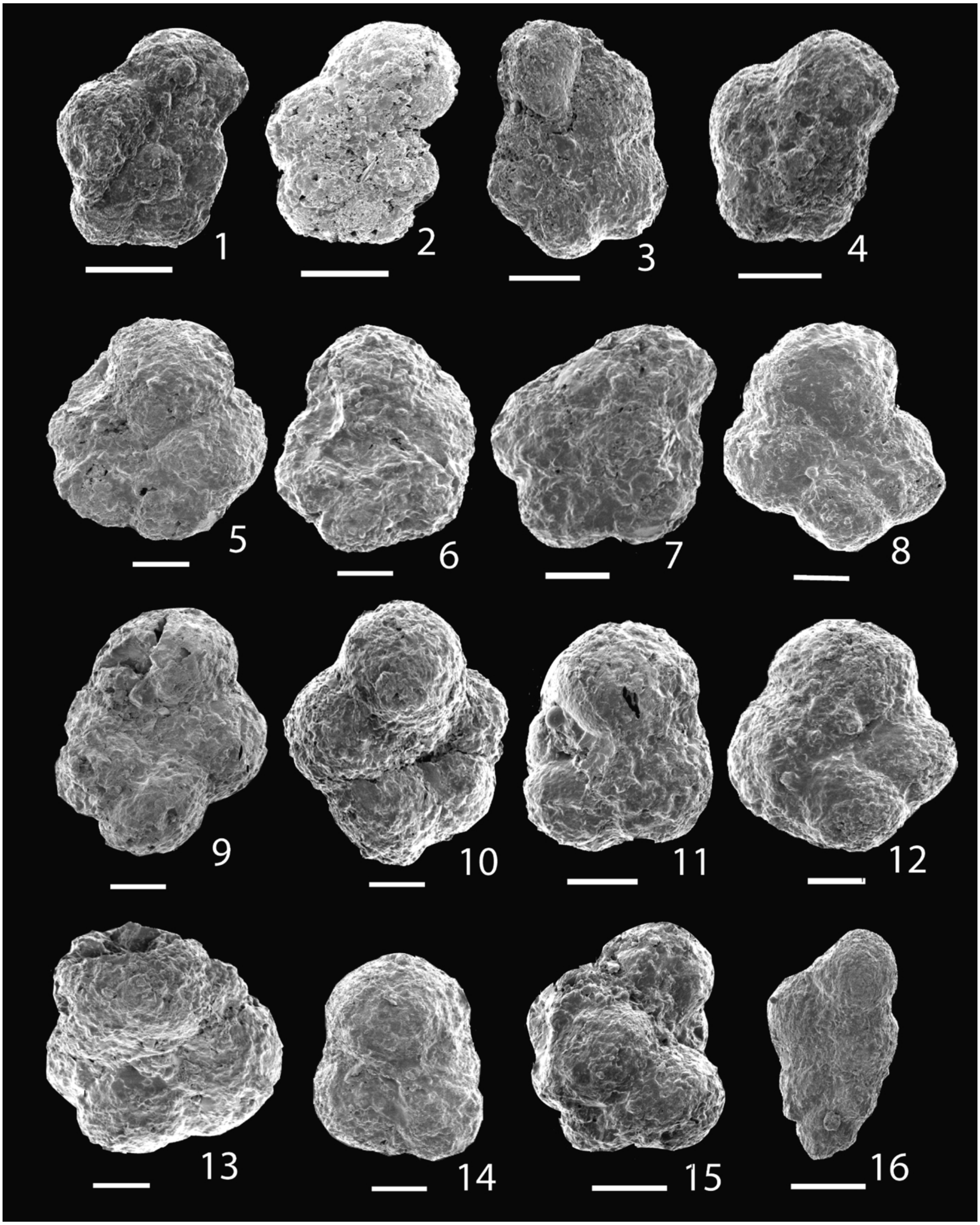

Plate 2. Tiny early Danian species from the lower *P. eugubina* Zone Pla(l) at Coxquihui, Mexico. All specimens are from the 20 cm thick interval between the 1 cm thin spherule layer 1 and 60 cm thick spherule layer 2. Note that Coxquihui and Beloc have the same tiny early Danian species associated with spherule layers within the early Danian *P. eugubina* Zone Pla(l). All specimens are from the 38–63 μm size fraction (scale bar = 20 μm). (1–3) *Parvularugoglobigerina longiapertura*, (4–8) *P. eugubina*, (9, 10) *Eoglobigerina edita*, (11) *Eoglobigerina eobulloides*, (12–14) *Globoconusa daubjergensis*, (15) *P. extensa* (= *G. conusa*), (16) *Woodringina hornerstownensis*.

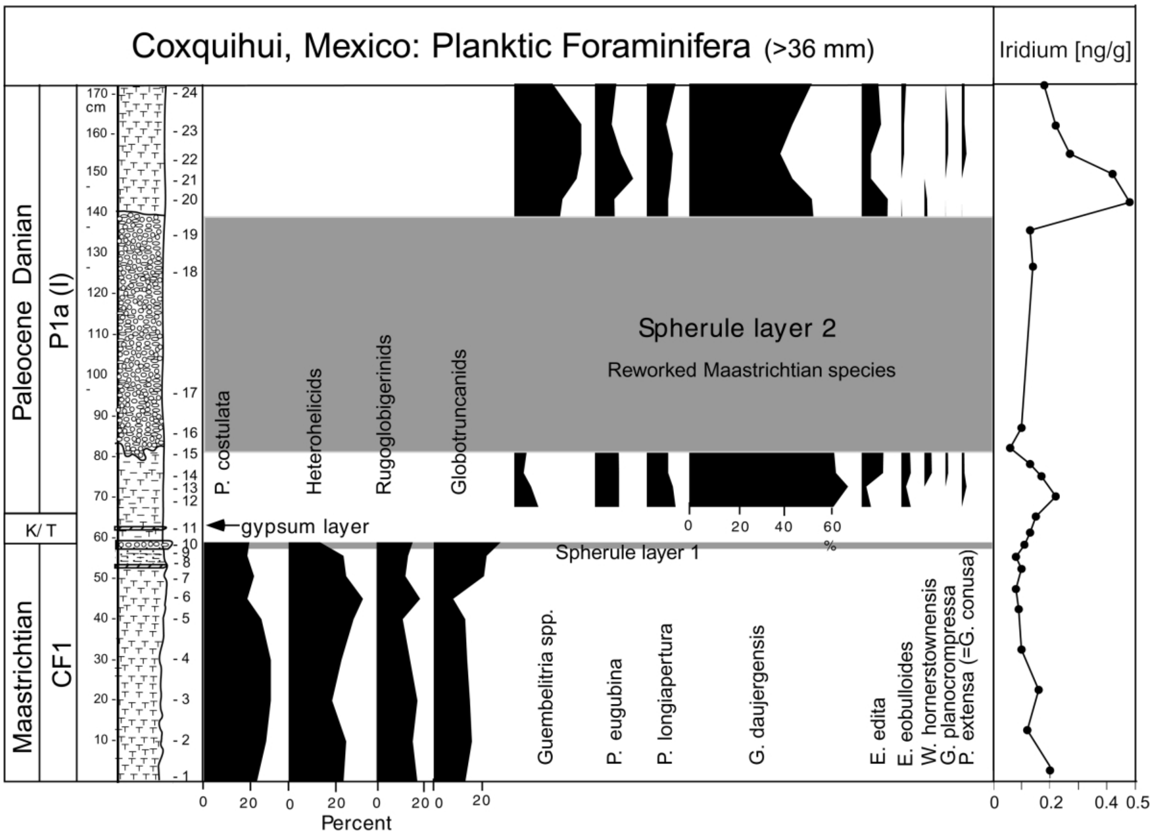

Fig. 6. Relative abundances of planktic foraminifera and Ir distribution across the K/T transition at Coxquihui. Note the high abundance of very small early Danian *P. eugubina* Zone Pla(l) assemblages below spherule layer 2, and the Ir anomaly in the marls above this spherule layer.

deposits of variable thickness at the K/T boundary. Our study of the Coxquihui section differs in some important aspects as presented here based on biostratigraphic, geochemical and pertrographic analyses.

3. Location and lithology

The village of Coxquihui is located in the State of Veracruz, Mexico, approximately 40 km west of Nautla, and can be reached by an unpaved road. The outcrop is located just east of the village along the road. A continuous sequence of approximately 2 m of marls and two intercalated spherule-rich layers are visible along the road and can be traced into the road surface where they are offset by a fault. Brown to beige clayey mottled marls of the Mendez Formation form the base of the section and reach a visible thickness of 50 cm (Fig. 3). A change to white sandy siltstone is observed in the uppermost 5 cm. A 1 cm thick red-colored layer with abundant altered spherules overlies the marls with a sharp and slightly undulose contact. The overlying 20 cm of beige clayey marls contain no spherules, though a gypsum layer is present 4 cm above the spherule layer. Above the marl layer is a 60 cm thick faintly layered spherule-rich brown-colored unit with an undulose and erosive contact at the base (Fig. 3). This spherule-rich unit contains abundant rounded marl and limestone clasts up to 2 cm in diameter. Terrigenous input (e.g. quartz, feldspar, mica) is minor. Grey marls overlie the spherule layer and reach a thickness of 40 cm (Fig. 3).

4. Petrology and origin of spherule layers

The SRDs at Coxquihui contain abundant light to dark brown altered shards of broken spherules and rare spherules in a matrix of spary calcite or micrite (Fig. 4A and B). The sediment texture is chaotic and no sedimentary structures were recognized, except for rough cross-bedding in the uppermost 20 cm. Spherule shards are highly irregular in outline and many of them are flaser-shaped and foamy. Spherules are mostly round and teardrop-shaped and range in diameter from 0.1 to approximately 1 mm. Some spherules are composite and contain bubbly internal structures. In addition, rounded marl and carbonate clasts and globules, shell fragments and foraminifera are frequently present, whereas terrigenous detritus (e.g. quartz, feldspar or mica) or volcanic input (e.g. feldspar, pyroxene) is rare to absent (Fig. 4A and B). In this aspect the Coxquihui section thus differs from other K/T boundary sections in the area (e.g. Tlaxcalantongo, La Ceiba) where a siliciclastic deposit is present.

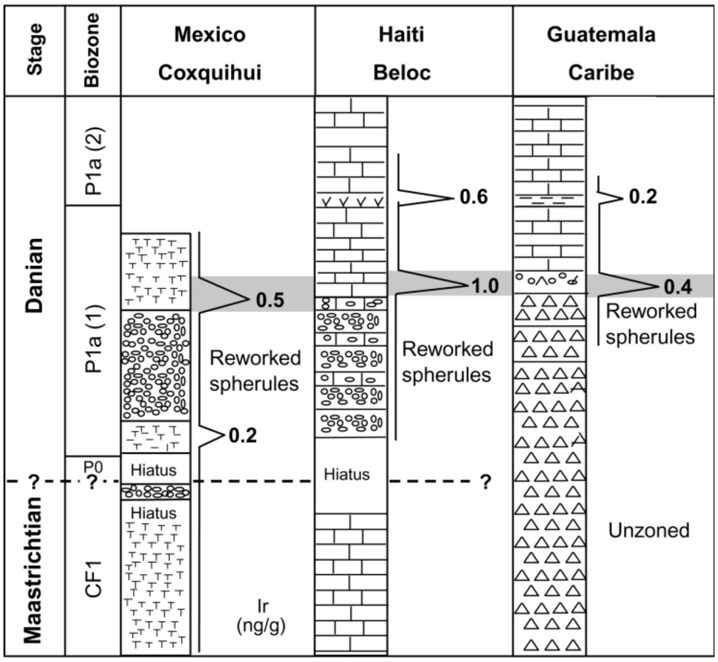

Fig. 7. Correlation of K/T boundary sections at Coxquihui, Haiti (Beloc) and Guatemala (Caribe). Note that at Caribe and Beloc the spherule-rich layers are in the early Danian Zone Pla(l), similar to the upper spherule layer at Coxquihui. All three sections contain small Ir anomalies in the Danian Zone Pla. At Coxquihui, the small Ir anomalies at the K/T boundary and Ir anomaly in Zone Pla are separated by pelagic marls. This suggests that in addition to the K/T boundary impact, a second Ir producing event occurred in Zone Pla.

Compositional changes exist between the base and top of the 60 cm-thick upper spherule layer. In the lower part of the unit, spherules are rare, poorly preserved and often fragmented. Abundant hollow individuals exist which are filled with blocky calcite. Spherules are often in-filled by radial fibrous spary cement. However, the overwhelming majority of constituents in the spherule layer are mm-sized flaser-like shards, which are mostly welded and show fluidal textures. In addition, rounded to subangular clasts of recrystallized limestone are frequent and reach diameters of 1 mm. In the upper part of the unit spherules are more abundant, well preserved though often fragmented into angular shards. Many well-rounded to teardrop-shaped carbonate globules show thin dark rims and inclusions of small opaque crystals (?rutile or hematite) and small micritic fragments.

Spherules and shards are similar in size, shape, texture and internal structures to those from Beloc, Haiti and northeastern Mexico, especially those from the La Sierrita area (Stinnesbeck et al., 2000, 2001). In these areas, spherules have been interpreted as impact-derived ejecta based on the glass geochemistry (Izett, 1991; Koeberl and Sigurdsson, 1992), oxygen isotope values (Blum and Chamberlain, 1992), Rb–Sr and Sm–Nd isotopic data (Blum et al., 1993), the presence of sulfate (Chaussidon et al., 1994) and very low water content (Koeberl, 1994). The data establish a strong link between spherules and the melt rock from the Chicxulub impact crater and suggest a common origin.

5. Platinum group elements

Twenty-four samples of spherule-rich sediments and marls were processed and analyzed for platinum group elements (PGEs) at the Institute for Mineralogy and Geochemistry of the University of Karlsruhe, in order to establish a possible relationship to the global K/T boundary Ir event (Fig. 5). A detailed description of the methods for PGE preconcentration and matrix elimination (by fire assay with nickel sulfide) is given in Kramar et al. (2001) and Stüben et al. (2002). Before the fire assay, samples were spiked with 500 μl of a solution containing about 16 ng of Ir and 33 ng Pt strongly enriched in the isotopes Ir^{191} and Pt^{198}, respectively. The analysis was carried out by isotope dilution mass spectrometry with a high resolution ICP/MS (AXIOM from VG Elemental, UK). Element contents were calculated from the isotope ratios Ir^{191}/Ir^{193} and Pt^{195}/Pt^{198} of the spiked and digested samples. Accuracy was checked by means of WPR-1 and SARM-7 standard reference materials. Detection limits are 0.05 ng/g Ir, and 0.4 ng/g Pt. Detection limits are mainly dependent on blanks of the NiS-fire assay.

A small Ir anomaly is centered at the base of the marls directly overlying the upper spherule layer, and tails upsection for approximately 15 cm (Fig. 3). The maximum Ir concentration of 0.5 ng/g correlates with the highest Pt content (1.7 ng/g), and with minor enrichments of Rh and Pd. These values, exceed the local background by approximately 0.4 ng/g for Ir and 0.9 ng/g for Pt and show a nearly chondritic Pt/Ir ratio. Subtracting the average background value (0.15 ng/g for Ir and 0.94 ng/g for Pt), an Ir_{excess}/Pt_{excess} ratio of 0.44 results, which is practically identical to the chondritic ratio of 0.45 and indicates a cosmic origin for the Ir anomaly. No significant PGE anomalies were detected within the spherule layers or the Maastrichtian marls. However, small but nevertheless significant increases in Ir (up to 0.22 ng/g) and Pt (up to 1.45 ng/g) are observed (in sample 12) within the 15 cm of marls just above the K/T boundary (Fig. 3). The nonchondritic Ir_{excess}/Pt_{excess} ratio of 0.15 implies that this enrichment is probably not linked to the K/T boundary event.

6. Biostratigraphy

6.1. Analyses of multiple size fractions

For planktic foraminiferal analysis, samples were processed based on standard techniques (Keller et al., 1995) and faunal assemblages were analyzed from the >63 and >150 μm size fractions for the late Maastrichtian, and also from the small 38–63 μm size fraction for the early Danian. Multiple-sized fraction analyses is necessary because late Cretaceous assemblages contain very large (>250 μm) tropical-subtropical species and abundant smaller sized (<150 μm) species. Moreover, recent investigations have shown that, in very high-stress environments, early Danian species are dwarfed (<63 μm) and therefore lost in routine biostratigraphic analysis of the larger size fraction (Keller et al., 2001).

Foraminifera are generally poorly preserved, recrystallized and difficult to wash free of adhering marls in Maastrichtian sediments of Coxquihui. Poor preservation makes it particularly difficult to analyze the small fragile, recrystallized early Danian species, and to obtain good scanning electron images for illustrations. However, because small foraminiferal species are not generally analyzed by other workers, leading to differing biostratigraphic interpretations, they are illustrated in Plate 2. The same tiny earliest Danian fauna has been observed from sections in Tunisia, Haiti, and elsewhere (Keller et al., 1995; 2001). For comparison, a similar earliest Danian Pla(l) assemblage from between two early Danian spherule layers at Beloc, Haiti, is illustrated in Plate 1. Although in both sections the foraminiferal tests are recrystallized, the early Danian morphologies of these species are easily recognized.

6.2. Biozonation

The basal 54 cm thick marl below the gypsum and pyrite enriched layer (sample 8) contains a typical late Maastrichtian low latitude Tethyan assemblage containing *P. hantkeninoides*, the index species for zone CF1 that spans the last 300 ky of the Maastrichtian (Fig. 5). However, the number of species in this interval is unusually low with a maximum of 30 species in any given sample, possibly as a result of poor preservation. A further decrease in species richness to 20 species is observed in the overlying 5 cm thick white sandy siltstone. Only very rare red-stained foramniferal species are present in the thin red spherule layer and the gypsum-enriched marl above it (sample 11).

The first early Danian species appear in the small size fraction (38–63 μm) in the 15 cm above the thin red spherule layer (samples 12–14, Fig. 5). This interval contains abundant *Globoconusa daubjergensis* and common *P. eugubina*, *P. longiapertura* as well as *Eoglobigerina edita*, *E. eobulloides*, *W. hornerstownensis*, *P. extensa* and *G. planolcompressa* (Figs. 5 and 6). This assemblage is characteristic of the lower part of the early Danian *P. eugubina* Zone, or Zone Pla(l) (Keller et al., 1995). The index species of the upper part of the *P. euguina* Zone, *Parasubbotina pseudobulloides* and *Subbotina triloculinoides*, are absent. The same low diversity early Danian Pla(l) assemblage is present in the marls above spherule layer 2 (Fig. 5). Reworked planktic foraminifera are present in the early Danian marl below the spherule layer 2, and rare reworked specimens are also observed within and above it (Fig. 5).

6.3. How complete is the K/T boundary transition?

Planktic foraminifera thus indicate that the K/T boundary is within the 10 cm interval encompassed by the thin red spherule layer and overlying 8 cm thick marl and thin gypsum layer. However, lithological and faunal assemblage changes suggest that there is a short hiatus at or just below the K/T boundary. For example, an undulating erosional surface separates the thin spherule layer 1 from the underlying sandy siltstone, suggesting that part of the latest Maastrichtian Zone CF1 may be missing. It also suggests the possibility that the thin spherule layer may have been reworked from an earlier deposit and redeposited. A K/T hiatus is also suggested by the absence of a clay layer and Ir anomaly.

However, there is little of the early Danian missing, as suggested by the presence of the lower part of the *P. eugubina* Zone Pla(l). The interval missing includes Zone P0 (or *G. cretacea* zone), which is generally characterized by abundant (~80%) *G. cretacea*, but missing at Coxquihui, and the evolutionary first appearances of Danian species in the lower part of *P. eugubina* Zone Pla(l) prior to the development of thriving populations of *P. eugubina* and *P. longiapertura*. A hiatus near the P0/Pla boundary has been observed in K/T sections worldwide (MacLeod and Keller, 1991a,b; Keller and Stinnesbeck, 1996).

The 60 cm thick spherule layer 2, which overlies an undulating erosional surface 20 cm above the K/T hiatus, suggests that these spherules may be reworked from an earlier Maastrichtian deposit. The presence of Maastichtian reworked sediments is indicated common break-resistant and abraded globotruncanids. These reworked specimens are mostly found at the base (sample 15) and top (sample 20) of the spherule deposit. There are no early Danian in situ species within the spherule deposit, which suggests rapid deposition. Above the spherule layer, the early Danian faunal assemblages are very much similar to the ones below, except that *Guembelitria* are more abundant (35%, Fig. 6). The similarity of these assemblages, and absence of Danian fauna within the spherule layer, are strong indications that redeposition of the spherule layer 2 occurred over a very short time period in the lower part of the early Danian *P. eugubina* Pla(l) Zone, or sometime within the first 100 ky of the Tertiary. However, since the spherule deposit rests on an undulating erosional surface, it is possible that some erosion of the underlying early Danian sediments occurred prior to deposition of spherule layer 2.

Our biostratigraphy of the Coxquihui section significantly differs from that recently published by Arz et al. (2001a), who noted one thick spherule layer directly overlying Maastrichtian sediments, with the first Danian species above it. They thus interpreted the spherule layer as of K/T age. The difference between our studies is due to two major factors. Firstly, they analyzed the >63 μm size fraction and missed the earliest Danian high-stress assemblages in the smaller 38–63 μm size fraction, leading to erroneous placement of the K/T boundary. Secondly, the section that they collected at Coxquihui appears to be less complete than ours, and missing the 1 cm thick red spherule layer followed by the 20 cm thick marl that contains the earliest Danian assemblages below the thick spherule layer. Topographic variability in the outcrops should be expected as a result of variable erosion, as indicated by the undulating erosional surface, particularly below the thick spherule layer 2 reported by Arz et al. (2001a).

7. Discussion

Recent re-examination of the spherule deposits in the Beloc sections of Haiti revealed that there are two or more spherule layers deposited at and above the K/T boundary (Fig. 7, Stinnesbeck et al., 2000; Keller et al., 2001). In these studies we concluded that the Haiti spherule layers are likely secondary deposits based on the presence of reworked clasts and foraminifera. These findings are at odds with previous research that considered the spherule layers as of precisely K/T boundary age. An Ir anomaly (1 ng/g) of roughly chondritic type is present in pelagic limestones directly overlying the SRDs (Fig. 7). At Caribe in Guatemala, an altered spherule layer with an Ir anomaly of 0.4 ng/g have been detected by Stinnesbeck et al. (1997) and Fourcade et al. (1998, 1999) in the top 10 cm of a limeclast breccia (Fig. 7). The breccia matrix contains small planktic foraminifera (*P. eugubina* and/or *E. fringa*). This suggests that the Caribe spherules and Ir anomaly were deposited in the early Danian Zone Pla similar to those at Haiti (Keller and Stinnesbeck, 2000).

Several features of the Coxquihui section show striking similarities in the stratigraphic position of the spherule layers and PGE anomaly, to the sections at Beloc and Caribe (Fig. 7). For example, at both Beloc and Coxquihui, the lowermost spherule layer rests on an undulating erosional surface that marks a hiatus at the K/T boundary. At Caribe, age control within the breccia is insufficient to place the K/T boundary precisely, but the presence of *P. eugubina* at the top of the breccia marks this as early Danian Zone Pla. In addition, in all three localities spherule layers are present in the early Danian *P. eugubina* Zone, and more specifically within the lower part, Pla(l) of this zone. The early Danian faunal assemblages in these localities are very similar, suggesting the same stratigraphic intervals (see Plates 1 and 2). In all three localities, a PGE anomaly was detected in zone Pla(l) directly overlying the Pla spherule layer. At Beloc and Coxquihui, this anomaly is clearly Ir dominated (only minor Pd, Pt, Rh), and PGE distributions are similar to patterns described for extraterrestrial origins (Ganapathy, 1980). No PGE data other than Ir are available for the Caribe section.

Although the presence of reworked Cretaceous foraminifera and other transported debris within the SRDs suggest reworking and redeposition, it remains unclear whether the PGE anomaly can be explained by reworking and transport. The postdepositional behavior of Ir and other PGE in sediments is still little understood (Sawlowicz, 1993). On the other hand, both the Coxquihui and Beloc PGE anomalies are distinctly peaked, rather than showing the diffuse enrichments that would be expected from reworking and transport. In addition, these PGE anomalies occur in marls or marly limestones that overlie the spherule-rich layers, and which show no indication of mechanical reworking from an anomaly deposited at the K/T boundary. It is difficult to invoke reworking as sole agent to explain the distinct peaked distributions of Ir and other PGE elements at about the same biostratigraphic time interval in three different countries. It thus remains a good possibility that the Ir anomalies represent a collision event in the early Danian that is independent from the impact at the K/T boundary. This scenario is supported at Coxquihui and Beloc, Haiti, by the clear stratigraphical separation of the early Danian Ir anomaly and the K/T boundary.

The stratigraphic similarities of SRDs in early Danian sediments at Coxquihui, Beloc and Caribe reveal deposition occurred at about the same time in all three localities. These similarities can be explained by several scenarios.

(1) The spherule layers at Coxquihui and Beloc represent the Chicxulub impact-generated fallout and hence mark the K/T boundary event. This is the favored scenario by most researchers and is consistent with the currently favored interpretation for all spherule deposits. The major problem with this interpretation is that it is inconsistent with stratigraphic data. At Coxquihui and Beloc, spherule deposition occurred within the early Danian *P. eugubina* Zone (Pla(l)), whereas in northeastern Mexico the earliest

spherule deposition occurred in the late Maastrichtian Zone CF1 (Keller et al., 2002a).

(2) Both early Danian spherule layers are reworked from a still older original spherule deposit in the latest Maastrichtian. This scenario is plausible in that it accounts for the above noted discrepancies in stratigraphic data. In this scenario, the original spherule deposition occurred about 200–300 ky before to the K/T boundary as indicated by the recent discovery of multiple spherule layers in northeastern Mexico (Stinnesbeck et al., 2001; Keller et al., 2002a,b). Stratigraphically higher spherule layers within the late Maastrichtian in northeastern Mexico and within the early Danian in Haiti, Guatemala and Coxquihui are interpreted as reworked. Studies detailing the geographic distribution of K/T and early Danian hiatuses (Macleod and Keller, 1991a,b; Keller and Stinnesbeck, 1996) indicate widespread erosion that could have redistributed K/T boundary and older (spherule-rich?) sediments. There is ample lithological and faunal evidence for erosion and redeposition in all spherule-bearing sections (e.g. erosional surfaces, clasts, reworked Cretaceous foraminifer which are often discolored and abraded).

(3) Multiple impact events across the K/T transition. This is likely the most radical scenario, though plausible. It is well-known that major Earth-crossing asteroid impacts tend to come in multiples (Hut et al., 1987; Bailey et al., 1994; Napier, 2001). If the oldest spherule layer predates the K/T boundary, as suggested by recent discoveries, then there is a second impact at the K/T boundary, marked by the widespread Ir anomaly and clay altered spherules that are distinctly different from the glass spherules of the Caribbean and Central America. In addition, the Ir anomaly in Zone Pla(l) may represent a third impact as suggested in this study.

8. Summary and conclusions

Spherule deposition in the Caribbean and Gulf of Mexico is widely considered to be a single event that originated with the K/T boundary impact at Chicxulub. However, our investigation of the Coxquihui section reveals the presence of two spherule layers at or near the K/T boundary and in the lower part of the early Danian *P. eugubina* Zone. Iridium is slightly enriched in the 10 cm thick marls that corresponds to the K/T boundary interval, and tails to background levels at the base of spherule layer 2 (Fig. 3). This minor Ir enrichment may represent mechanical reworking from the K/T boundary Ir anomaly, though the nonchondritic Ir/Pt ratio does not permit a clear link to the K–T boundary event. The second Ir anomaly of 0.5 ng/g immediately above spherule layer 2 contains only minor amounts of Pt, Pd, and Rh and hence the PGE distribution is similar to patterns described for extraterrestrial origins. The stratigraphic position of the two spherule layers and Ir anomalies at Coxquihui is similar to those observed at Beloc, Haiti, and Caribe, Guatemala. These data together with recent discoveries of multiple spherule layers in late Maastrichtian sediments of northeastern Mexico (Stinnesbeck et al., 2001; Keller et al., 2002a), indicate that spherule deposition and Ir anomalies are not restricted to the K/T boundary. Current evidence suggests that Central America may have suffered not only a major extraterrestrial impact at the K/T boundary, but also impacts during the last 200–300 ky of the Maasrichtian and possibly in the early Danian Zone Pla(l), approximately 100 ky after the K–T boundary.

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