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Earth-Science Reviews 1283 (2002) 1–37
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Multiple impacts across the Cretaceous–Tertiary boundary

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Received 5 August 2002; accepted 3 December 2002

Abstract

The stratigraphy and age of altered impact glass (microtektites, microkrystites) ejecta layers from the Chicxulub crater are documented in Late Maastrichtian and Early Danian sediments in Mexico, Guatemala, Belize and Haiti. In northeastern Mexico, two to four ejecta layers are present in zone CF1, which spans the last 300 ky of the Maastrichtian. The oldest ejecta layer is dated at 65.27 ± 0.03 Ma based on sediment accumulation rates and extrapolated magnetostratigraphy. All younger ejecta layers from the Maastrichtian and Early Danian *Parvularugoglobigerina eugubina* zone Pla(l) may represent repeated episodes of reworking of the oldest layer at times of sea level changes and tectonic activity. The K/T boundary impact event (65.0 Ma) is not well represented in this area due to widespread erosion. An Early Danian Pla(l) Ir anomaly is present in five localities (Bochil, Actela, Coxquihui, Trinitaria and Haiti) and is tentatively identified as a third impact event at about 64.9 Ma. A multiimpact scenario is most consistent with the impact ejecta evidence. The first impact is associated with major Deccan volcanism and likely contributed to the rapid global warming of 3–4 °C in intermediate waters between 65.4 and 65.2 Ma, decrease in primary productivity and onset of terminal decline in planktic foraminiferal populations. The K/T boundary impact marks a major drop in primary productivity and the extinction of all tropical and subtropical species. The Early Danian impact may have contributed to the delayed recovery in productivity and evolutionary diversity.

Keywords: Multiple impacts; Maastrichtian–Danian; Microtektites; Microkrystites; Ir; PGE anomalies

1. Introduction

The Chicxulub structure in Yucatan, Mexico, is generally considered the K/T boundary impact that caused one of the major mass extinctions in the Earth's history (Hildebrand et al., 1991). Impact ejecta layers have now been widely recognized in numerous localities around the Gulf of Mexico (see review by Smit, 1999) and linked to the Chicxulub impact based on their geographic distribution, $^{39}Ar/^{40}Ar$ ages close to the K/T boundary (Sigurdsson et al., 1991; Swisher et al., 1992; Dalrymple et al., 1993) and chemical similarity to Chicxulub melt rock (Izett et al., 1991; Blum et al., 1993; Koeberl et al., 1994; Chaussidon et al., 1996). Controversies persist with respect to the stratigraphic position of the ejecta layer at or near the K/T boundary, and the nature and tempo of emplacement, whether by tsunami (Smit et al., 1996) or

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0012-8252/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
doi:10.1016/S0012-8252(02)00162-9

gravity flows and sea level changes (Adatte et al., 1996; Bohor, 1996; Stinnesbeck et al., 1996; Keller et al., 1997), and the presence of multiple altered impact glass spherule layers in the Late Maastrichtian and Early Danian (Keller et al., 2001, 2002a,b; Soria et al., 2001). A better understanding of these events may reconcile the two divergent K/T mass extinction hypotheses. The impact–extinction hypothesis calls for sudden mass extinctions due to a single large impact (Alvarez et al., 1980) now considered to be the Chicxulub structure. Paleontologists have long argued that the fossil record does not support a single cause for the mass extinction and, therefore, proposed multievent scenarios that include major volcanism, rapid climate and sea level changes (Archibald, 1996; Keller, 1996; MacLeod et al., 1997) and one or more impacts (Keller et al., 1997, 2002a; Keller, 2001).

These controversies have remained unsolved, in part, because most impact-related investigations have been geographically limited to a narrow region surrounding Chicxulub, and temporally limited to an interval spanning the K/T boundary clay, the ejecta layer and a few samples above and below. No significant effort has been made to examine older or younger sediments for additional impact ejecta or other environmental signals. The wider context of the mass extinction event, including the half million years before and after the K/T boundary, is well studied based on fossil assemblages, climate and sea level changes, all of which show major changes preceding the K/T boundary (see review in Keller, 2001). Only recently have investigations of impact ejecta in Haiti and Mexico included the upper part of the Late Maastrichtian and Early Danian and revealed the presence of multiple impact ejecta layers (microtektites and microkrystites) in both Late Maastrichtian and Early Danian sediments, as well as Ir and Platinum group elements (PGE) anomalies in the Early Danian (Keller et al., 2001, 2002a; Stinnesbeck et al., 2001, 2002; Odin et al., 2001; Stüben et al., 2002).

In this paper, we review the stratigraphy and biochronology of the K/T boundary ejecta deposits and provide new evidence of multiple ejecta deposits from sections in central and southern Mexico, southern Belize and eastern Guatemala (Fig. 1). The first part introduces the biostratigraphic scheme of the K/T

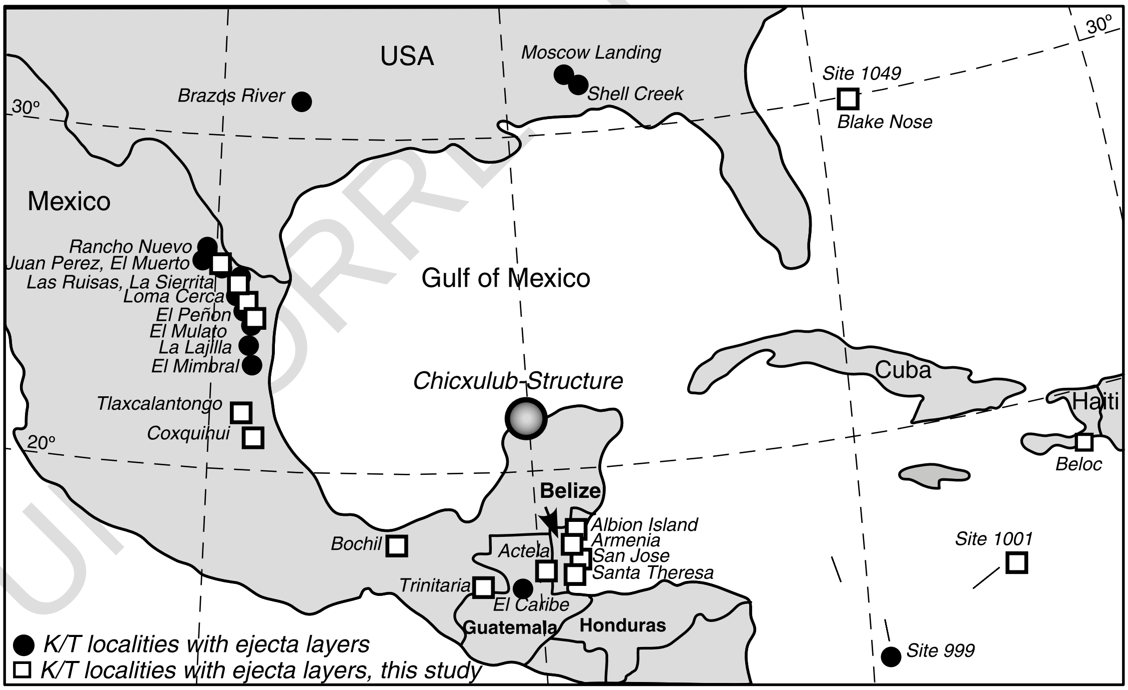

Fig. 1. Localities with Cretaceous–Tertiary boundary sequences that contain vesicular altered impact glass spherules (microtektites and microkrystites). Squares mark localites discussed in text.

boundary, the globally recognized boundary markers and the age and biozonation control of the Late Maastrichtian and Early Danian based on which the age and continuity of the sedimentary record is evaluated. In the second part, we review and document the stratigraphy and age of thick microtektite and microkrystite ejecta deposits from Mexico, Guatemala, Belize, Haiti and deep-sea sites, and provide new mineralogical (Cheto smectite) analyses that suggest a common glass origin. Finally, we provide a regional synthesis of the age of spherule deposition in Central America and the Caribbean and propose a multievent scenario for the K/T transition that is consistent with current impact, climate and fossil data.

1.1. Methods

Field sections were examined, measured and sampled based on standard methodologies. Biostratigraphic analysis was based on planktic foraminifera processed following the standard method of Keller et al. (1995). The smaller (36–63 μm) size fraction was examined for the first occurrence of tiny Early Danian species. Individual clasts from breccias, conglomerates and spherule layers were processed separately and analyzed for planktic foraminifera in order to determine the biostratigraphic ages of these sediments prior to erosion and redeposition.

Clay mineral analyses were conducted at the University of Neuchatel, Switzerland, based on XRD (SCINTAG XRD 2000 Diffractometer, Geological Institute) and ESEM (Phillips environmental microprobe equipped with EDEX analyzer, Institute of Microtechnique) following the procedures outlined by Kübler (1987) and Adatte et al. (1996). Platinum group elements (PGE) were analyzed at the Institute for Mineralogy and Geochemistry, University of Karlsruhe, by isotope dilution HR-ICP-MS after preconcentration and matrix reduction by Ni-fire assay (Kramar et al., 2001; Stüben et al., 2002).

2. Stratigraphy of the K/T boundary transition

2.1. Continuous K/T records

Our understanding of the Cretaceous–Tertiary boundary events largely depends on two critical factors: (1) the quality and continuity of the stratigraphic record that holds evidence for impacts, mass extinctions, climate and sea level changes, and (2) the age resolution that can be achieved for these events based on biostratigraphy, cyclostratigraphy and magnetostratigraphy. To evaluate the temporal distribution of impact ejecta, it is essential to understand the stratigraphy of the K/T boundary transition in areas of high sedimentation and unencumbered by impact ejecta beyond fine scale fallout (e.g. iridium, Ni-rich spinels).

There are numerous K/T boundary sections worldwide and the boundary horizon can easily be identified in both outcrops and drill cores as a sharp lithological break, but the continuity of the stratigraphic record is variable and depends on the paleoenvironment and depth of sediment deposition. In shallow water sequences (< 150 m), sedimentation is often interrupted by erosion or nondeposition due to global cooling, intensified current activity and sea level changes or tectonic activity. The K/T boundary is, therefore, usually marked by a disconformity with a greater interval missing than in continental margin settings (e.g. Brazos, Texas (Keller, 1989; Yancey, 1996; Heymann et al., 1998), Stevns Klint, Denmark (Schmitz et al., 1992), Qreiya, Egypt, and Seldja, Tunisia (Keller et al., 1998, 2002c). Redeposition of eroded sediments tends to occur in shallow basins and incised valleys which may preserve impact evidence.

Deep-water open ocean pelagic sequences (>600 m) also tend to be incomplete or condensed. This is largely due to low productivity, extremely low sedimentation rates, increasing dissolution with depth (lysocline and calcium carbonate compensation depth) and erosion or nondeposition due to intensified currents during global cooling. Erosion associated with global cooling periods at 65.5 Ma, during the last 100 ky of the Maastrichtian and during the Early Danian, is commonly identified in both shallow and deep-water sections by bioturbated erosional surfaces and major faunal breaks (MacLeod and Keller, 1991a,b; Kucera and Malmgren, 1998; Li and Keller, 1998a,b; Abramovich et al., 2003; Stinnesbeck et al., 1997). The K/T boundary is generally marked by a sharp bioturbated bedding surface, disconformity, a condensed thin clay layer and Ir anomaly.

The most complete sequences with the highest rates of sedimentation occur in continental margin settings spanning outer shelf to upper slope environments. The circum-Mediterranean Tethys has yielded the most complete K/T sequences to date (Tunisia, Egypt, Spain, Italy and Bulgaria, Groot et al., 1989; Pardo et al., 1996; Keller et al., 1995, 2002d; Luciani, 1997, 2002, Adatte et al., 2002). These pelagic to hemipelagic facies are deposited in high productivity and upwelling zones of the outer shelf to the upper slope (200–600 m) with often-cyclic sedimentation (Herbert and D'Hondt, 1990; Kate and Sprenger, 1993). The K/T boundary is easily identified in the field by a thick, dark, organic-rich clay layer with a millimeter thin red layer at the base that contains the Ir anomaly. These Tethyan sequences provide the best age resolution and fingerprint the order of events during the K/T transition. In Central America, the thickest impact ejecta deposits are found in continental margin settings at depths of about 500 m (e.g. Mexico, Haiti, Guatemala; Smit, 1999; Stinnesbeck et al., 1996; Keller et al., 1997, 2001).

2.2. K/T boundary criteria

There is an internationally accepted set of criteria that defines the K/T boundary worldwide with the official K/T boundary Global Stratotype Section and Point (GSSP) accepted by the International Commission on Stratigraphy (ICS) at El Kef, Tunisia (Cowie et al., 1989; Keller et al., 1995; Remane et al., 1999). The El Kef section was chosen for its continuous and expanded sedimentary record, excellent preservation of microfossils, geochemical and mineralogical marker horizons, absence of disconformities, hard grounds or any other breaks in sedimentation across the K/T boundary. The El Kef stratotype and co-stratotype at Elles 75 km to the east (Remane et al., 1999; Keller et al., 1995, 2002d) remain the most expanded and complete K/T sections and the standard against which the completeness of faunal and sedimentary records are judged worldwide.

At El Kef and Elles, the Upper Maastrichtian consists of monotonous gray marls marked by the mass extinction of all tropical and subtropical species by the end of the Maastrichtian. The K/T boundary is marked by a 2-mm-thick red layer enriched in iridium, nickel-rich spinels (Robin et al., 1991), and clay spherules interpreted as altered microkrystites (Smit and Romein, 1985). Above the red layer is a 50-cm-thick dark

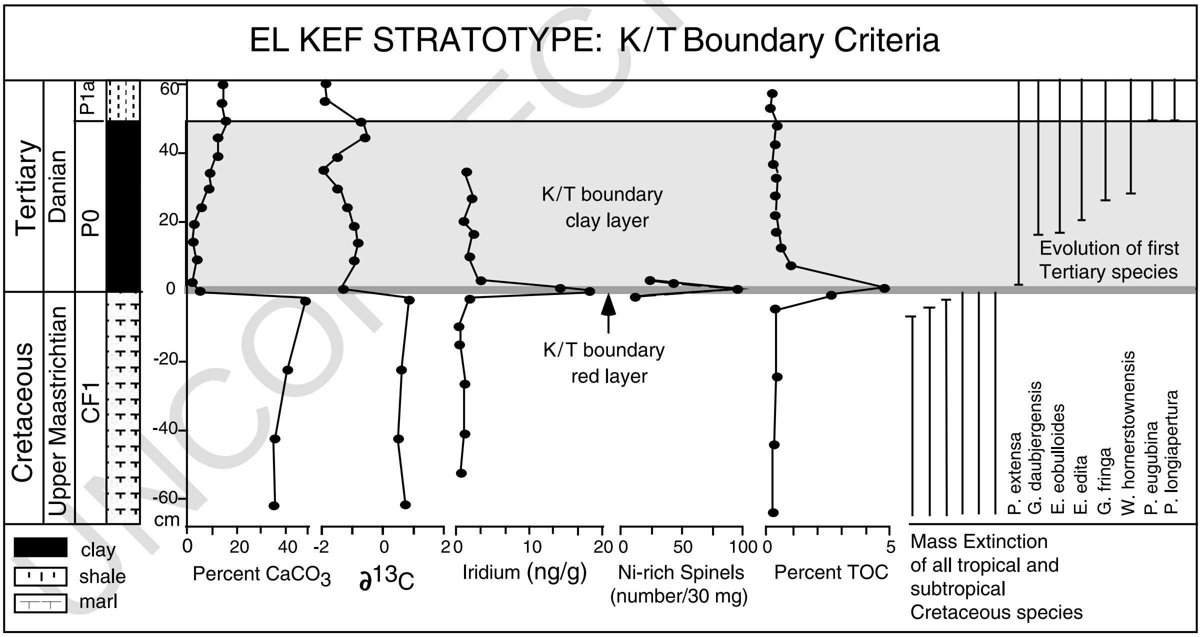

Fig. 2. K/T boundary defining criteria based on the El Kef stratotype. The K/T boundary is defined by unique biomarkers—the extinction of tropical and subtropical species and the first occurrence of Tertiary species. Lithological changes (boundary clay, red layer), geochemical signals (drop in $\delta^{13}C$, high TOC, low $CaCO_3$), iridium and Ni-rich spinels are additional markers for identifying the boundary, but by themselves do not define it.

organic-rich but carbonate-poor clay with a 2–3‰ δ^{13}C negative shift that marks the crash in plankton productivity (Keller and Lindinger, 1989). It is tempting to define the K/T boundary by the thin red layer, widely considered the K/T impact ejecta (Smit, 1999). But thin red layers are not unique and are usually present at the base of clay layers, whereas biomarkers are unique events. The clay layer is rich in first appearances of very tiny (36–63 μm) Early Danian planktic foraminifera including the sequential evolution of the first eight Tertiary species beginning immediately above the red layer (Fig. 2, Keller et al., 1995). The ICS commission placed the K/T boundary at the base of the clay and red layer, as defined by the mass extinction below and the first appearance of the first Tertiary species above (Fig. 2). All other criteria (e.g. clay layer, red layer, Ir anomaly, Ni-rich spinels, peak in total organic matter, δ^{13}C shift and clay spherules) can be used as additional boundary markers, but are not part of the K/T boundary definition.

2.3. K/T boundary biomarkers

Planktic foraminifera provide excellent biomarkers because they suffered the most severe mass extinction across the K/T transition with all tropical and subtropical species extinct by K/T boundary time, followed by the rapid evolution and diversification of new species in the Early Danian (Keller et al., 1995). Biomarkers are based on the first and last appearances of species that have been shown to be synchronous over wide geographic areas. Most evolving Early

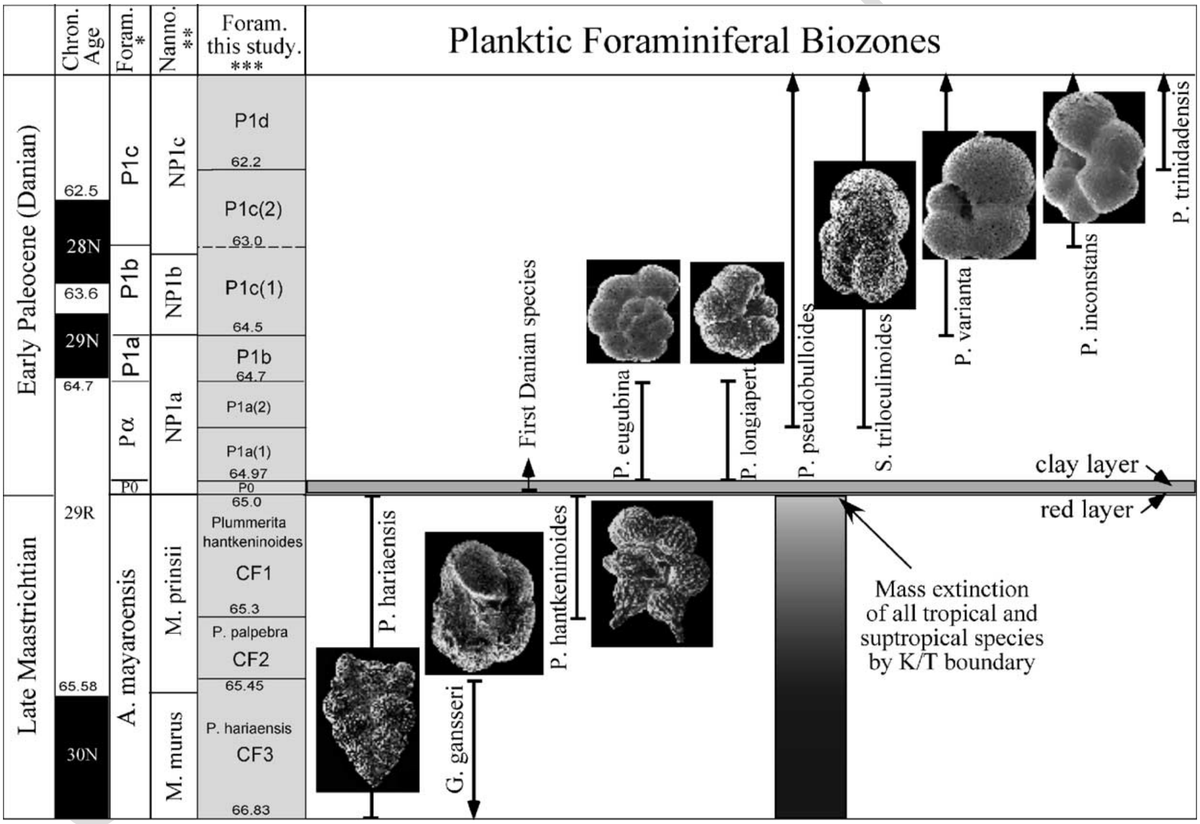

Fig. 3. High-resolution planktic foraminiferal biozonation for the Cretaceous–Tertiary transition used in the stratigraphic analysis of impact ejecta deposits (***Keller et al., l995; Li and Keller, 1998a). Note this biozonation significantly refines the resolution for the Late Maastrichtian zonal scheme (*Berggren et al., 1995) by replacing the upper *A. mayaroensis* zone by three biozones and by subdividing the *P. eugubina* zone Pla into two subzones based on the first appearances of *P. pseudobulloides* and *S. triloculinoides*. The calcareous nannofossil zonation is by Tantawy (2003).

Danian species have synchronous datum levels and global distributions because they evolved in generally cool, low productivity, high-stress surface water environments (Keller et al., 2002d). Critical biomarkers for the boundary clay zone P0 are the first evolving species at the base and first *Parvularugoglobigerina eugubina* at the top of the boundary clay (Fig. 2). The range of *P. eugubina* from first to last occurrences marks the critical zone Pla (Fig. 3). The interval of these two zones spans about 300,000 years (from the K/T boundary to the top of chron 29R (Fig. 3, Pardo et al., 1996) with zone P0 estimated at about 30,000 years at the El Kef stratotype (MacLeod and Keller, 1991a,b; Berggren et al., 1995). The 270,000-year interval of zone Pla can be further subdivided into Pla(l) and Pla(2) by the first appearances of *Parasubotina pseudobulloides* and *Subotina triloculinoides* in the small (< 100 μm) size fraction.

The most important Late Maastrichtian biomarker for K/T studies is *Plummerita hantkeninoides*, which

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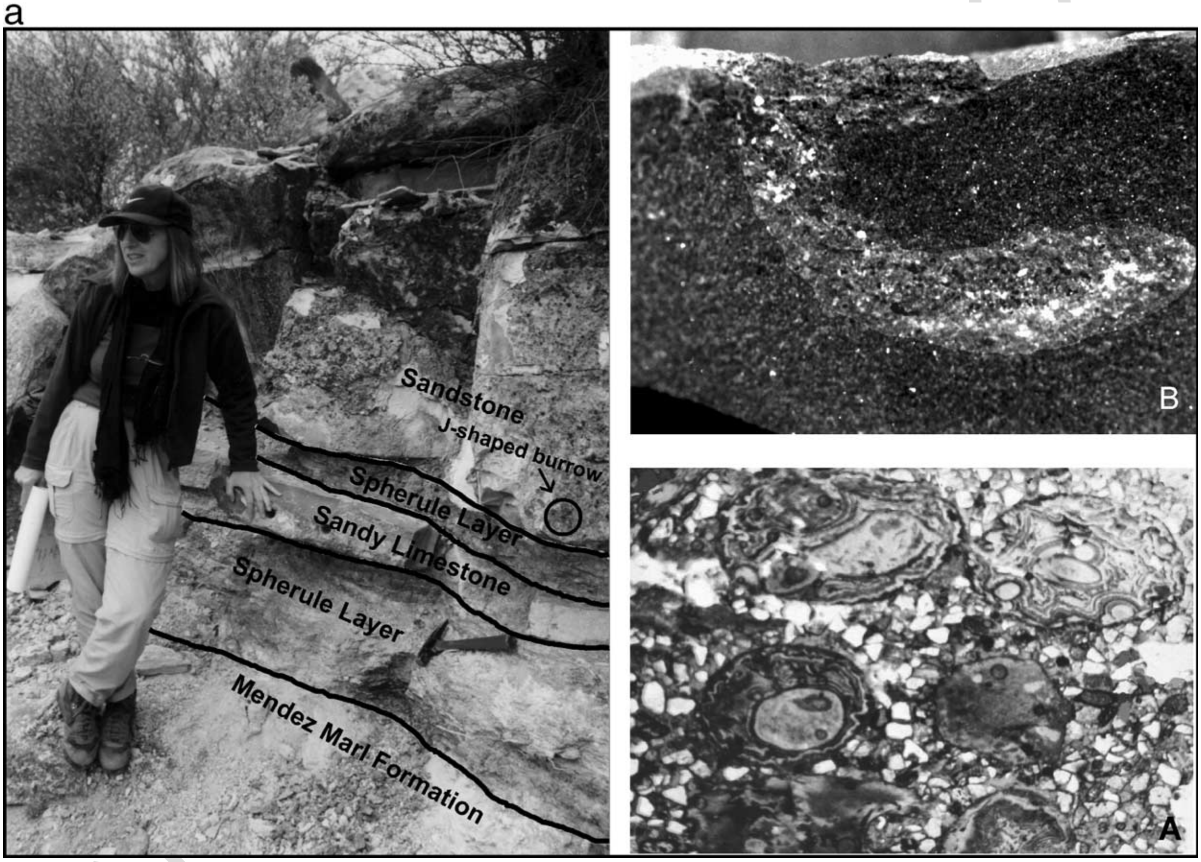

Fig. 4. (a) The siliciclastic deposit overlying the Mendez Formation at El Penon I in northeastern Mexico (author GK for scale). Unit 1 consists of two altered vesicular glass (microtektites and microkrystites) spherule layers with abundant reworked clastics and shallow water foraminifera. Spherules average 1 mm in diameter (A). A 10–20-cm-thick sandy limestone separates these two spherule layers. Sandstone unit 2 disconformably overlies unit 1. J-shaped burrows (5–10 cm long) infilled with spherules from the underlying unit 1 sherule layer and truncated at the top are found near the base of unit 2 (B). These burrows indicate colonization of the ocean floor during deposition of the sand unit 2 and negate rapid deposition by an impact-generated tsunami. (b) El Penon II, about 300 m from El Penon. The siliciclastic deposit with the altered vesicular impact glass spherule layer of unit 1, the sandstone unit 2 and alternating sand, silt and shale layers of unit 3 that form the top of the outcrop mesas in the area. Bioturbation and trace fossils are relatively rare in unit 2 (see B), but common to abundant in the fine-grained layers of unit 3. *Chondrites* burrows seen as vertical shafts in fine-grained silt layers (A) or exposed on bedding planes (B) are abundant. These burrows indicate repeated colonization of the ocean floor during deposition of unit 3 and negate rapid deposition by an impact-generated tsunami.

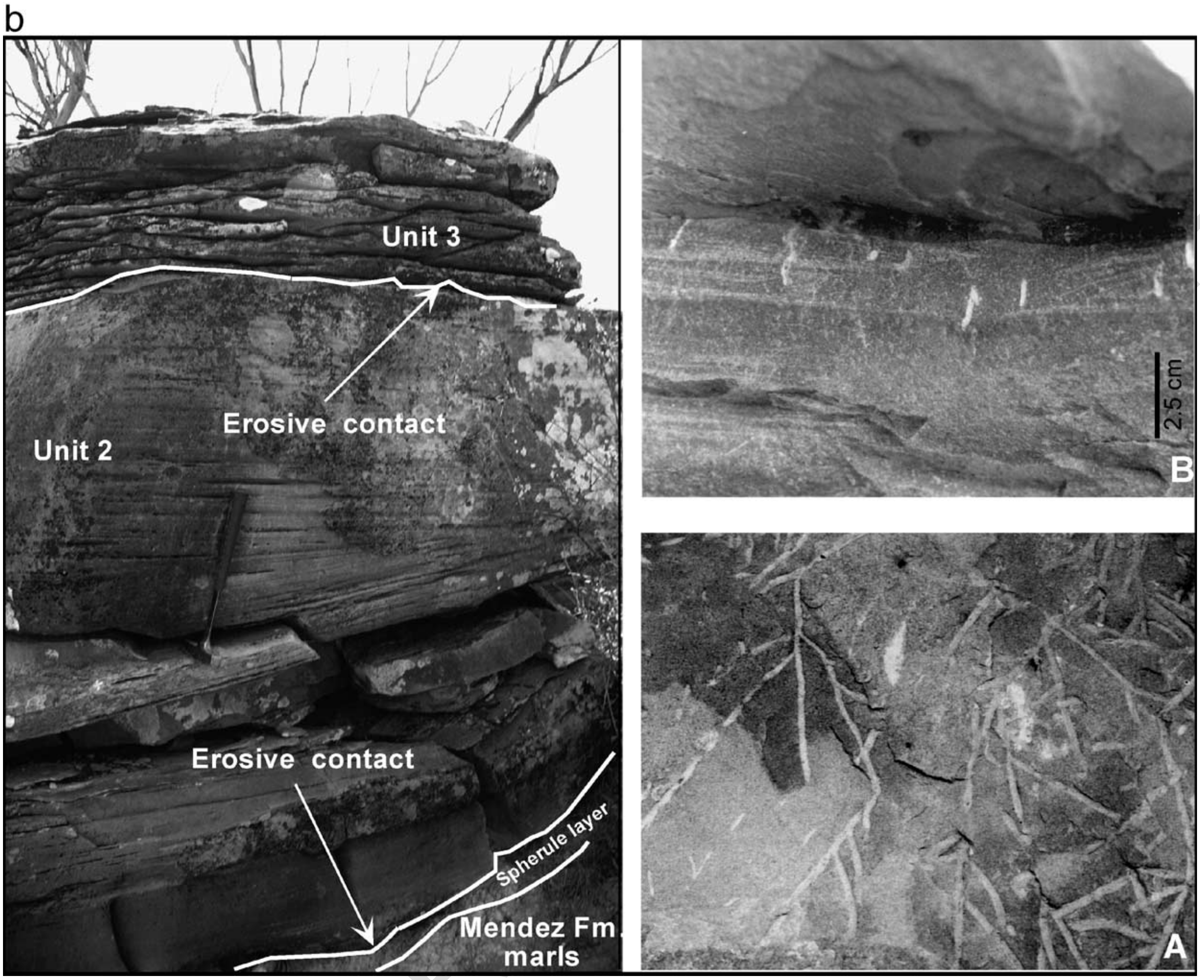

Fig. 4 (*continued*).

spans the last 300 ky of the Maastrichtian (Fig. 3). The temporal resolution for the Late Maastrichtian is based on the range of *P. hantkeninoides*, which spans the last 300,000 ky of the Maastrichtian, the extinction of *Gansserina gansseri* at 65.45 Ma and first appearance of *Pseudoguembelina hariaensis* at 66.8 Ma (Fig. 3). Age estimates are based on foraminiferal datum events of DSDP Site 525A and Agost, Spain, tied to the paleomagnetic stratigraphy of the same sections (Pardo et al., 1996; Li and Keller, 1998a,b). Zones CF1 and CF2 span chron 29R below the K/T boundary (65.0–65.58 Ma) and are approximately equivalent to the calcareous nannofossil zone *Micula prinsii*.

3. Impact ejecta database

The most diagnostic and easily recognized impact ejecta within < 1000 km of Chicxulub are layers of tiny altered glass spherules (0.3–4 mm) characterized by abundant internal vesicles. These altered glass spherules have been identified as tektites or microtektites produced by melting and quenching of terrestrial rocks during a hypervelocity impact (Izett et al., 1991; Sigurdsson et al., 1991; Blum and Chamberlain, 1992; Blum et al., 1993; Koeberl, 1993), or microkrystites, a product of impact vapor condensates, as indicated by the presence of crystallites of quartz and calcite (Griscom et al., 1999). Microtektites and microcrystites may occur together in the same ejecta layers around the Gulf of Mexico and Central America. Smit (1999) suggested that microtektites predominate in proximal ejecta sites within 2500 km of Chicxulub, whereas microkrystites dominate in more distal localities.

3.1. Northeastern Mexico

3.1.1. K/T boundary and siliciclastic deposits

The originally discovered altered impact glass spherule layer in northeastern Mexico, which contains both microkrystites and microtektites (henceforth labeled MM), disconformably overlies marls of the Mendez Formation and disconformably underlies the base of thick siliciclastic deposits. At El Penon I, this ejecta deposit forms two layers separated by a 15–20-cm-thick sandy limestone (Fig. 4a) that is also observed in sections from Mimbral, La Lajilla and Rancho Grande (Keller et al., 1997). The overlying siliciclastic deposit is 8-m-thick at El Penon I and about 2-m-thick at the nearby El Penon II outcrop (Fig. 4b). The lithologies are generally subdivided with unit 1, the altered glass spherule layer at the base (see Fig. 4a,b). The overlying unit 2 consists of well-sorted sandstone in often-lenticular bodies that infill channels. The topmost unit 3 consists of alternating layers of sandstone, silt and shale (Stinnesbeck et al., 1996). Bohor (1996) interpreted these deposits as turbidite or gravity flows triggered by the Chicxulub impact. Based on paleocurrent direction changes, Smit et al. (1996) and Smit (1999) assumed that units 2 and 3 indicate the passage of successive tsunami waves after the settling of melt rock and vapor condensates in unit 1. This could not be confirmed by subsequent paleocurrent measurements throughout the La Sierrita, Las Ruisas and Loma Cerca areas which revealed a nearly uniform direction east–southeast with only 3% showing the opposite trend (Affolter, 2000). This paleocurrent direction is consistent with clastic runoff from the Sierra Madre Oriental and transports into deeper waters via a large submarine canyon system (e.g. Lavaca and Yoakum paleocanyons of Texas and Chicontepec in central–eastern Mexico, Galloway et al., 1991).

Trace fossils are relatively rare in unit 2, but have been observed at Rancho Canales and El Penon I as 5–10-cm-long J-shaped burrows infilled with spherules from unit 1 and truncated at the top by overlying sand layers (Fig. 4a-B; Keller et al., 1997). Trace fossils are common in the finer grained layers of unit 3. *Chondrites* burrows are particularly abundant in the fine silt layers of unit 3 (Fig. 4b), but *Ophiomorpha*, *Thalassinoides*, *Planolites* and *Zoophycos* are also present (see Ekdale and Stinnesbeck, 1998). The burrowed horizons indicate that sediment deposition occurred episodically with periods of erosion and rapid deposition alternating with periods of normal pelagic sedimentation and colonization of the ocean floor by bottom dwellers. Units 2 and 3 could, therefore, not have been deposited by a tsunami over a period of hours to days (Smit et al., 1996), but may be related to sea level changes and gravity flows as suggested by the presence of reworked shallow water microfossils and terrigenous debris (Adatte et al., 1996; Stinnesbeck et al., 1996). Unit 1 is also reworked and transported as indicated by reworked shallow water foraminifera and abundant terrigenous clastic debris (Fig. 4a-A). The age of units 1–3 is uncertain largely because of the abundance of reworked sediments (Keller et al., 1997). Below the siliciclastic deposits, the presence of *P. hantkeninoides*, the zone CF1 biomarker, indicates that deposition probably occurred within the last 100,000 years of the Maastrichtian (Fig. 3). Above unit 3, Tertiary shales of early *P. eugubina* zone Pla(1) age are enriched with iridium and suggest that the K/T boundary is very condensed (e.g. La Lajilla, Mimbral, El Mulato, La Parida and La Sierrita; Stinnesbeck et al., 1996; Smit, 1999).

The juxtaposition of the unit 1 altered impact glass spherule (MM) layer at the base and Danian sediments above the siliciclastic deposits has led some workers to argue for a K/T age based on three assumptions: (1) the altered glass spherules represent vapor condensates and melt droplets from the Chicxulub impact, (2) the impact occurred at the K/T boundary and (3) the siliciclastic sediments represent impact-generated tsunami deposits (Smit et al., 1993, 1994, Smit et al., 1996; Smit, 1999; Arz et al., 2002). As noted above, assumption 3 is contradicted by the presence of multiple horizons of bioturbation in units 2 and 3 that indicate deposition occurred over an extended period of time during which benthic faunas repeatedly colonized the ocean floor (Keller et al., 1997, 2002a;

Ekdale and Stinnesbeck, 1998). If the microtektites and microkrystites originated from the Chicxulub impact, for which there is strong chemical evidence (Sigurdsson et al., 1991; Swisher et al., 1992; Blum et al., 1993), their stratigraphic position below the K/T boundary and below the siliciclastic deposit also jeopardizes assumption 2 that Chicxulub is of precisely K/T age.

3.2. Multiple altered impact glass spherule layers

Recent investigations of the Mendez Formation marls below the microcrystite and microtektites (MM) layer of unit 1 at the base of the siliciclastic deposits have revealed one to three additional and sometimes lens-like MM layers separated by up to 2–4 m of marls, as shown in Fig. 5, for a series of outcrop between Loma Cerca and Mesa Juan Perez spanning a distance of 9 km (Keller et al., 2002a). The thickness of these MM layers is variable and ranges from 5 to 10 cm to over 3.5 m, with the thickest layers containing abundant marl and marl clasts of the Mendez Formation (Fig. 5, Loma Cerca A and Las Ruisas B). Unit 1 MM layer is absent in only a few outcrops (Las Ruisas C), and in some only unit 1 was observed (Las Ruisas A, El Muerto, Fig. 5). This is likely due to erosion as well as limited and poor outcrop exposures along the wooded hillside of these mesas. Occasionally, a MM layer may be syndepositionally deformed and folded (Soria et al., 2001; Schulte et al., in press), but there is no evidence of regional large-scale slump deposits (Keller and Stinnesbeck, 2000). In over 40 localities investigated over a region of 60 km^2, multiple altered glass spherule (MM) layers are commonly present in the Late Maastrichtian planktic foraminiferal zone *P. hantkeninoides* CF1 which spans the last 300 ky of the Maastrichtian (Fig. 3, Schulte, 1999; Affolter, 2000; Schilli, 2000; Ifrim, 2001). ICP-MS analysis of MM layers revealed no PGE or Ir anomalies.

The Loma Cerca B section, located on the western flank of the Mesa Loma Cerca about 40-km east of Montemorelos, has one of the most expanded Late Maastrichtian zone CF1 records with four altered microtektite and microkrystite (MM) layers (labeled SR-1 to SR-4 with SR-4 being unit 1, Fig. 6). The lowermost MM layer SR-1 is 10 m below the siliciclastic deposit and 1 m above the base of the *P. hantkeninoides* CF1 zone (Fig. 3). Normal pelagic marls (2 m) separate SR-1 from the two closely spaced 50-cm-thick MM layers SR-3 and SR-2, and 6.5 m of normal pelagic marls separates SR-3 from SR-4 (the unit 1 spherule layer) at the base of the siliciclastic deposit. MM layer SR-1 consists almost entirely of closely packed vesicular altered glass spherules and fragments up to 5–7 mm in diameter with a blocky calcite matrix (Fig. 6A–C). Spherules are often compressed and welded with concave–convex contacts (Fig. 6B) suggesting that deposition occurred while the glass was still hot and ductile, possibly as rapidly sinking rafts. There is no evidence of significant reworking in the lowermost MM layer SR-1. In contrast, the upper three MM layers (SR-2, SR-3 and SR-4) contain a mixture of irregularly shaped marl clasts, lithic fragments and in SR-4 abundant terrigenous input (Fig. 4a-A). This suggests that the oldest layer represents the original deposition and the three younger layers are the result of subsequent reworking and transport, possibly at times of lower sea levels. Detailed documentation of structure, texture and compositions of these spherule layers is provided in Schulte et al. (in press).

Planktic and benthic foraminifera yield clues to the nature of deposition, whether chaotic reworking or normal pelagic sedimentation. At Loma Cerca B, species abundance changes are consistent with normal pelagic sedimentation and there is no evidence of significant reworking in the marls between MM layers SR-1 to SR-4 (Keller et al., 2002a). Species populations show a strong climatic trend with increased abundance of deeper dwelling tropical–subtropical globotruncanids and decreased surface dwellers marking climate warming beginning at the base of MM layer SR-1 and continuing through SR-2 and SR-3 (Fig. 7). This warming correlates with global climate warming in CF1 between 65.2 and 65.4 Ma (Li and Keller, 1998b). A sharp peak in globotruncanids and benthic foraminifera at the base of MM layers SR-2 and SR-3 indicates selective preservation consistent with reworking and transport. MM layer SR-4 contains abundant reworked benthic foraminifera from shallow shelf areas (Keller et al., 1997).

The age of the four MM layers can be estimated based on planktic foraminiferal zone CF1 which spans

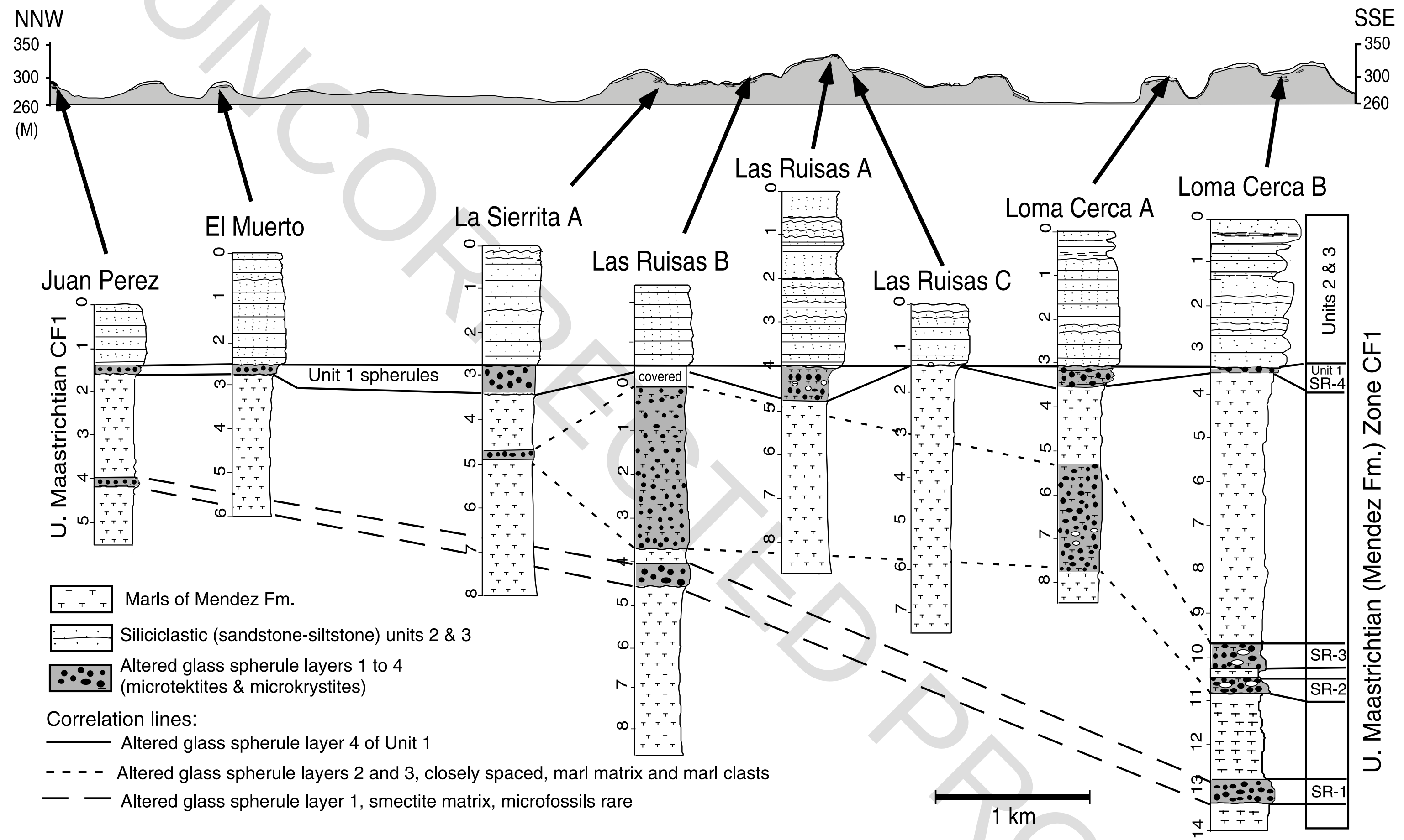

Fig. 5. Stratigraphic and lithologic correlation of Late Maastrichtian sections with several layers of altered impact spherule deposits (microtektites, microkrystites) from Mesa Loma Cerca to Mesa Juan Perez in northeastern Mexico (Fig. 1). The siliciclastic deposits of units 2 and 3 form the top of the sections and the mesas as shown by the topographic relief. All spherule deposits are within the Mendez marl Formation and within zone CF1 that spans the last 300 ky of the Maastrichtian. Lines mark correlation of spherule layers.

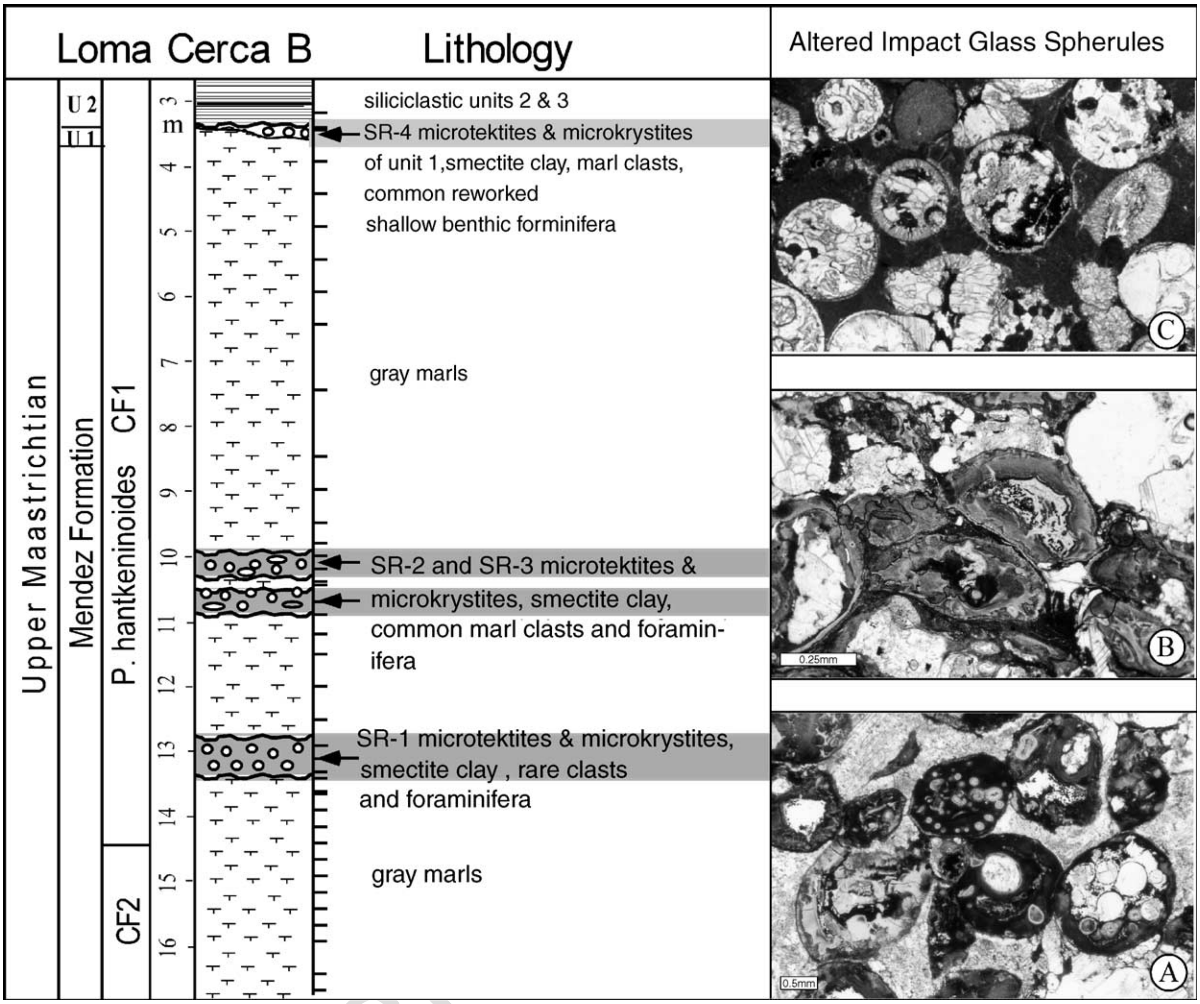

Fig. 6. Lithostratigraphy of the altered impact glass spherule-rich deposits labeled SR-1 to SR-4 at Loma Cerca, Mexico. Note that three spherule layers are interbedded with marls of the Mendez Formation and the fourth is unit 1 at the base of the siliciclastic deposit. Vesicular glass spherules of layer SR-1 contain a matrix of smectite clay; clasts and foraminifera are rare (A and C). Welded glass spherules are common in SR1, SR2 and SR3 and may represent rapidly sinking rafts (B). Average size of spherules is 1 mm.

the last 300 ky of chron 29R in the Maastrichtian (Fig. 3). Assuming that most of zone CF1 is present at Loma Cerca B, an assumption that is justified based on the climate warming signal and presence of unique *Guembelitria* peaks (Abramovich and Keller, 2002), the average sediment accumulation rate is 3 cm/ky. This rate compares favorably with 2 cm/ky at El Kef and 4 cm/ky at Elles for pelagic marls during zone CF1 (Li et al., 1999). On the basis of these accumulation rates, MM layer SR-1 was deposited at ~270 ky, SR-2 at ~215 ky, SR-3 at ~210 ky and SR-4 probably within < 5–10 ky before the K/T boundary. An error of 30,000 years is estimated.

3.3. Central Mexico

Tlaxcalantongo and Coxquihui are two K/T boundary sections with spherule deposits that are known from the State of Veracruz in east central Mexico (Fig. 1). At Tlaxcalantongo (also called La Ceiba), a thin

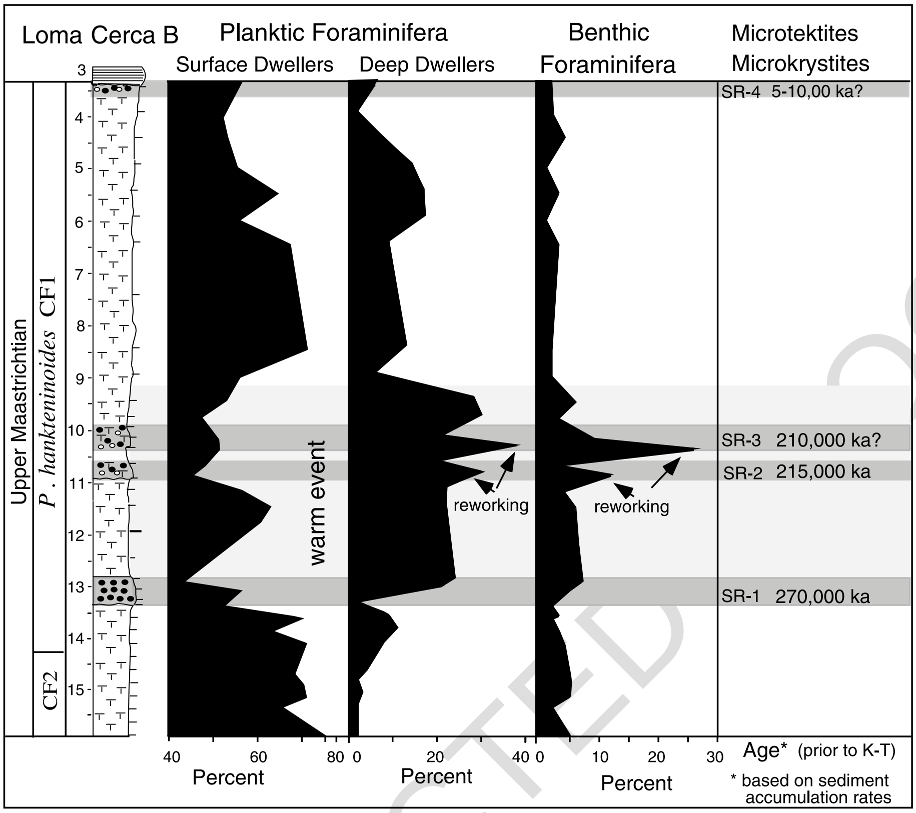

Fig. 7. Planktic foraminiferal proxies as indicators for climate change and reworking at Loma Cerca, Mexico. The overall increase in the relative abundance of the deeper dwelling globotruncanids and decrease in surface dwellers mark climate warming within zone CF1 and correlate to global warming between 65.4 and 65.2 Ma (Li and Keller, 1998b). Peak abundances in globotruncanids and benthic foraminifera at the base of spherule layers SR-2 and SR-3 mark reworking and suggest that these layers are redeposited from an older spherule deposit (SR-1?).

MM layer (SR-4 of unit 1) is present below an 80-cm-thick siliciclastic deposit (units 2–3, Stinnesbeck et al., 1996; Smit et al., 1996; Arz et al., 2001a,b). At Coxquihui to the south, only about 50 cm of Late Maastrichtian sediments is exposed and no siliciclastic deposit is present, though two MM layers are present (Fig. 8). The first MM layer is 2-cm-thick and truncates the Cretaceous fauna. No microfossils are present in the first 6 cm of the overlying sediments, but a rich Early Danian Pla(l) assemblage is present above, including a minor enrichment in Ir and Pd (Fig. 8). Above this interval is the second 60-cm-thick MM layer well within the Early Danian zone Pla(l). Ir and Pd anomalies are observed above this MM layer. Both Smit (1999) and Arz et al. (2001b) identified this thick spherule layer and Ir anomaly as K/T boundary age, possibly due the presence of reworked Maastrichtian species within the Danian Pla assemblage.

3.4. Southern Mexico

The best-known K/T section from southern Mexico is near Bochil, Chiapas (Fig. 1). We collected two sections at this locality, Bochil-1 and Bochil-2. Both outcrops are located along an unpaved road that crosses the hamlet of San Pedro Martir and leads to the PEMEX well Soyalo 1. Bochil-2 is about 8 km from the intersection with the main road, whereas Bochil-1 is 9.5 km from the same intersection and easily recognized by drill holes for paleomagnetic studies. Bochil-1 was previously studied by Monta-

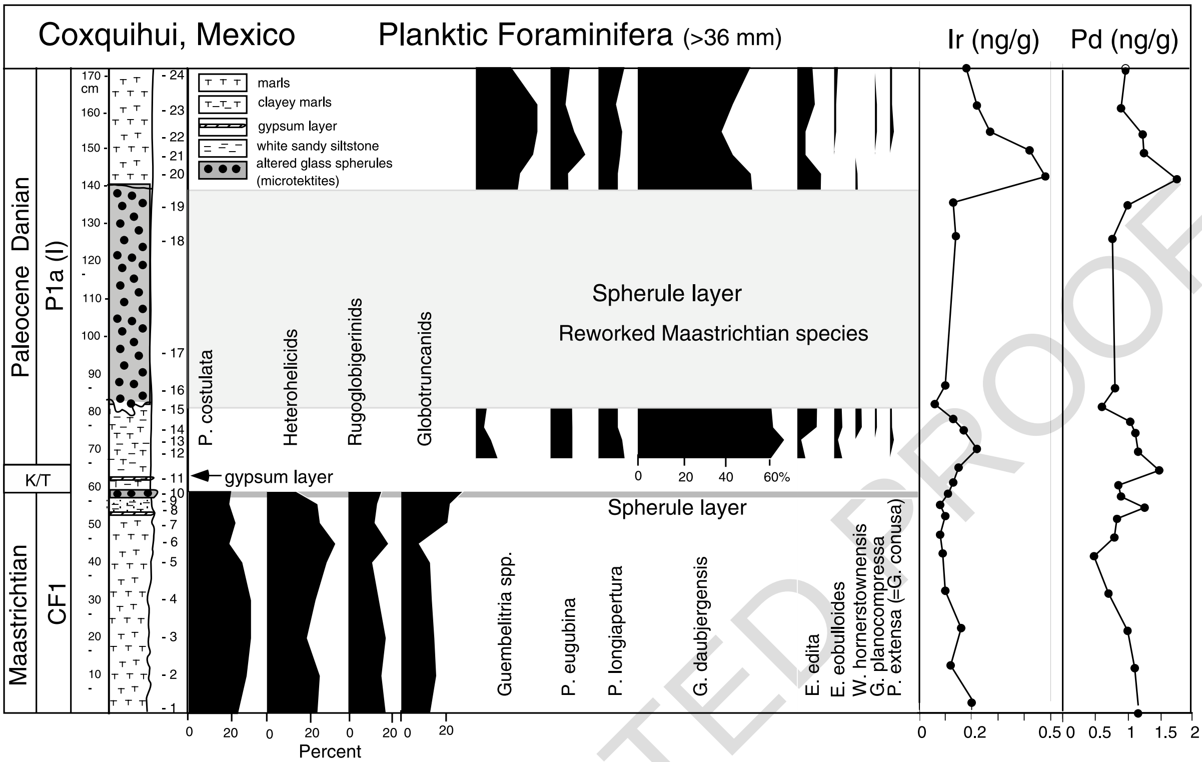

Fig. 8. Litho-, bio- and chemostratigraphy of the Coxquihui section in east Central Mexico. A thin (2 cm) altered glass spherule layer truncates the K/T boundary. A 60-cm-thick altered glass spherule layer with reworked Maastrichtian species is within the lower part of the *P. eugubina* subzone Pla(l). The reworked species indicate that the spherules are reworked and redeposited from an older probably Late Maastrichtian spherule deposit. The sudden appearance of abundant Danian species in the Early Danian marks a hiatus. Note the Ir and Pd anomalies in the marls above the reworked spherule deposit.

nari et al. (1994), Smit et al. (1996), Smit (1999) and Grajales-Nishimura et al. (2000).

3.4.1. Bochil-1

At Bochil-1, typical reefal limestone breccias with rudists and larger foraminifera, indicative of Campanian–Maastrichtian age, underlie a 1-m-thick microconglomerate with altered glass spherules (Fig. 9). The first Danian species of subzone Pla(l) appear above this microconglomerate in a 3-cm-thick white marl with common Fe-rich spherules and Ir enrichment. Maximum Ir enrichment occurs in a gray marl 8 cm above associated with a relatively diverse Early Danian planktic foraminiferal assemblage indicative of the *P. eugubina* subzone (Pla(l). Reworked Cretaceous species, including *P. hantkeninoides*, are also present and indicate that the Latest Maastrichtian zone CF 1 is eroded. Almost pure Cheto smectite is present in the 2-cm-thick microconglomerate above the limestone and persists into the marls of subzone Pla(2) (Fig. 9). Smectite with the best crystallinity and highest intensity is observed in the upper white marl of P1a(2), coincident with the Pd anomaly (Fig. 5) and indicates weathering of impact glass into Na–Mg Cheto-smectite (Debrabant et al., 1999; see Belize section). The stratigraphic positions of the Ir and Pd enrichments in Pla(l) and the Pla(l)/Pla(2) boundary at Bochil-1 appear to be equivalent to the Ir and Pd enrichments in Pla(l) at Coxquihui (Fig. 8) and Haiti (Keller et al., 2001; Stüben et al., 2002).

3.4.2. Bochil-2

Bochil-2 is located 1.5 km from Bochil-1. At this locality, a polymict limestone breccia disconformably underlies brown shales and gray marls (Fig. 10a). The section was sampled in order to determine the age of

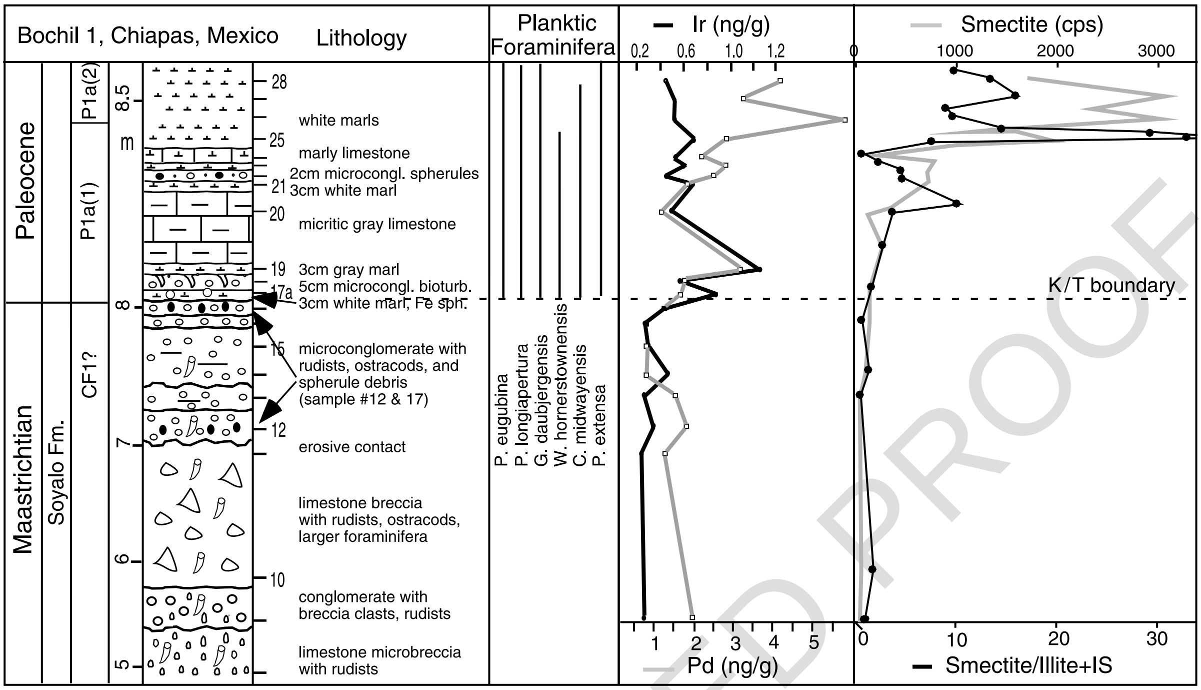

Fig. 9. Litho-, bio- and chemostratigraphy of Bochil 1, Chiapas, Mexico. Altered glass spherules are present at the base and top of a microconglomerate layer of probable latest Maastrichtian age. The first marl layer above the Maastrichtian microconglomerate contains Early Danian planktic foraminifera of the *P. eugubina* subzone Pla(l) as well as Ir and Pd anomalies. Altered glass spherules and Cheto smectite and a Pd anomaly are present near the Pla(l)/Pla(2) boundary, as previously observed at Beloc, Haiti (Keller et al., 2001; Stüben et al., 2002).

the breccia and its relationship to the K/T boundary and the spherule layer. The breccia matrix and overlying shales and marls contain an assemblage of large and well-developed Early Paleocene species including *S. triloculinoides*, *S. trivialis*, *P. pseudobulloides*, *G. compressa*, *Praemurica inconstans* and *Chiloguembelina midwayensis* that indicate an Early Paleocene age of the upper Plc or lower Pld zones (Fig. 2). The breccia contains rare but well-preserved translucent glass spherules including teardrop and elongate shapes. These spherules differ from those in latest Maastrichtian, K/T and Early Danian intervals by their pristine preservation, smaller size and geochemistry with a composition of predominantly of SiO2, with minor Ba, Ca and Ir contents (Fig. 10b). Additional collections are needed to determine their origin.

3.4.3. Trinitaria

The section is located 14 km south of La Trinitaria, Chiapas, at the km 202 sign on the main road between Comitan and Ciudad Cuahtemoc. This section was described previously by Cros et al. (1998) and Gonzales Lara (2000). The outcrop consists of a 15-m-thick limestone breccia with upward fining angular to subangular clasts. The top 10 cm of the breccia unit consists of a size-graded microconglomerate (Fig. 11). Overlying the microconglomerate is a 2-cm-thick laminated micritic limestone and thin red clay layer with abundant pyrite spherules (sample 7) that contain the first Tertiary species (38–63 μm size fraction) including *P. eugubina*, *E. edita*, *E. fringa*, *G. daubjergensis* and common *Guembelitria cretacea*. This assemblage is characteristic of the Early Danian *P. eugubina* subzone Pla(l) (Fig. 3). The tan marls above this sample are enriched in Ir and Pd (Fig. 11) at an interval that is stratigraphically equivalent to the Ir and Pd enrichments at Bochil-1, Coxquihui and Haiti. The limestone breccia (sample 4) contains smectites and zeolites that suggest the presence of weathered glass. The fine clay fraction (<2 μm) of the Ir-enriched interval (samples 7–9, Fig. 11) consists of an almost single smectite phase

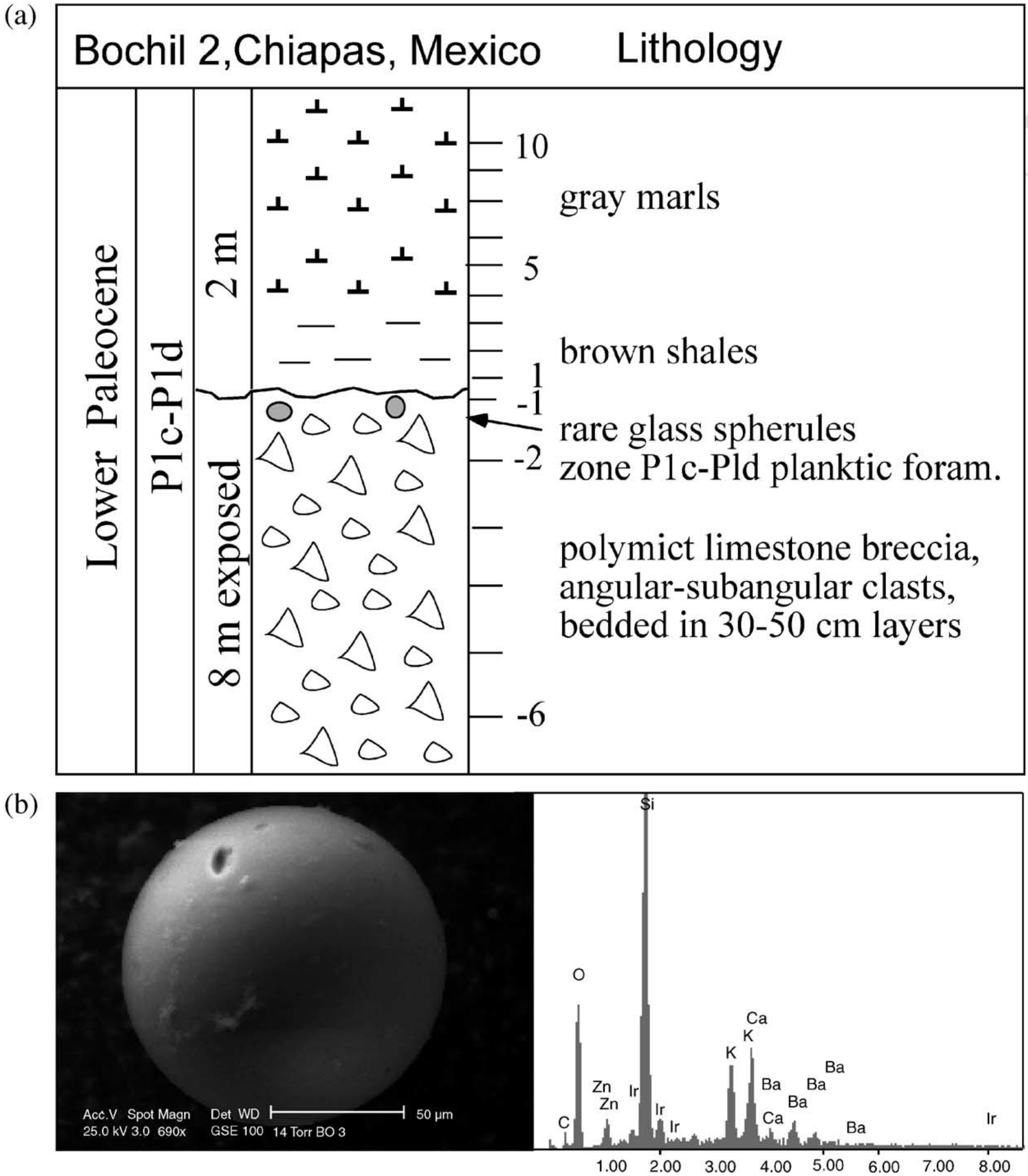

Fig. 10. (a) Litho- and biostratigraphy at Bochil 2, Chiapas, Mexico. The section is of Danian zone Plc–Pld age (Fig. 3) and consists of a polymict breccia with rare glass spherules at the top. The glass is high in SiO_2, Ca, K and minor Ir (10b). Microfossil-rich shales overlie the breccia.

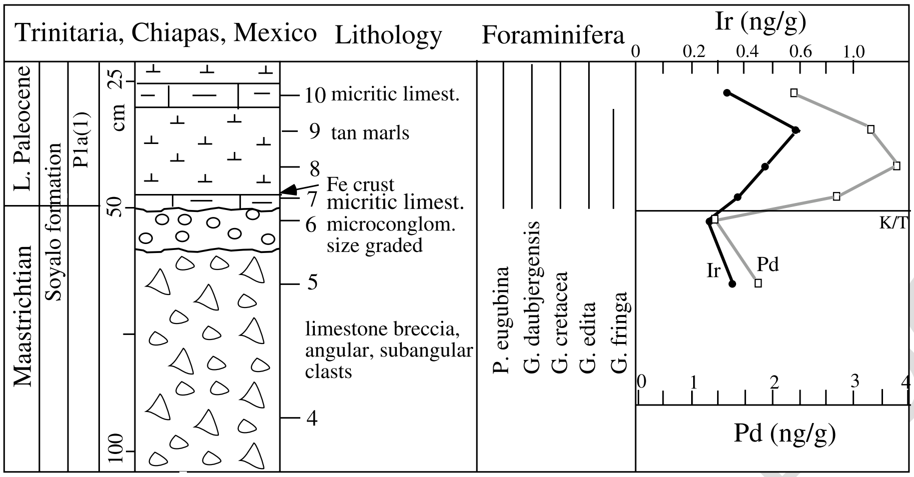

Fig. 11. Litho-, bio- and chemostratigraphy of the K/T transition at Trinitaria, Chiapas, Mexico. The Late Maastrichtian sequence consists of breccia followed by a microconglomerate and micritic limestone. The marls overlying this limestone contain planktic foraminifera indicative of the Early Danian *P. eugubina* Pla(l) subzone. Ir and Pd anomalies are present within this Early Danian marl layer.

(probably Cheto smectite) similar to Bochil, but unlike Bochil also contains a significant amount of zeolite in the 2–16-μm size fraction that may indicate volcanic input.

4. Guatemala

At El Caribe, Guatemala, Cretaceous limestone breccias with altered glass spherules underlie Early Danian Pla(l) sediments enriched with iridium, similar to Bochil-1, Chiapas (Stinnesbeck et al., 1997; Fourcade et al., 1998, 1999; Keller and Stinnesbeck, 2000). Thick deposits of altered vesicular spherules, similar to the microtektite and microkrystite deposits in northeastern Mexico, have recently been discovered at Actela located 30-km southeast of San Luis, El Peten, near the Guatemala/Belize border (Fig. 1, Keller et al., in preparation). At this locality, Cretaceous limestone breccias underlie a 2-m-thick spherule-rich microbreccia that contains an Early Danian zone Pla(l) assemblage (Fig. 12). A 5-cm-thick spherule layer is present near the top of the microbreccia and spherules are reworked up to the Pla(l)/Pla(2) boundary marked by a bentonite layer with the overlying marl enriched in Pd and Ir.

These data indicate reworking of MM spherules into Early Danian sediments as also suggested by frequent erosional surfaces. The Ir anomaly is clearly well within the *P. eugubina* zone (near Pla(l)/Pla(2 boundary), similar to that observed at Bochil, Coxquihui and Haiti (Figs. 8 and 9) and marks an Early Danian event that appears to be independent of impact spherule deposition (Keller et al., 2001; Stüben et al., 2002).

Mineralogical analysis of the altered MM layers (samples 0 and 2, Fig. 12) reveals a Cheto smectite typical of weathered glass spherules, similar to Bochil and Belize, though not as well crystallized. Debrabant et al. (1999) reported similar results from both the microbreccia and spherule-rich deposits of this section based on thermoanalytic techniques (DTA). Above this interval, the marls and shales of the Sepur Formation are characterized by more heterogeneous clay mineral assemblages with typical Cheto smectite layers alternating with Al–Fe smectite related to soil weathering, similar to clays found in the Maastrichtian limestones. Debrabant et al. (1999) concluded that these Early Danian Cheto smectites most likely reflect multiple reworking episodes of the K/T spherule bearing level, an interpretation that is consistent with our analysis.

5. Belize

Most investigations in Belize have focused on the Albion Island quarry and its unusual spheroid and

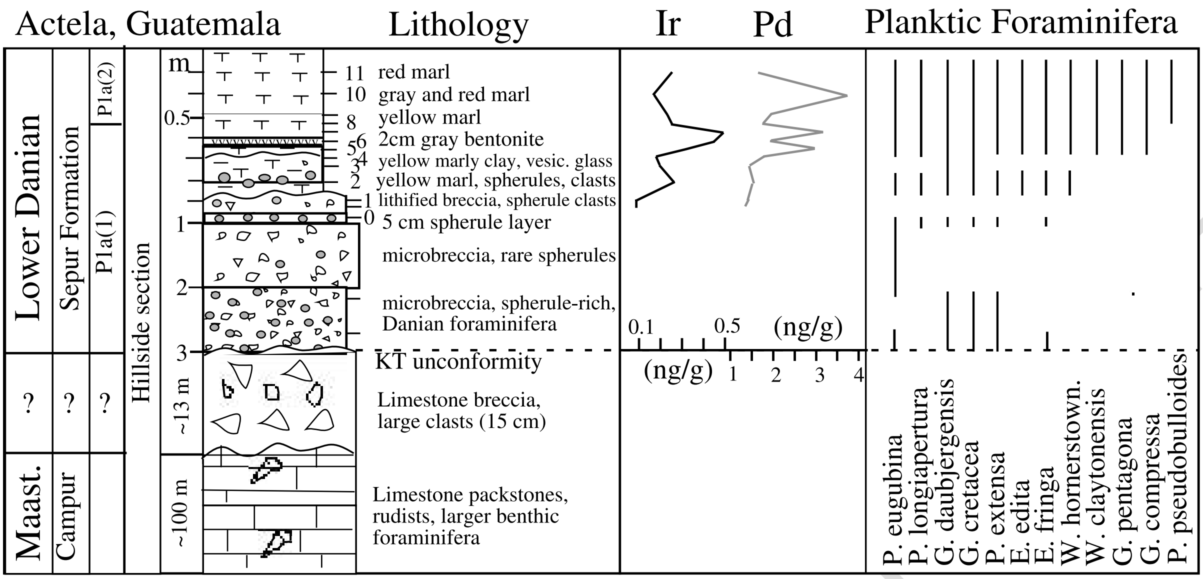

Fig. 12. Litho-, bio- and chemostratigraphy of the K/T transition at Actela in eastern Guatemala. The first altered impact glass spherules are present in a microbreccia which also contains Early Danian *P. eugubina* subzone Pla(l) planktic foraminiferal assemblages. Variable abundance of altered glass spherules is present (reworked?) in the lower 2.4 m of the Danian Pla(l). Maximum Ir concentration occurs in a yellow marl and bentonite above the last spherule-rich deposit and just below the Pla(l)/Pla(2) transition. A Pd enrichment occurs 15 cm above this interval near the base of Pla(2) as also observed at Coxquihui, Bochil, Trinitaria and Beloc, Haiti.

diamictite deposits that overlie the Barton Creek Formation (Ocampo et al., 1996; Pope et al., 1999; Fouke et al., 2002), and similar deposits are also present at Armenia in central Belize along the Hummingbird Highway (Fig. 13, Keller et al., in preparation). The absence of age diagnostic fossils in these deposits has prevented age determination or stratigraphic correlation to the impact ejecta deposits of Mexico, Guatemala and Haiti. Recently, thick altered vesicular glass spherule deposits with abundant reworked Cretaceous limestone clasts, foraminifera and lenses of spherules similar to Actela and Mexico have been discovered in the San Jose Quarry and Santa Theresa sections of southern Belize (Fig. 13). Planktic foraminifera indicate that these deposits are reworked and redeposited in the Early Danian zone Pla(l), similar to Actela, Coxquihui, Trinitaria and Beloc, Haiti (Figs. 8, 11, 12 and 14).

A stratigraphic correlation between the Armenia and Albion Island spheroid deposits and the southern Belize altered glass spherule deposits can be made based on a Al and Mg-rich smectite (Cheto smectite). Cheto smectite is an almost pure high Mg-smectite that forms up to 100% of the clay fractions derived from weathering of impact glass (e.g. melt rock and vapor condensates; Debrabant et al., 1999; Bauluz et al., 2000). Cheto smectite is characterized by a high percentage of expendable layers (>95%), excellent crystallinity, very high intensity of the 001 reflection and a webby morphology. Debrabant et al. (1999) observed Cheto smectite in altered impact glass spherule deposits of El Caribe in Guatemala and Ceibo (Tlaxcalantongo) in Central Mexico, and Bauluz et al. (2000) observed this smectite in the boundary clay of Stevns Klint, Denmark. Our analyses (SCINTAG XRD 2000 Diffractometer and a Phillips ESEM equipped with EDEX analyzer) indicate the presence of Cheto smectite in the large spheroid deposits of Albion Island and Armenia, as well as the altered glass spherule deposits of Santa Theresa, San Jose Quarry and Actela (Figs. 12 and 13, Keller et al., in preparation), the microtektite and microkrystite deposits of Beloc (Haiti), Coxquihui, Bochil and Trinitaria in Mexico. The wide distribution and almost ubiquitous presence of Cheto smectite in altered impact glass layers provides a good proxy for correlating these deposits as shown for Belize (Fig. 13). In addition to Cheto smectite, a significant amount of

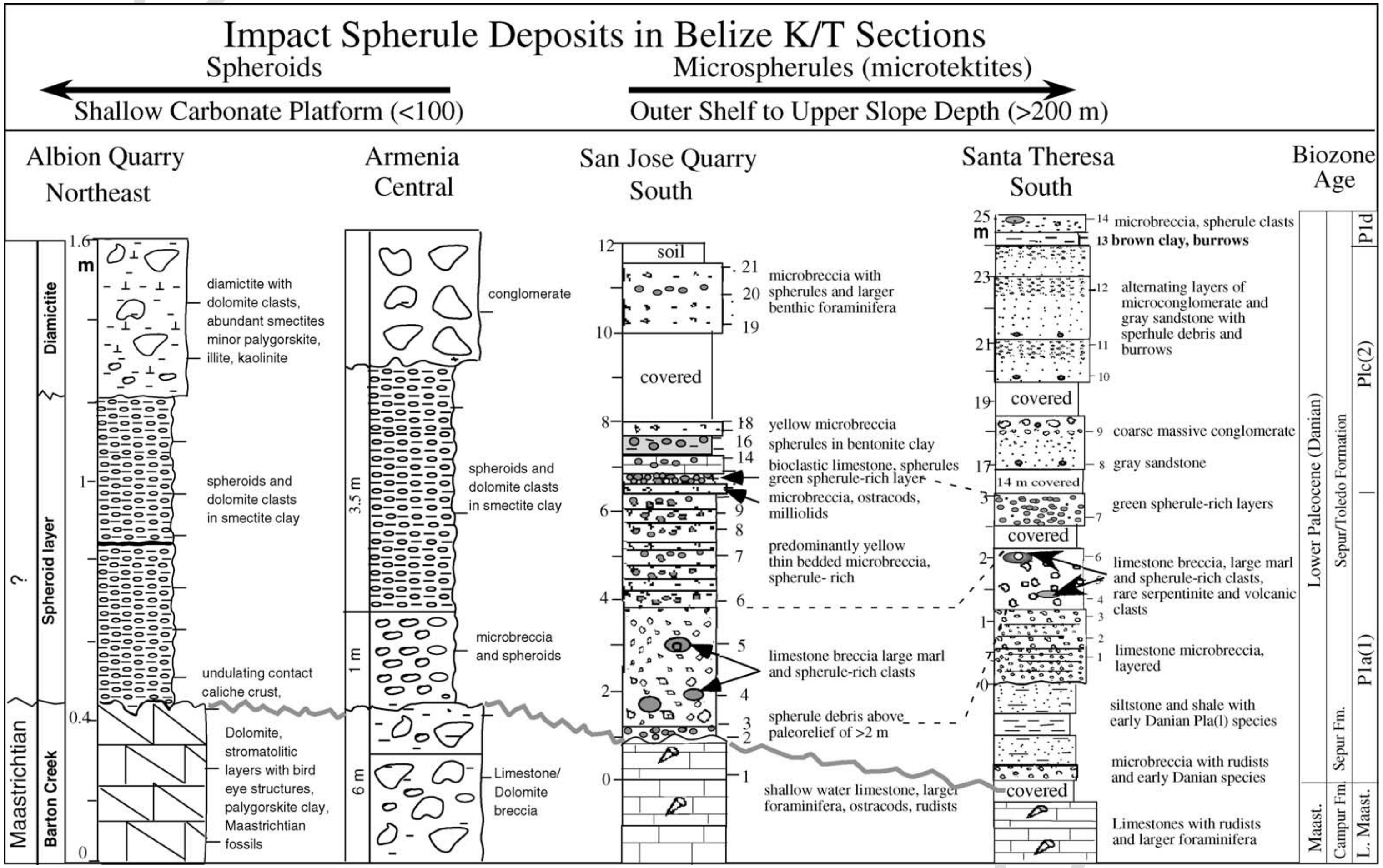

Fig. 13. Litho- and biostratigraphy of the Santa Theresa and San Jose quarry sections in Belize and their probable correlation with Armenia and the Albion Island Quarry based on the Cheto smectite that is interpreted to represent weathered impact glass spherules from the Chicxulub impact on Yucatan.

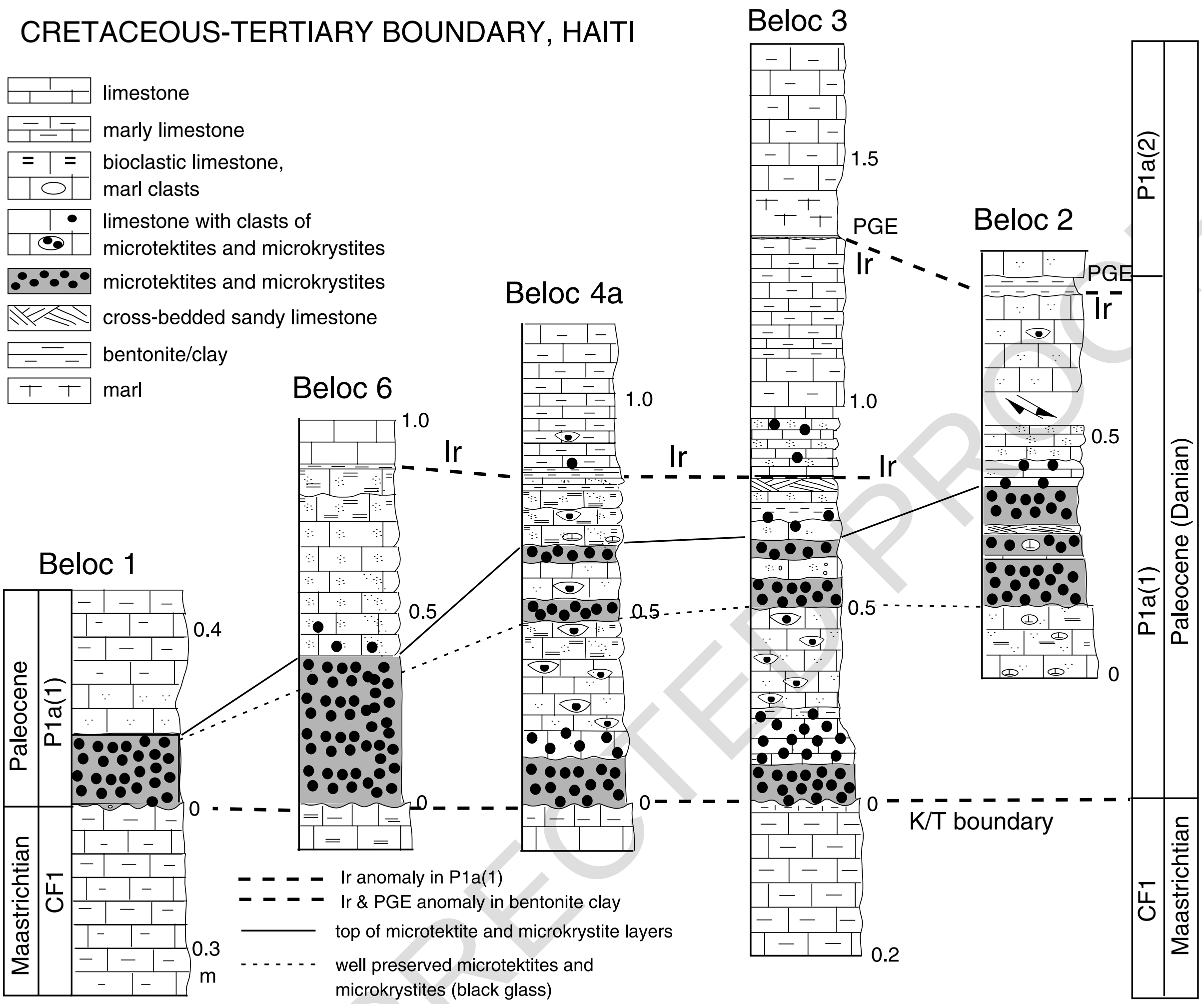

Fig. 14. Litho- and biostratigraphic correlation of the K/T boundary transition at Beloc, Haiti, modified after Keller et al. (2001). Impact glass spherule deposits (microtektites and microkrystites) disconformably overlie marly limestone of Late Maastrichtian age. Expanded sections at Beloc 3 and Beloc 4 show multiple impact glass spherule layers in the Danian zone Pla(l). An Ir anomaly occurs well above the glass spherule deposits. A bentonite near the Pla(l)/Pla(2) boundary is enriched in Ir and PGE.

zeolite (heulandite–clinoptilolite) is present that suggests a volcanic input (Elliot, 1993; Elliot et al., 1989) probably derived from arc related volcanism.

6. Haiti

The biostratigraphy of the Beloc sections has been previously reported in several studies including Maurasse and Sen (1991), Sigurdsson et al. (1991), Jéhanno et al. (1992), Leroux et al. (1995) and Lamolda et al. (1997). Most of these studies focused on roadside outcrops which have a prominent spherule layer that is folded, faulted and slumped. Stinnesbeck et al. (2000) and Keller et al. (2001) reported on several new and undisturbed sections that contain expanded K/T transitions with spherule layers, Ir and PGE anomalies (Stüben et al., 2002) within the Early Danian *P. eugubina* subzone Pla(l) (Fig. 14).

In all Beloc sections, the latest Maastrichtian consists of a pelagic marly limestone that contains an impoverished tropical planktic foraminiferal assem-

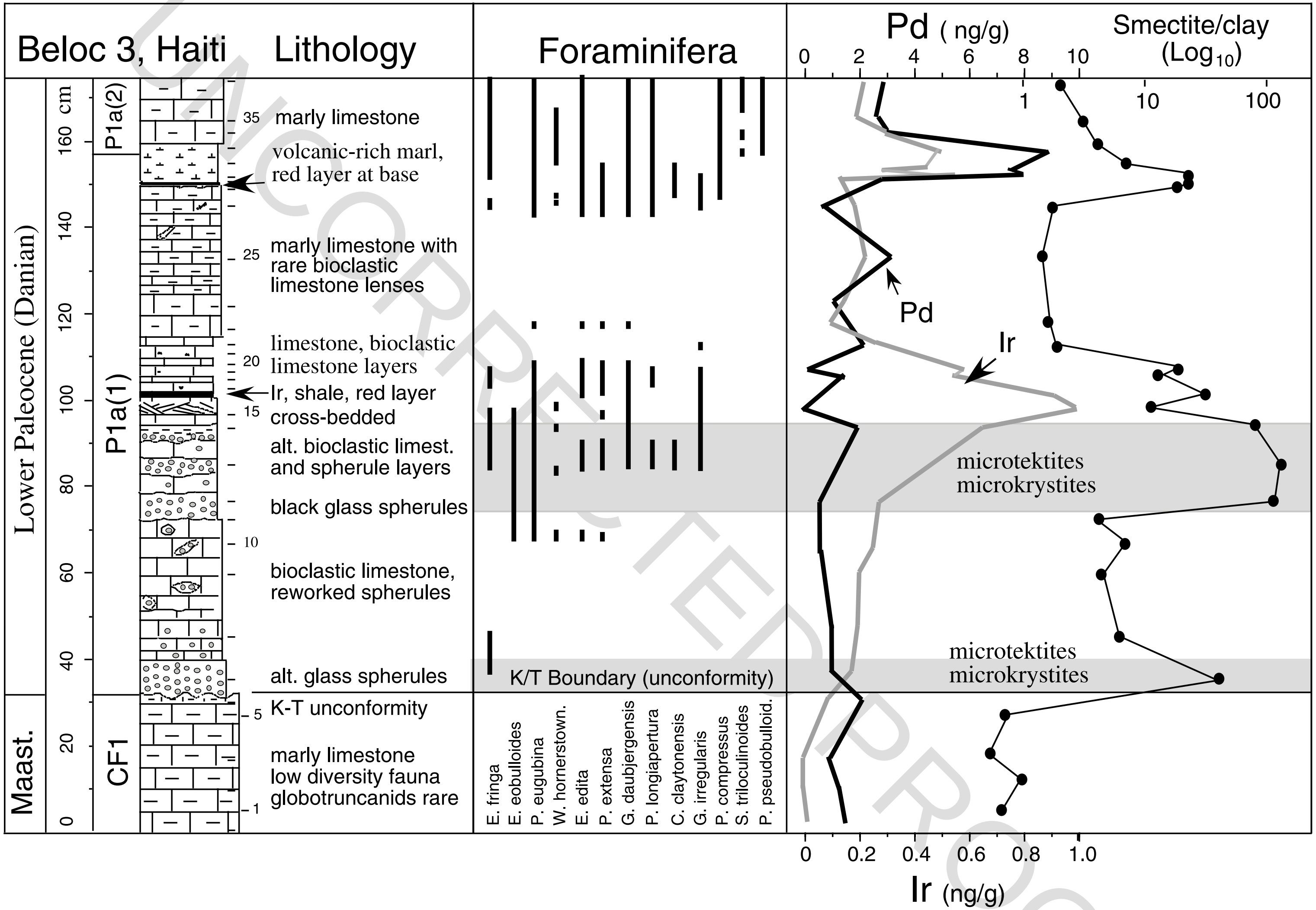

Fig. 15. Litho-, chemo- and biostratigraphy of the Beloc 3 section, Haiti, modified after Keller et al. (2001). The K/T Ir anomaly is missing due to erosion, the subzone Pla(l) Ir anomaly above the spherule deposits marks an Early Danian impact event, whereas the Pd and minor Ir anomalies at the Pla(l)/Pla(2) transition mark a regional volcanic event. Cheto smectite is present in the altered impact glass spherule layers (shaded).

blage of the *P. hantkeninoides* zone CF1. A 20–30-cm-thick volcanoclastic tuff layer at 10 m below the K/T boundary has a K–Ar date of 66.5 ± 0.8 Ma and is within the calcareous nannofossil *M. prinsii* zone (Odin et al., 2001). The K/T boundary unconformity is marked by an erosional surface with clasts of micritic limestones underlying an altered MM layer that varies between 10 and 40 cm in thickness (Fig. 14) and contains the first Tertiary species that define zone Pla(l) (Fig. 15, Keller et al., 2001). A 30-cm-

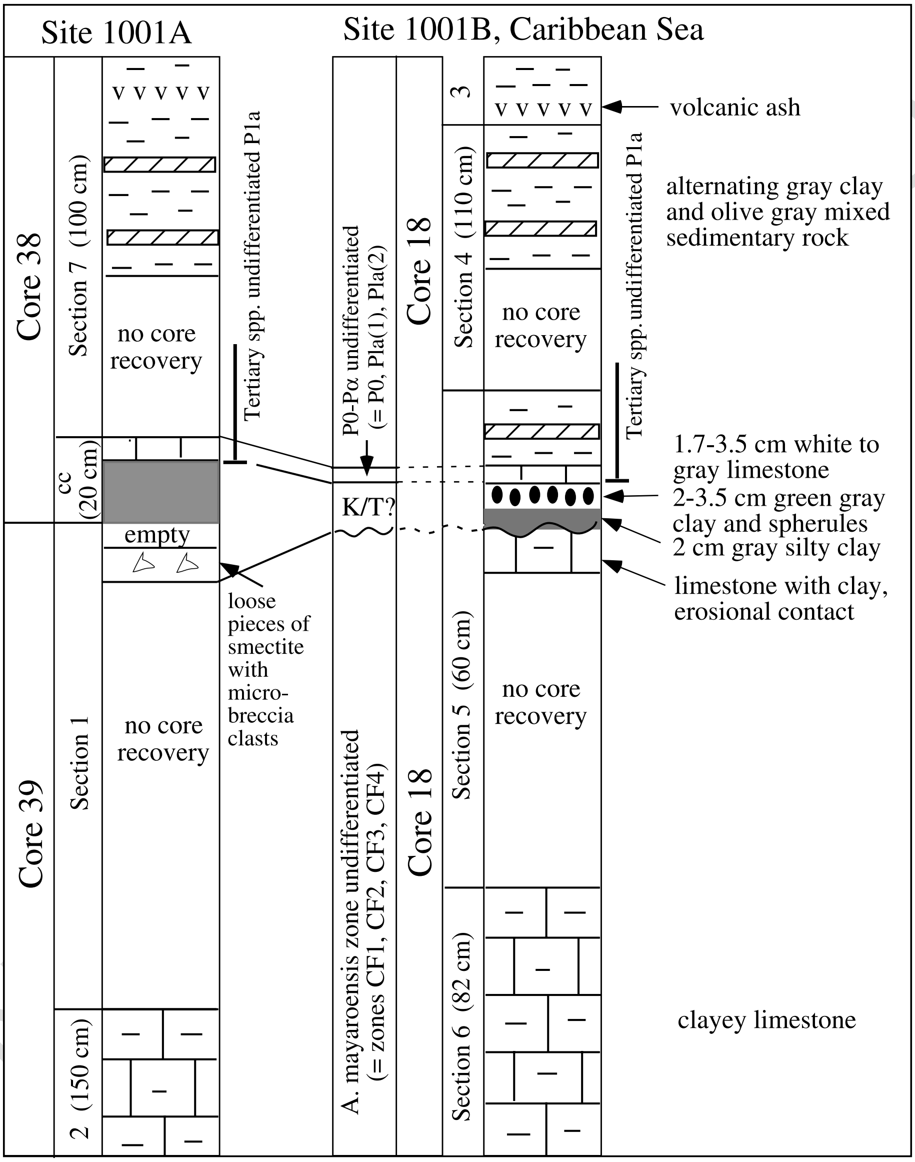

Fig. 16. Litho- and biostratigraphy of ODP Site 1001 Holes A and B in the Columbian Basin based on published data from Sigurdsson et al. (1997). Note that an incomplete K/T transition was recovered in a 2-cm thick gray silty clay and 2–3.5-cm-thick green clay and spherule layer that overlie an erosional surface of Late Maastrichtian limestone. Core recovery is poor and published biostratigraphic data provide poor age control that permit no conclusion regarding the precise placement of the spherule layer with respect to the K/T boundary.

thick bioclastic limestone with reworked spherules and spherule lenses overlies this unit in the more expanded sections and underlies a 5–15-cm-thick layer with well preserved black microtektites and microkrystites (Beloc 4a, Beloc 3, Figs. 14 and 15). An Ir anomaly was observed in zone Pla(l) in a clay layer in three outcrops above the spherule layers (Fig. 14, Stüben et al., 2002), and shocked minerals were reported by Leroux et al. (1995). A second Ir and PGE enrichment occurs in a 10-cm-thick volcanoclastic layer near the Pla(l)/Pla(2) boundary (Fig. 14). The clay fraction of the MM layers consists of an almost pure and very well crystallized Cheto smectite, similar to that observed in Belize, Guatemala and Mexico sections.

7. Deep sea sites

7.1. Caribbean ODP Sites 999 and 1001

Caribbean ODP Leg 165 cored several localities with the expectation of recovering an undisturbed and complete K/T transition to complement the MM deposits in Beloc, Haiti, 350 km to the north. The K/T boundary was recovered in two localities. At Site 999, located on Kogi Rise in the Colombian Basin at 2828-m depth, an incomplete K/T transition was recovered in a 2-cm-thick clayey layer in a calcareous limestone (Sigurdsson et al., 1997). At Site 1001, located on the Hess Escarpment at 32,600-m depth, the K/T boundary layer was recovered in two holes

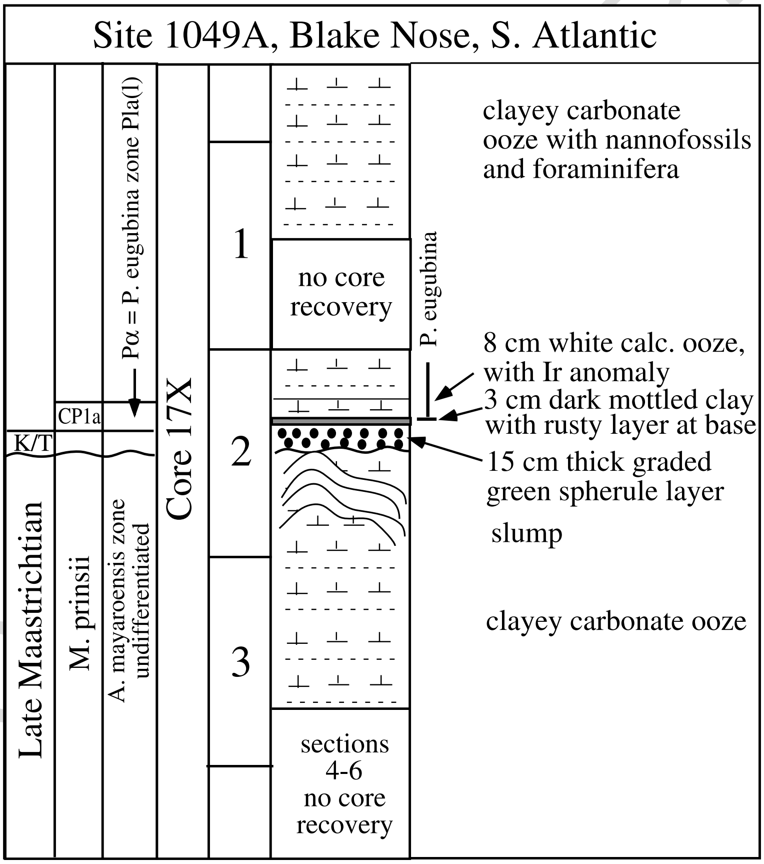

Fig. 17. Litho- and biostratigraphy of ODP Site 1049, Hole A, on Blake Nose off Florida based on published data from Norris et al. (1998) and Klaus et al. (2000). This section is very condensed as compared with Haiti or Mexico. The spherule layer overlies slumped Maastrichtian sediments where the latest Maastrichtian is missing. The Early Danian is condensed with Pla(l) directly above the spherule layer. The Ir anomaly is present in the 8-cm-thick calcareous ooze of subzone Pla(l) above the clay layer, similar to Beloc, Coxquihui and Actela and does not appear to be the K/T boundary anomaly.

only a few tens of meters apart, though core recovery is poor (Fig. 16). Hole 1001A recovered four loose pieces of green–gray smectite with microbreccia clasts in the core catcher (38Rcc) tentatively identified as the K/T boundary (Fig. 16, Sigurdsson et al., 1997). The first Danian planktic foraminifera are reported from the overlying gray limestone as a *G. cretacea* dominated undifferentiated P0–Pα interval (equivalent to zones P0, Pla(l) and Pla(2) of this study, Fig. 3). Hole1001B recovered a condensed undisturbed K/T boundary interval (Fig. 16). The K/T boundary consists of a 2-cm-thick clay and 2–3.5-cm-thick altered glass spherule layer that disconformably overlies Late Maastrichtian limestone. Above the clay layer is a 2–3.5-cm-thick green gray smectite clay with altered glass spherules. As in Hole 1001A, the fist Tertiary assemblage (undifferentiated P0–Pα) occurs in the overlying gray limestone. No iridium enrichment was detected in these two sections.

7.2. Northwest Atlantic ODP site 1049

ODP Site 1049 located on Blake Nose off eastern Florida at 2656-m depth contains a very condensed and incomplete K/T transition (Norris et al., 1998, 1999; Klaus et al., 2000), compared with sections in Haiti (Figs. 14 and 15). Hole 1049A contains the least disturbed K/T transition recovered in a dark layer of core 17X, Section 2 between 58 and 75 cm (Fig. 17). A 15-cm-thick graded green spherule layer (altered microtektites, microkrystites) with reworked Cretaceous foraminifera and clasts of limestone, chalk, and dolomite disconformably overlies slumped clayey carbonate ooze of *M. prinsii* zone age (Klaus et al., 2000). The Danian zone Pla index species *P. eugubina* first appears in the dark clay above this spherule layer (Huber et al., 2002). Ir anomaly and diverse Pla(1) assemblage are present in the overlying calcareous ooze (Martinez-Ruiz et al., 2001a,b).

8. Discussion

8.1. Early Danian Ir and Pd anomalies

There is widespread evidence for an Early Danian *P. eugubina* subzone Pla(l) Ir anomaly in Haiti, Guatemala and Mexico (Figs. 8–15; Keller et al., 2001; Stinnesbeck et al., 2002; Stüben et al., 2002). This Ir anomaly is generally above the altered microtektite and microkrystite deposits of the Early Danian and represents a unique unrelated event. In contrast, no spherule deposits are directly associated with Ir enrichments above background values. Stüben et al. (2002) and Stinnesbeck et al. (2002) concluded that at Beloc and Coxquihui, the chondrite-normalized PGE patterns associated with the Ir anomalies indicate a cosmic origin with higher Ir values compared to Pt and Pd. As a result of different chemical behaviors, the PGE distribution patterns are modified during endogenic and exogenic evolution. During evolution of evolving magmas, chondrite-normalised PGEs tend to become increasingly enriched as compared to Ir (Keays, 1995).

Above the *P. eugubina* subzone Pla(l)/Pla(2) boundary is a second PGE anomaly (Pd, and minor Ir enrichments) in marly or volcanoclastic layers at Beloc and Bochil (Figs. 5 and 10). All PGEs are enriched in this interval and the PGE pattern is basalt-like, suggesting a volcanic source (Stüben et al., 2002). Clayey or volcanoclastic layers at this stratigraphic interval have also been observed in sections from Belize, Guatemala, Mexico and ODP Site 1001 (Sigurdsson et al., 1997). The origin of this Pd anomaly is discussed in Stüben et al. (2002, in preparation).

8.2. Biostratigraphy of impact ejecta layers

Impact spherule deposits from Central America, Haiti and the Gulf of Mexico are often interpreted as of K/T boundary age based on the dual assumptions that they are ejecta from the Chicxulub impact, and that this impact occurred precisely at the K/T boundary. Frequently, these assumptions are made in the absence of biostratigraphic data (e.g. Sigurdsson et al., 1991; Smit et al., 1996; Smit, 1999), or contrary to biostratigraphic data that reveal Early Danian species in the microtektite and microkrystite deposits, but nevertheless lead authors to interpret the deposits as of K/T boundary age (e.g. Maurasse and Sen, 1991; Lamolda et al., 1997; Fourcade et al., 1998, 1999; Smit, 1999). We have demonstrated that there is clear stratigraphic separation of altered impact glass spherule layers, iridium and PGE anomalies that indicate multiple impacts (Figs. 4–17). Furthermore, biostratigraphic data based on planktic foraminifera provide consistently high resolution age control that reveals

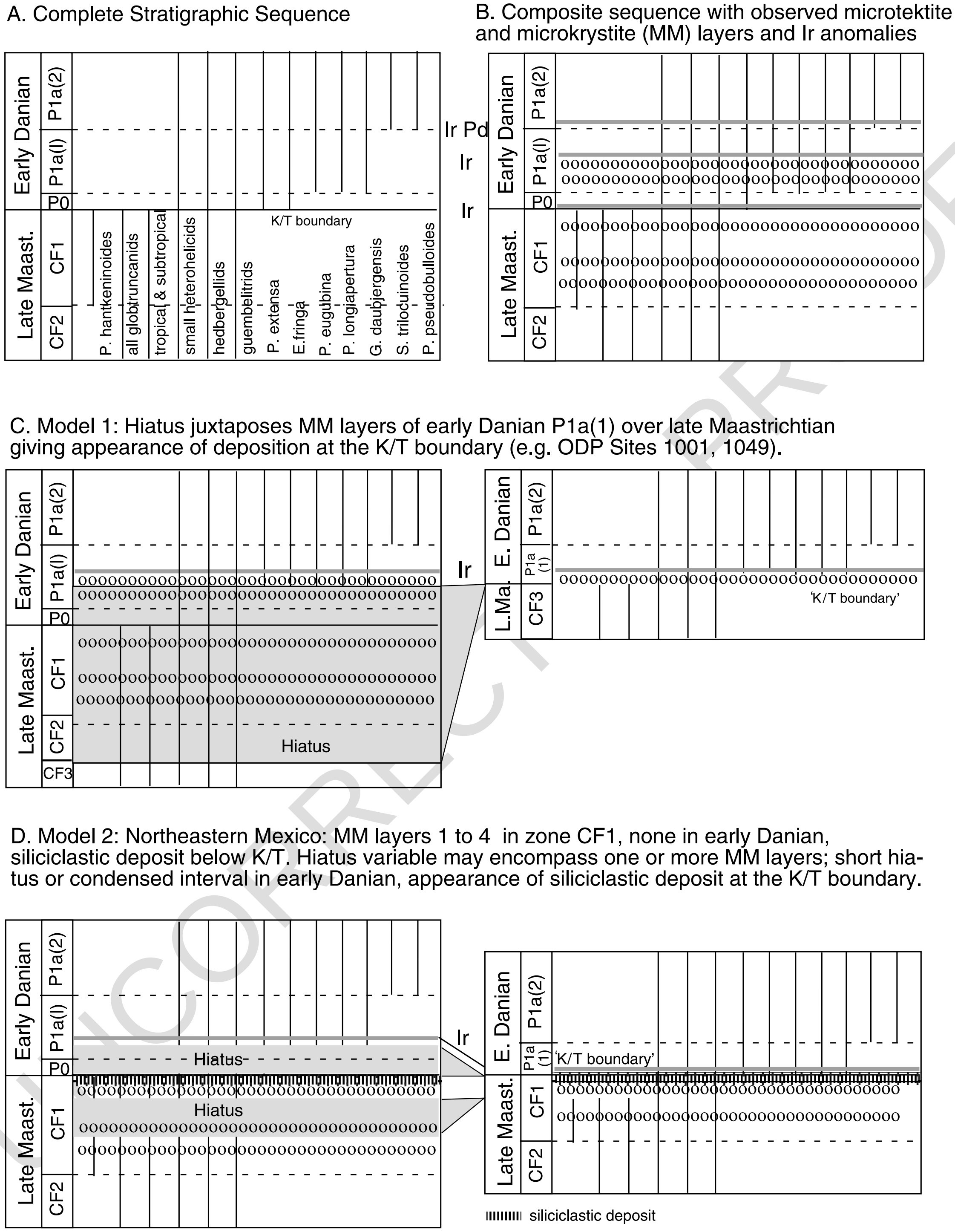

Fig. 18. (A, B) Model showing how variable erosion and reworking can explain the presence of multiple spherule layers above and below the K/T boundary as originating from one single Late Maastrichtian event. See text for details.

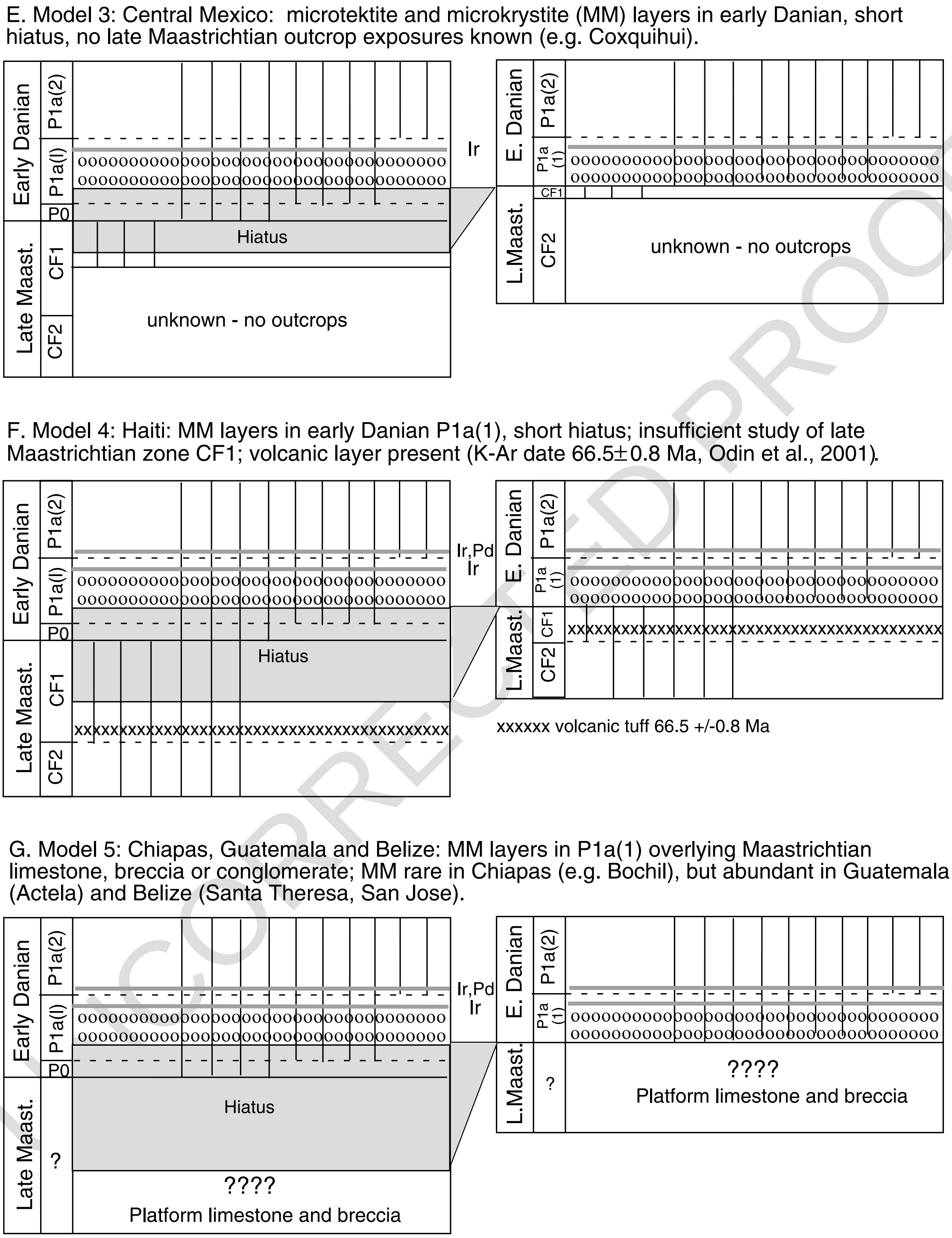

Fig. 18 (*continued*).

impact ejecta deposits in the Late Maastrichtian zone CF1 and Early Danian zone Pla(l) and indicate multiple impacts occurred over a period of at last 400,000 years.

We have also shown that the biostratigraphy of altered impact glass ejecta is complex and variable throughout Mexico, Guatemala, Belize, Haiti and the Caribbean Sea as a result of paleodepths, depositional environments and hiatuses. Known sections with microtektite and microkrystite (MM) deposits include depositional environments spanning from shallow carbonate platforms where MM are often found in microconglomerates, microbreccias or breccias (e.g. Belize, Guatemala and Chiapas in southern Mexico), to outer shelf–upper bathyal (central Mexico) or upper bathyal environments with shallow water transport and terrigenous influx from the Sierra Madre Oriental (northeastern Mexico) and to the deep-sea bathyal environments with predominantly pelagic deposition (Sites 1001 and 1049). Each of these paleoenvironments was affected differently by sediment deposition and erosion due to tectonic activity, sea level changes and paleocurrents, as well as slumps and channelized current transport that acted independently of the MM spherule deposition event(s), although the latter likely produced additional disturbances.

Determining the original MM depositional event(s) is, therefore, a daunting task that requires a regional approach and the integration of sections from shallow to deep and spanning up to a million years encompassing chron 29R. Determining whether impact ejecta deposits represent a single impact event precisely at the K/T boundary, predate or postdate the boundary, or represent multiple impact events, requires detailed quantitative biostratigraphy, analysis of the nature of impact glass as well as iridium and PGE anomalies. Age control for the altered impact glass (MM) layers, microbreccias and microconglomerates with altered glass spherules can be obtained by biostratigraphic analysis of characteristic Late Cretaceous and small (36–100 μm) Early Danian planktic foraminifera within matrix and clasts. Foraminiferal species of marl and MM-rich clasts provide the age of deposition prior to erosion and redeposition, whereas the matrix between the MM clasts indicates the age of redeposition. High-resolution biostratigraphy allows deconstruction of the depositional sequences as shown in models 1–5 (Fig. 18A,B).

8.3. Deconstructing the depositional sequence

A complete biostratigraphic sequence contains all biozones and biomarkers as shown in Fig. 18A. A composite sequence with the observed spherule layers, Ir and Pd anomalies is shown in Fig. 18B. The observed variable number of spherule layers and their stratigraphic positions can be explained by the depositional environment and hiatuses (Fig. 18A,B).

Model 1 shows a possible scenario for deep sea Sites 1001 and 1049 (Figs. 16 and 17), where the MM layer juxtaposes part of the Early Danian subzone Pla(l) over Late Maastrichtian sediments with zone CF1 missing (Fig. 18C). This gives the appearance of a "K/T boundary" MM deposit, though it could have been deposited anytime between CF1 and the lower part of Pla(l). Microfossil and paleomagnetic data indicate that the Late Maastrichtian zones CF1 and CF2 and most of the Early Danian *P. eugubina* zone are missing (Figs. 16 and 17, Sigurdsson et al., 1997; Norris et al., 1998; Huber et al., 2002). Model 2 shows deposition in the upper bathyal environment of northeastern Mexico where the variable number of MM layers can be explained by variable erosion and topography (Fig. 18D). The absence of (reworked) MM layers in the basal Tertiary may be due to depletion of the original source deposit from which reworking occurred. Model 3 shows MM deposition in an outer shelf to upper bathyal environment at Coxquihui in central Mexico where the siliciclastic deposit is absent and the MM layers are in the Early Danian subzone Pla(l) (Figs. 8 and 18E). A 1-cm MM layer juxtaposes part of the Early Danian subzone Pla(l) over Late Maastrichtian zone CF1 (Stinnesbeck et al., 2002). A 60-cm-thick MM layer in the Early Danian subzone Pla(l) has been previously identified as K/T age (Smit, 1999; Arz et al., 2002). No evaluation of latest Maastrichtian spherule layers or sediment deposition can be made at Coxquihui (or Tlaxcalantongo) due to limited outcrop exposures. Model 4 shows MM deposition in an upper bathyal environment in Haiti (Beloc, Figs. 14 and 15) where spherule layers are in Early Danian sediments and a volcanic ash layer is present in the Late Maastrichtian zone CF1 (Fig. 18F). The base of the lowermost MM layer in subzone Pla(l) disconformably overlies Late Maastrichtian zone CF1 sediments marking a short hiatus. A systematic examination of Late Maastrichtian sediments for possible spherule deposits has yet to be done. Model 5 shows spherule deposition on carbonate platform environments in Chiapas, Guatemala and Belize (Fig. 18G). In these shallow water environments, thick MM deposits are present in Belize and Guatemala in microconglomerate, microbreccia and breccia deposits of the Early Danian subzone Pla(l) (Figs. 12 and 13), but relatively rare in Chiapas (Bochil, Fig. 9). A hiatus marks the lower part of the Early Danian and the MM-rich deposits overlie platform limestone, conglomerate or breccia of indeterminate Late Maastrichtian age.

We conclude that MM deposits in Central America and the Caribbean show two distinct temporal and spatial distribution patterns in the Late Maastrichtian and Early Danian (Fig. 19). But it cannot be demonstrated that the impact event that produced the microtektites and microkrystites occurred precisely at the K/T boundary, as identified by standard criteria (e.g. first Danian species of zone P0, boundary clay, red layer, Ir and PGE anomalies, carbon-13 shift, Fig. 2). Though the ubiquitous presence of disconformities, hiatuses and condensed sequences tend to create the appearance of a K/T boundary event. The data support a pre-K/T impact event in zone CF1 and a post-K/T impact in zone Pla(l), in addition to the well-known K/T event.

8.4. Age of impacts and impact craters

8.4.1. Late Maastrichtian zone CF1 impact

The age of the pre-K/T impact is 65.27 ± 0.03 Ma based on average sediment accumulation rates of 3 cm/ky for zone CF1 as determined from northeastern Mexico sections (Figs. 5 and 6, details in Section 3.1). This age is supported by planktic foraminiferal assemblages that indicate the oldest MM layer (as well as MM layers 2 and 3) was deposited within an interval of global warming between 65.4 and 65.2 Ma (Fig. 20, Li and Keller, 1998b).

8.4.2. K/T boundary impact

There is strong evidence from Ir and PGE anomalies worldwide for a major K/T boundary impact (65.0 Ma), but this record is largely missing in the Caribbean, Gulf of Mexico and surrounding continental shelf area due to widespread erosion (Keller et al., 1993).

8.4.3. Early Danian P. eugubina subzone Pla(l) impact

An Ir anomaly with a chondritic PGE pattern has been observed in subzone Pla(l) above the spherule deposits at five localities (Actela, Beloc, Coxquihui, Trinitaria and Bochil; (Figs. 8, 9, 11, 12 and 15)) and is tentatively identified as an Early Danian impact event (see Stüben et al., 2002; Kramer et al., 2001). The Early Danian subzone Pla(l) MM layers are below the Ir and PGE anomalies.

8.4.4. Impact craters

Three impact craters have now been dated as near K/T boundary age and provide strong support for multiple impacts. The 24-km-wide Boltysh crater of Ukraine is dated at 65.2 ± 0.6 Ma (Kelley and Gurov, 2002), and the 12-km-wide Silverpit crater of the North Sea at about 65 Ma (Stewart and Allen, 2002). The 120-km-wide Chicxulub crater has $^{40}Ar/^{39}Ar$ ages varying from 65.0 to 65.2 and 65.4 Ma (Izett et al., 1991; Sharpton et al., 1992; Swisher et al., 1992). Based on the presence and stratigraphic position of impact glass spherule layers in northeastern Mexico, we conclude that the oldest microtektite and microkrystite layers represent the Chicxulub. The altered MM layer(s) of northeastern Mexico was previously linked to Chicxulub based on the chemical similarity of melt rock (Izett et al., 1991; Sigurdsson et al., 1991; Koeberl et al., 1994), the abundance and geographic distribution of impact ejecta within a 1000-km radius of Chicxulub. The variable $^{40}Ar/^{39}Ar$ ages of Chicxulub are well within the estimated age of 65.27 ± 0.03 Ma for the oldest ejecta layer in northeastern Mexico based on stratigraphic evidence. Impacts that created the Boltysh and Silverpit craters may have been too small to register very large and geographically widespread ejecta layers, though a systematic search has yet to be done. These impacts, however, would have significantly contributed to the greenhouse effect and climate warming that imperiled an already fragile ecosystem and hastened the terminal decline of planktic foraminifera. If the Chicxulub crater predates the K/T boundary, the K/T boundary impact crater is still to be found. A potential candidate that deserves serious consideration is the Shiva structure on the western continental shelf of India that may have triggered eruption of the Deccan volcanic eruptions (Chatterjee, 1997).

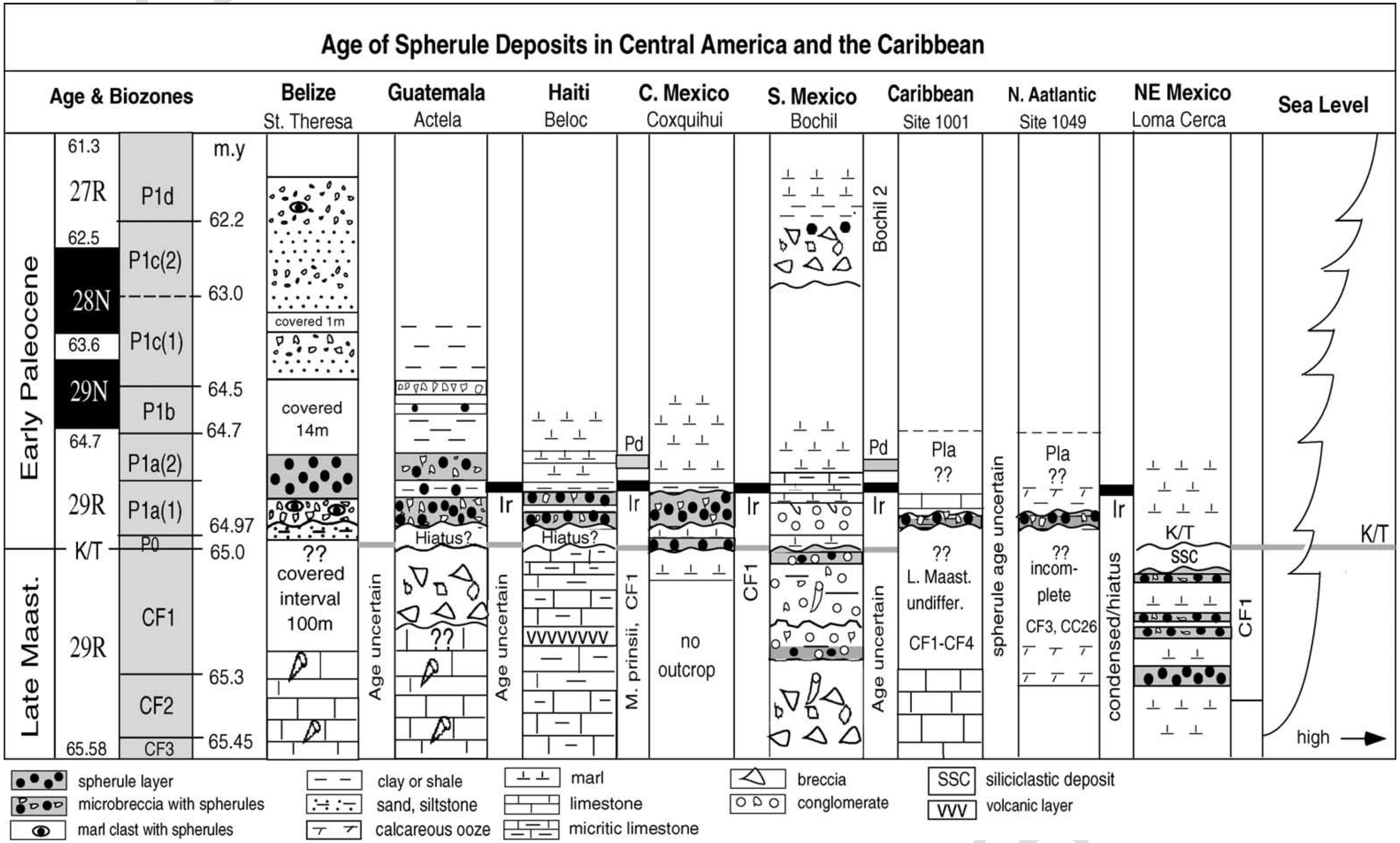

Fig. 19. Stratigraphic summary of altered impact glass spherule deposits and Ir anomalies in Central America, Gulf of Mexico and Caribbean. Note that no spherule deposits are known from precisely the K/T boundary. In all sections, the spherules are either in Early Danian sediments and likely reworked, or stratigraphically within the Late Maastrichtian (NE Mexico) where the oldest spherule layer predates the K/T boundary by 270–300 ky. Widespread erosion across the K/T transition is generally related to sea level fluctuations. Note that the Ir anomaly in the Early Danian subzone Pla(l) is tentatively identified as an impact event.

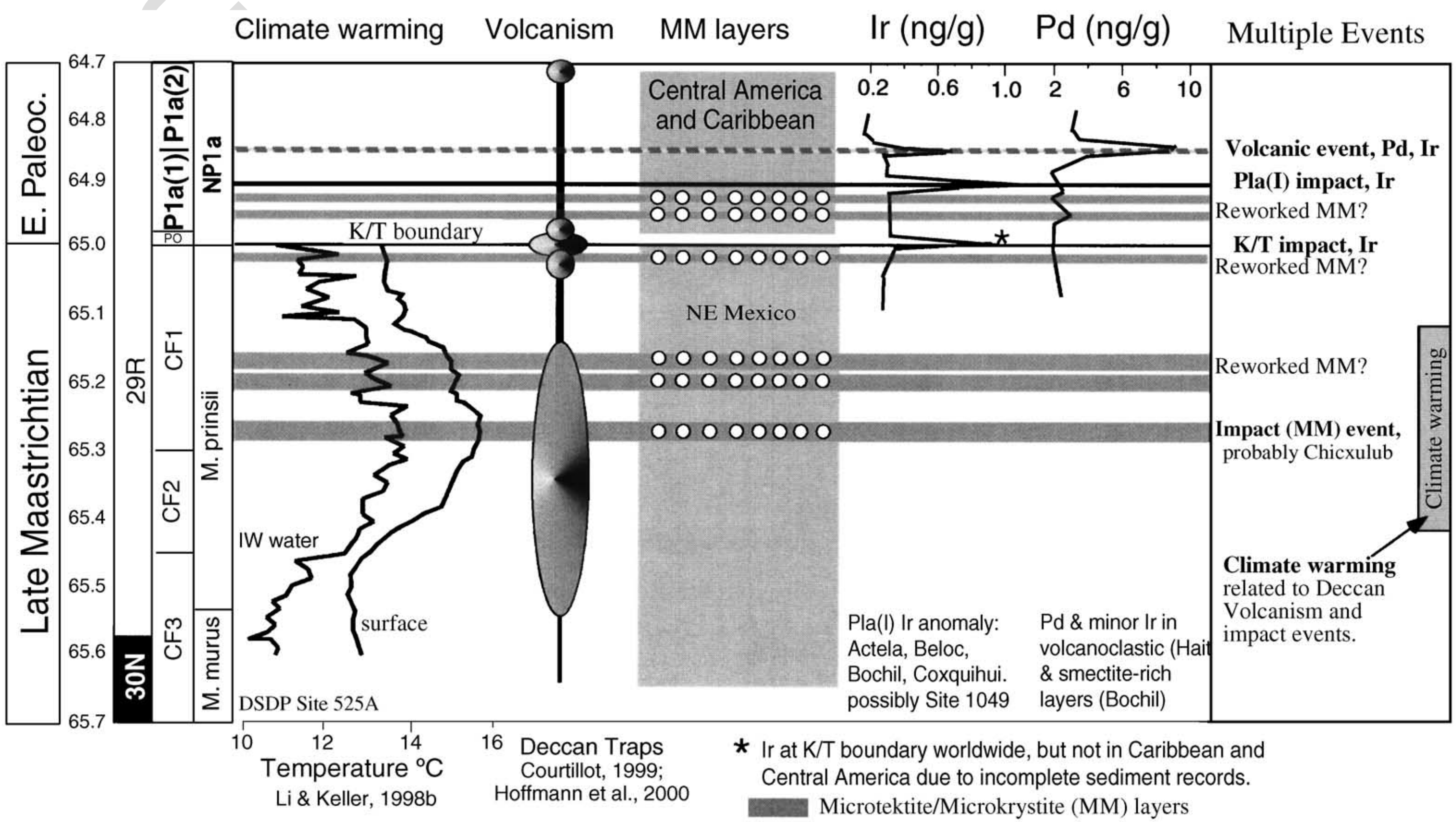

Fig. 20. Multiple impact K/T scenario based on impact glass spherule deposits and Ir anomalies in the Gulf of Mexico, Caribbean and Central American. The oldest impact glass spherule layer is dated at 65.27 ± 0.03 Ma and is linked to the Chicxulub event based on glass chemistry. This impact event coincides with the global climate warming between 65.2 and 65.4 Ma (Li and Keller, 1998b) and peak intensity of Deccan volcanism (Hoffman et al., 2000). Younger impact glass spherule layers in the Late Maastrichtian and Early Danian may be repeatedly reworked as a result of sea level fluctuations. The K/T boundary event is generally absent in the region due to erosion and tectonic activity (Keller et al., 1993). A widespread Ir anomaly in the Early Danian subzone Pla(1) is tentatively identified as an Early Danian impact event, and a Pd anomaly and minor Ir anomaly at the Pla(l)/Pla(2) transition may be related to a regional volcanic event.

The Early Danian subzone Pla(l) impact at about 64.9 Ma is tentatively identified based on Ir anomalies in five sections (Beloc, Bochil, Trinitaria, Coxquihui and Actela) and requires further study. Most impact related studies have concentrated on the K/T boundary and neither Early Danian nor Late Maastrichtian sediments have been systematically analyzed for impact ejecta and PGEs. No likely crater is known to us. New evidence for multiple impacts justifies systematic evaluation of both these time intervals. One such study currently concentrates on deep-sea cores where impact markers have been determined in pre-K/T sediments from the Pacific Ocean (Hagstrum and Abbott, 2002). Multiple impacts have been advocated for some time based on astrophysical theories (see Hut et al., 1987; Bailey et al., 1994; Napier, 1998, 2001). The increasing number of impact craters detected in Paleozoic sediments of Australia and elsewhere (Glikson, 2001) provides solid evidence that extraterrestrial events are neither unique nor uncommon.

8.5. Biotic crisis

The sudden mass extinction of planktic foraminifera is often cited as the defining criteria for the single impact scenario (Smit, 1999). Though this simplified view does not account for the complexities of faunal turnovers preceding the K/T boundary (see review in Keller, 2001). Cretaceous planktic foraminifera reached maximum sustained diversity of 55–65 species between 69.5 and 65.5 Ma. This time period was associated with a global cooling trend, upwelling, high productivity and increased watermass stratification that resulted in increased niche availability for species (Li and Keller, 1998a,b; Abramovich et al., 2003). The last 0.5 my of the Maastrichtian are characterized by a series of extreme climate changes including maximum global cooling at 65.5 Ma, followed by 3–4 °C warming between 65.4 and 65.2 Ma (Li and Keller, 1998c) that resulted in reduced watermass stratification, decreased productivity and decreased abundance of most subsurface dwellers (e.g. globotruncanids) which became very rare and disappeared from many regions (Keller, 1996, 2001; Abramovich et al., 1998, 2003; Kucera and Malmgren, 1998). This biotic crisis occurred at a time of major Deccan volcanism (Hoffman et al., 2000) and a major impact (Chicxulub?) that produced the microtektite and microkrystite deposits in Mexico, Guatemala, Belize and Haiti.

The extinction of all large complex tropical and subtropical species, or two-thirds of the species assemblage, culminated at the K/T boundary coincident with another major impact. Although the extinct group reduced diversity by two-thirds, these species accounted for less than 10% of the total foraminiferal population, whereas the bulk of the survivor species population dramatically decreased and disappeared during the Early Danian zone Pla. The mass extinction of the tropical–subtropical species by K/T boundary time, thus, provides a reliable biomarker, but the kill-effect of the K/T impact event is often overestimated since these species were already on the brink of extinction due to preceding environmental changes. The terminal decline in species abundance populations of this group began at the onset of the global warming between 65.4 and 65.2 Ma and accelerated during the last 100 ky of the Maastrichtian (Keller, 2001). The only survivors of the K/T mass extinction were small species able to tolerate a wide range of environmental conditions (e.g. hedbergellids, heterohelicids and guembelitrids). Most of these species disappeared in the Early Danian zone Pla possibly as a result of competition from the rapidly evolving Early Danian species and further environmental deterioration associated with a third impact.

9. Impact scenarios

9.1. K/T impact at Chicxulub

All spherules originated from the Chicxulub impact at the K/T boundary and their stratigraphic emplacement in Late Maastrichtian and Early Danian sediments is the result of slumps, gravity flows, mass wasting, margin collapse due to seismic shaking, tsunamis and reworking into younger sediments as a result of current activity.

This is the standard K/T impact scenario. It gains some support from slumps on the slope of Blake Nose, off Florida (Klaus et al., 2000; Norris et al., 2000), and small-scale folds (2–10 m) at Beloc, Haiti and in the La Sierrita area of northeastern Mexico (Soria et al., 2001; Keller et al., 2002a,b). But small-scale slumps are common occurrences in any upper bathyal and slope settings. The scenario suffers from the lack of evidence for large-scale pervasive slumping throughout the region that would be expected in response to the cataclysmic seismicity generated by the Chicxulub impact. The age of the 700-m-thick clastic sequence of the Cacarajicara Formation of Cuba that includes breccia and boulder is attributed to the K/T impact (Bralower et al., 1998; Kiyokawa et al., 2002), but the age remains uncertain. The 70-m-thick graded breccia with large (5 m) platform limestone blocks at Bochil has been interpreted as impact-related margin collapse (Smit, 1999), though only the 1-m-thick microconglomerate at the top contains impact evidence (Fig. 9). Similar breccias occur repeatedly in the Campanian–Maastrichtian sequences and have been interpreted as collapsed platform carbonates due to tectonic activity (Michaud and Fourcade, 1989). The siliciclastic deposits of northeastern Mexico, previously interpreted as tsunami deposits, are bioturbated and indicate deposition over a longer time period (Keller et al., 1997; Ekdale and Stinnesbeck, 1998). Moreover, the impact-induced slump hypothesis can only attempt to explain spherules in Maastrichtian sediments but not those in the Early Danian, which must have been reworked from an older deposit.

One explanation for the multiple spherule layers interbedded in normal pelagic sediments of the Mendez Formation in northeastern Mexico is downslope movement of large slump blocks that essentially preserve the stratigraphic succession as suggested for Blake Nose (Klaus et al., 2000; Norris et al., 2000). In northeastern Mexico, where two and three spherule layers are separated by up to 4 m of normally stratified marls without evidence of disturbance, slump blocks would have had to occur in triple succession, each preserving the spherule layer and gently depositing the next slump block without disturbing the underlying slump and spherule layer. This seems highly unlikely if not impossible but also begs the question as to where the additional spherule layers came from once the original deposit slumped downslope and was emplaced.

9.2. Pre-K/T impact at 65.27 Ma

The stratigraphically oldest microtektite and microkrystite layer represents an impact event about 270 ± 30 ky before the K/T boundary and subsequent spherule deposits are reworked by periodic current activity.

This hypothesis is supported by the stratigraphic position of the oldest altered impact MM layer in many sections in northeastern Mexico (Affolter, 2000; Lindenmaier, 1999; Schilli, 2000; Keller et al., 2002a), the high concentration of altered MM and absence of reworked clasts or foraminifera, presence of amalgamated and fused spherules suggesting rapid sinking as rafts (Figs. 4a,b and 5, Schulte et al., in press) and the gradation to normal hemipelagic sedimentation at the top. Support for reworking of the other MM layers in Late Maastrichtian sediments includes the presence of common marl clasts, reworked planktic and benthic foraminifera and transported shallow water benthic foraminifera. Support for reworked MM layers into Early Danian sediments includes the frequent presence of Maastrichtian limestone clasts and foraminifera, although clasts with Early Danian foraminiferal assemblages are also present and suggest a phase of Danian reworking. In the Beloc, Haiti sections, Cretaceous tropical species are commonly present in the MM layers of the Early Danian zone Pla and clearly indicate a reworked component from Late Maastrichtian sediments (Keller et al., 2001).

9.3. Multiple impacts

The K/T transition is a time of multiple impact and volcanic events and accompanying climate changes during the last 500 ky of the Maastrichtian and continuing into the Early Danian *P. eugubina* zone.

A sequence of three impact events and one volcanic event can be identified in the Gulf of Mexico, Caribbean and Central America as summarized in Fig. 20. The oldest ejecta (microtektite and microkrystite) layer in northeastern Mexico provides strong support for a pre-K/T impact at about 65.27 ± 0.03 Ma. Closely associated with this time interval is a major pulse in Deccan volcanism (Courtilot, 1999; Hoffman et al., 2000), coeval major greenhouse warming (Fig. 20), decrease in productivity (Barrera, 1994; Li and Keller, 1998b) and decline in planktic foraminiferal populations (Keller, 1996, 2001). This impact ejecta may represent the Chicxulub event, as suggested by glass geochemistry, abundance and geographic distribution.

Younger ejecta layers may have been reworked and redeposited from the original event by current and tectonic activity, though an additional impact event in the Late Maastrichtian cannot be ruled out. The second impact at the K/T boundary is characterized worldwide by an Ir anomaly, major drop in primary productivity and mass extinction of all tropical and subtropical planktic foraminifera. Sediments representing this event are largely absent in the Caribbean and Central America as a result of erosion due to tectonic and current (Gulf Stream) activities (Keller et al., 1993).

A third impact is tentatively identified based on an iridium anomaly in the *P. eugubina* subzone (Pla(l)) (Figs. 8, 9, 11, 12, 15 and 19). In each locality, the Ir anomaly is stratigraphically above the spherule layer and separated from it by a layer of marl, shale, clay or cross-bedded bioclastic limestone. Diffusion or reworking from the K/T boundary event and re-deposition into distinct peaked anomalies some 100,000 years later in widely separated localities is very unlikely (Sawlowicz, 1993; Kramar et al., 2001). In a detailed analysis of the REE and PGE elements of the Beloc and Coxquihui sections, Stüben et al. (2002) and Stinnesbeck et al. (2002) concluded that the Ir-dominated anomaly of platinum group elements (PGEs) has an almost chondritic abundance pattern and appears to be of cosmic, rather than volcanic, origin. The widespread nature of this anomaly indicates an Early Danian impact event in the *P. eugubina* subzone Pla(l) about 100 ky after the K/T boundary.

A volcanic event is identified near the *P. eugubina* subzone Pla(l)/Pla(2) boundary based on a volcanic-rich layer at Beloc, Haiti, that contains a second anomaly enriched in all PGEs, but particularly Pd (8.9 ng/g), Pt (6.2 ng/g) and Ir (0.6 ng/g, Fig. 15). A PGE anomaly in the same stratigraphic interval is also observed at Bochil-1 with Pd (5.8 ng/g) and Ir (0.6 ng/g) enrichments and a basalt-like PGE pattern that suggests some volcanic input (Fig. 5). A systematic investigation of this event is in progress (Stüben et al., in preparation).

10. Conclusion

A multiimpact scenario is most consistent with current evidence of altered impact glass (microtektites, microkrystites), Ir anomalies, PGEs, volcanic activity and climate change during the Late Maastrichtian to Early Danian as summarized in Fig. 20. Current evidence supports three impact events over a period of about 400 ky. The first impact, marked by the oldest deposit of altered microtektites and microkrystites (MM) occurred at about 65.27 ± 0.03 Ma nearly coincident with major Deccan volcanism that likely contributed to the rapid global warming between 65.4 and 65.2 Ma and began the terminal decline in planktic foraminiferal populations. Subsequent Late Maastrichtian and Early Danian altered MM layers may have been repeatedly reworked and redeposited from this event by currents during low sea levels and tectonic activity, though an additional spherule-producing event cannot be completely ruled out. The second impact is the well-known K/T boundary event (65.0 Ma) marked worldwide by an Ir anomaly and other cosmic signals, though this event is not well represented in the Caribbean and Central America due to erosion as a result of current and tectonic activity. The K/T boundary impact coincides with the demise of all tropical and subtropical planktic foraminiferal species and a drop in primary productivity. The third impact is more tentatively identified by an Ir anomaly in five sections (Haiti, Guatemala and Mexico) in the Early Danian *P. eugubina* subzone Pla(l) about 100 ky after the K/T boundary (64.9 Ma). This event may have been responsible for the demise of Cretaceous survivor species and the delayed recovery after the K/T impact event. Late Maastrichtian and Early Danian sequences need to be investigated for impact signals outside the Caribbean and Central America to determine the global physical and biotic effects of these cosmic events.

Acknowledgements

We thank Andrew Glikson for a tremendously helpful review and for liberally sharing his knowledge with us. We also thank Robert Hargraves for his many stimulating discussions and his untiring pursuit of impacts. This study has benefited from various student projects in Mexico over the past 6 years and we gratefully acknowledge the contributions by W. Affolter, C. Ifrim, M. Lindinger, L. Schilli and P. Schulte. We also thank Brian Holland, Belize Minerals, and Jorge de la Cruz and Carlos de Leon, Perenco, Guatemala, for many lively discussions and field guidance in Belize and Guatemala. We are grateful to J.G. Lopez-Oliva for logistical support and making facilities available at the Geology Department of the University of Nuevo Leon, Linares, G. L. Julio Cesar (Instituto Mexicano del Petroleo) for logistical information of the Bochil-1 and Trinitaria sections and Markus Harting (Institut for Minearlogy and Geochemistry, University of Karlsruhe) for PGE analysis of the Actela section. Research was supported by the German Science Foundation grants STI 128/7-1 and -2 and STU 169/10-2, the Swiss National Fund no. 8220-028367 (TA) and NSF Grant EAR-0207407 (GK).

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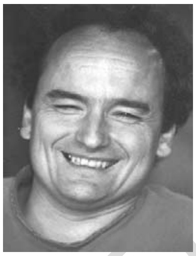

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