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Multiple spherule layers in the late Maastrichtian of northeastern Mexico

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ABSTRACT

The discovery of as many as 4 spherule layers within 10 m of pelagic marls below the sandstone-siltstone complex and Cretaceous-Tertiary (K-T) boundary in the La Sierrita area of northeastern Mexico reveals a more complex K-T scenario than previously imagined. These spherule layers were deposited within pelagic marls of the Mendez Formation; the oldest layer is as much as 10 m below the K-T boundary. The marls are of latest Maastrichtian calcareous nannofossil *Micula prinsii* zone and planktic foraminiferal zone CF1 (*Plummerita hantkeninoides*) age; the latter spans the last 300 k.y. of the Maastrichtian. The oldest spherule layer was deposited near the base of zone CF1 and marks the original spherule-producing event. This is indicated by the presence of a few marl clasts and benthic foraminifera that are frequently surrounded by welded glass, and many welded spherules with schlieren features, indicating that deposition occurred while the glass was still hot and ductile. It is possible that some, or all, of the three stratigraphically younger spherule layers have been reworked from the original spherule deposit, as suggested by the common marl clasts, terrigenous input, reworked benthic and planktic foraminifera, and clusters of agglutinated spherules. These data indicate that at least one spherule-producing event occurred during the late Maastrichtian and provide strong evidence for multiple catastrophic events across the K-T transition.

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INTRODUCTION

In 1990, glass spherule deposits were discovered in sediments at the Cretaceous-Tertiary (K-T) boundary at Beloc, Haiti, and subsequently similar glass spherule deposits were discovered in K-T deposits at Mimbral and many other localities in northeastern Mexico (Izett et al., 1990; Smit et al., 1992, 1996; Stinnesbeck et al., 1993; Keller et al., 1997). The chemical similarity of the glass spherules with melt rock in subsurface samples at Chicxulub led many workers to interpret an impact origin for the glass spherules and Chicxulub as the impact crater (Izett et al., 1990; Sigurdsson et al., 1991; Koeberl, 1993; Koeber et al., 1994).

However, on the basis of the Haiti sections, some workers suggested that volcanism (Lyons and Officer, 1992), two impacts (Leroux et al., 1995), or one impact and one volcanic event (Jéhanno et al., 1992) produced the stratigraphically separated glass spherules, shocked quartz, and iridium anomaly. Recent analyses of new and more complete K-T boundary sections at Beloc, Haiti, revealed that the glass spherules were deposited in the early Danian *Parvularugoglobigerina eugubina* zone ~100 k.y. after the K-T boundary (Stinnesbeck et al., 2000; Keller et al., 2001). A spherule deposit in the *P. eugubina* zone was also observed above a thick breccia in the Caribe section of Guatemala (Fourcade et al., 1998, 1999; Keller and Stinnesbeck, 2000). In addition, a new K-T section at Coxquihui, Mexico, also revealed deposition of a spherule layer within the early Danian *P. eugubina* zone (Stinnesbeck et al., in press). In all three localities, and in addition to the well-known K-T Ir anomaly, a small but significant iridium anomaly was also observed immediately above the early Danian spherule layer, and rare shocked minerals are also present. Although it is possible that the early Danian spherule layer and Ir anomalies in Haiti, Guatemala, and Mexico are reworked from older original deposits, an early Danian impact event cannot be ruled out.

An impact event at the K-T boundary is generally accepted and well documented based on a global iridium anomaly, shocked quartz, and Ni-rich spinels (Alvarez et al., 1992; Robin et al., 1992; Rocchia et al., 1996), the extinction of all tropical and subtropical planktic foraminifera and many calcareous nannofossil species (see summaries in D'Hondt et al., 1996; Keller et al., 1995; Pospichal, 1996). It is also widely accepted that the Chicxulub crater represents this K-T boundary impact event, based on the stratigraphic position of the glass spherules near the K-T boundary in sections in Haiti and Mexico (Alvarez et al., 1992; Smit et al., 1992, 1996), their chemical similarity with melt rock in subsurface cores at Chicxulub (Izett et al., 1990; Sigurdsson et al., 1991; Blum and Chamberlain, 1992; Blum et al., 1993; Koeberl, 1993; Koeberl et al., 1994), and an $^{40}Ar/^{39}Ar$ age of ca. 65 Ma of the spherules and melt rock (Izett et al., 1990; Swisher et al., 1992; Dalrymple et al., 1993). However, the age and origin of the glass spherules are still disputed.

In a continuing effort to determine the age and origin of the glass spherules in northeastern Mexico, a major study was undertaken by us and a group of students to map and examine the sandstone-siltstone complex and underlying late Maastrichtian sediments over 50 km in the La Sierrita area of northeastern Mexico (Fig. 1, Lindenmaier, 1999; Schulte, 1999; Schilli, 2000, Affolter, 2000). The results are surprising: of more than 24 sections examined below the sandstone-siltstone complex, nearly all contain as many as 4 distinct spherule layers, often separated by several meters of pelagic marls of the Mendez Formation (Fig. 2). Here we report the stratigraphic results of one of these sections at Loma Cerca, and address specifically: (1) the age of the spherule layers; (2) the likelihood that the oldest layer is the original spherule-producing event and that the other layers are reworked; (3) environmental changes associated with the spherule event(s); and (4) the implications of this discovery for impact scenarios.

Lithology of spherule-bearing deposits

Cretaceous-Tertiary (K-T) boundary sequences in the La Sierrita area form a northwest-southeast-trending series of low-lying hills that consist of Maastrichtian marls of the Mendez Formation. The top of these hills is formed by a resistant sandstone-siltstone complex that varies in thickness from 0.20 cm to 4 m in the La Sierrita sections (Figs. 2 and 3) and 8 m in the Peñon section (Stinnesbeck et al., 1996). A small iridium anomaly is generally present beginning at the top of this depositional complex and reaches peak abundance in the overlying early Danian marls (Smit et al., 1992; Keller et al., 1997). Some workers suggested that this sandstone-siltstone complex (including the spherule layer at its base) and Ir anomaly represent a megatsunami deposit generated by the Chicxulub impact, and was deposited over a few hours or days (Smit et al., 1992, 1996; Bralower et al., 1998). However, this interpretation is no longer tenable based on the presence of several horizons of trace fossils within this sedimentary complex.

Evidence of trace fossils in the sandstone-siltstone complex is present in numerous outcrops. In the past workers typically subdivided this depositional complex into three distinct sedimentary units that represent distinct depositional events. At the base is unit 1, the spherule layer that is generally not bioturbated. Above the spherule layer is unit 2, a sandstone that is mostly not bioturbated (Fig. 3), but generally contains a few J-shaped, 5–10-cm-long, spherule-filled burrows near the base (Fig. 4, A and B) that are often truncated by overlying sand layers. Ekdale and Stinnesbeck (1998, p. 593) interpreted these burrows as having been "excavated following deposition of the first sand layers and then filled with spherules, scoured, and overlain by more of unit II sand." The uppermost unit 3 consists of alternating sandstone, siltstone, and shale that contain abundant trace fossils (Fig. 3). These trace fossils were abundantly illustrated and discussed in Ekdale and Stinnesbeck (1998) and include *Chondrites*, *Ophiomorpha*, *Planolites*, and *Zoophycos*. Additional illustrations are shown in Figure 4 (C–E). The burrows of unit 3 indicate that sediment deposition occurred epi-

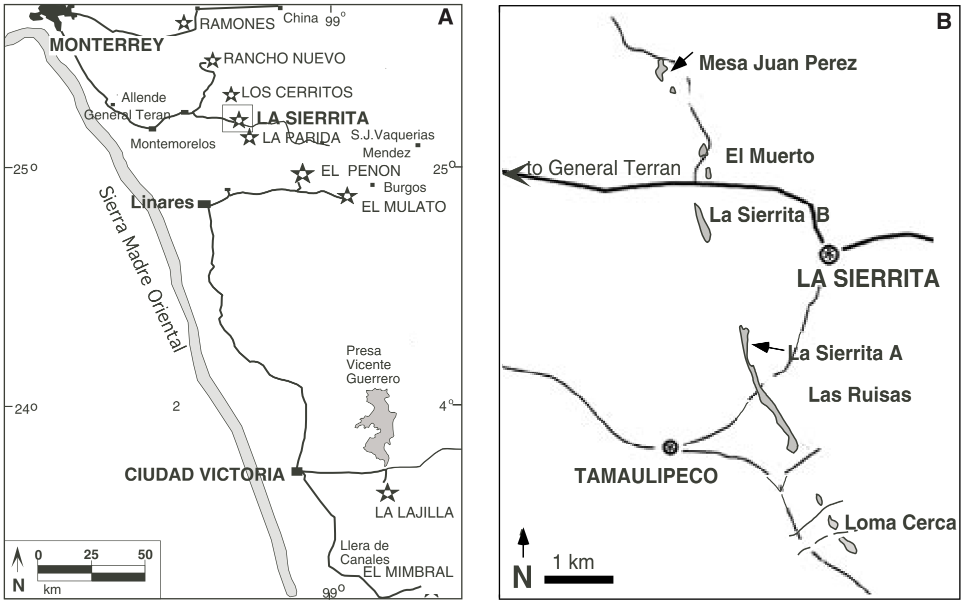

Figure 1. A: Location map of Cretaceous-Tertiary boundary sections with spherule-rich deposits below sandstone-siltstone complex in northeastern Mexico. Stars mark localities of sections. B: Location map of La Sierrita area with low-lying northeast-southwest–trending hills of Mendez Formation topped by sandstone-siltstone complex. There are 2–4 spherule layers within upper 10 m of pelagic marls of Mendez Formation. Series of lithologs of these sections are illustrated in Figure 2.

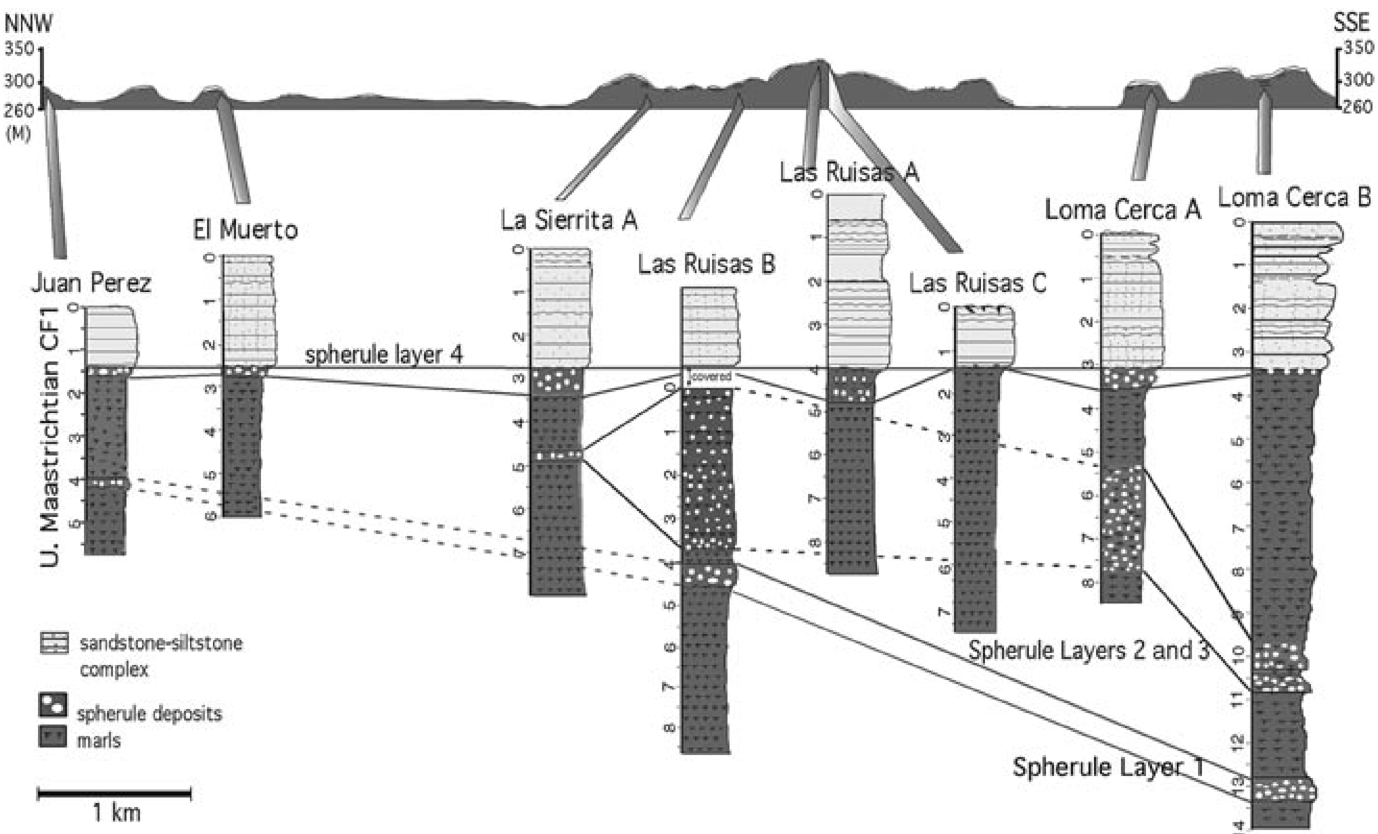

Figure 2. Stratigraphic and lithologic correlation of eight late Maastrichtian sections in La Sierrita area, from Loma Cerca in southwest to Mesa Juan Perez in northeast (see Fig. 1B). Topographic relief illustrates positions of these sections from sandstone-siltstone complex at top to Mendez Formation marl that makes up slopes of hills. Each section contains spherule layer directly below sandstone-siltstone complex and as many as three additional spherule layers in 10 m of pelagic marls below it. Age of oldest spherule layer at Loma Cerca B predates Cretaceous-Tertiary boundary by ~270 k.y. Numbers on lithological columns indicate meters. Solid lines mark correlation of spherule layers. Dashed correlation lines indicate where particular spherule layer is missing in some sections.

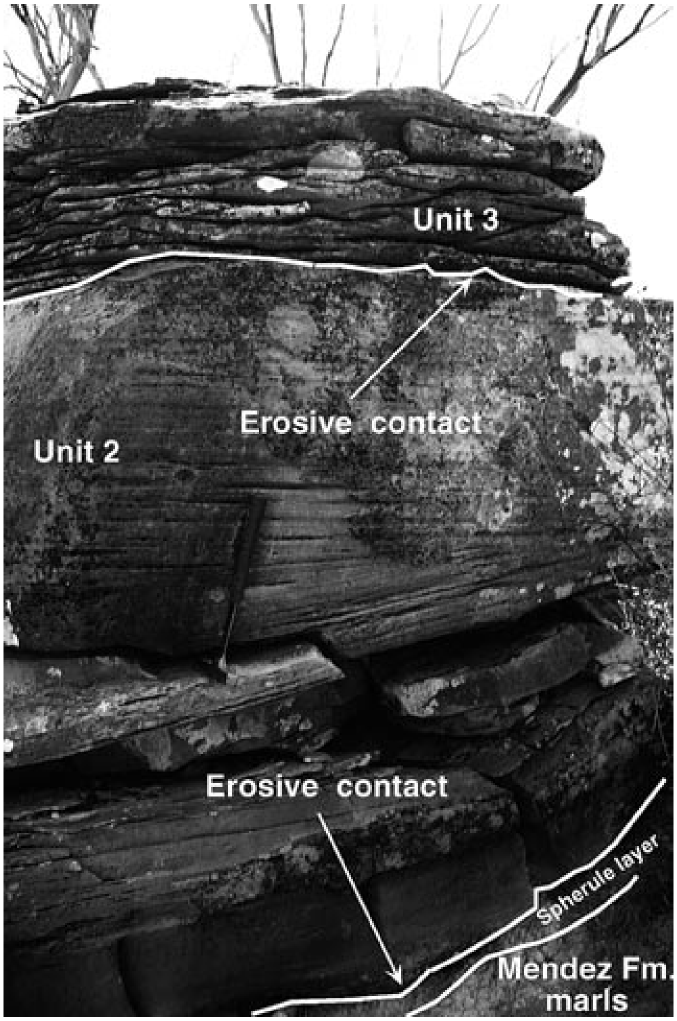

Figure 3. Sandstone-siltstone complex at La Sierrita A showing marl of Mendez Formation and spherule layer (unit 1) at base, sandstone (unit 2) in middle, and overlying alternating sand, silt, shale layers (unit 3). Trace fossils are rare in unit 2 and very common in unit 3. Hammer, 30 cm, for scale. Fm.—Formation.

sodically and that burrowing occurred during periods of deposition, not after deposition had ceased.

Trace-fossil evidence indicates that the entire sandstone-siltstone complex of units 2 and 3 was deposited over a long period of time during which periods of normal pelagic sedimentation and colonization of the ocean floor alternated with periods of erosion followed by rapid deposition. The entire sandstone-siltstone complex (units 1–3) could therefore not have been deposited by a tsunami over a period of hours to days, as suggested by Smit et al. (1992, 1996). However, this evidence does not question the reality of a K-T boundary impact, or even the possibility that the rippled upper beds (20–25 cm) of the sandstone-siltstone complex beneath the iridium anomaly could have been deposited by a tsunami event. These data, however, contradict the interpretation that the spherule layer (unit 1) is directly related to the planktic foraminiferal extinctions at the K-T boundary and the Ir anomaly at the top of the burrowed sandstone-siltstone complex. The K-T boundary and the spherule event are temporally separated by the trace-fossil horizons of units 2 and 3 in the sandstone-siltstone complex in northeastern Mexico.

Throughout the La Sierrita area, a spherule layer (unit 1) that varies from a few centimeters to 1 m thick typically underlies the sandstone-siltstone complex (Fig. 2). As many as 3 additional spherule layers are present in the top 10 m of the underlying marls in more than 24 sections examined (Figs. 2 and 5A). These spherule layers may be separated by 2–6 m of pelagic marls, indicating that deposition occurred in a normal marine environment. The contact between the stratigraphically lowermost spherule layer and overlying marl is often sharp, suggesting little erosion (Fig. 5B). The Loma Cerca B section is one of these sequences located on the western flank of the Loma Cerca hill, ~40 km east of Montemorelos. The top of the hill is capped by a 3.5-m-thick sandstone-siltstone complex that has a 5–10-cm-thick spherule layer at its base. More than 15 m of marls of the Mendez Formation are exposed below it; there are two closely spaced 50-cm-thick spherule layers between 6.8 and 7.5 m. Both of these layers show decreasing spherule abundance upward and mark two depositional events. Another 50-cm-thick spherule layer, without upward decreasing abundance, is present between 9.5 and 10 m below the base of the sandstone-siltstone complex. Thus four spherule layers are present in these late Maastrichtian Mendez marls. No iridium anomaly is associated with any of the four late Maastrichtian spherule layers, and shocked quartz grains are rare.

Methods

In the field, samples were collected at 10–20 cm intervals for biostratigraphic, mineralogical, and stable isotope analyses. For biostratigraphic analysis, samples were processed for foraminifera using standard laboratory techniques (Keller et al., 1995). The washed residue (>63 µm size fraction) was examined for planktic foraminifera and a species census was taken to evaluate the age of the sediments. Changes in species populations indicative of climatic variations, reworking and transport of species, and hiatuses were evaluated based on quantitative analysis of ~250–300 individuals per sample. Microfossils are abundant, although generally recrystallized, in the Mendez marls and exhibit no evidence of preservational bias due to carbonate dissolution or breakage. For hard marls, thin sections were also made and examined to counter possible bias in washed residues. No major bias was observed. Thin sections were also made of the spherule layers and examined for glass and to identify the nature of the spherules, reworked clasts, terrigenous influx, and transported foraminifera. The biostratigraphic zonal scheme of Pardo et al. (1996) and Li and Keller (1998b) was used where the last 300 k.y. of the Maastrichtian, or the upper interval of chron 29r below the K-T boundary, are

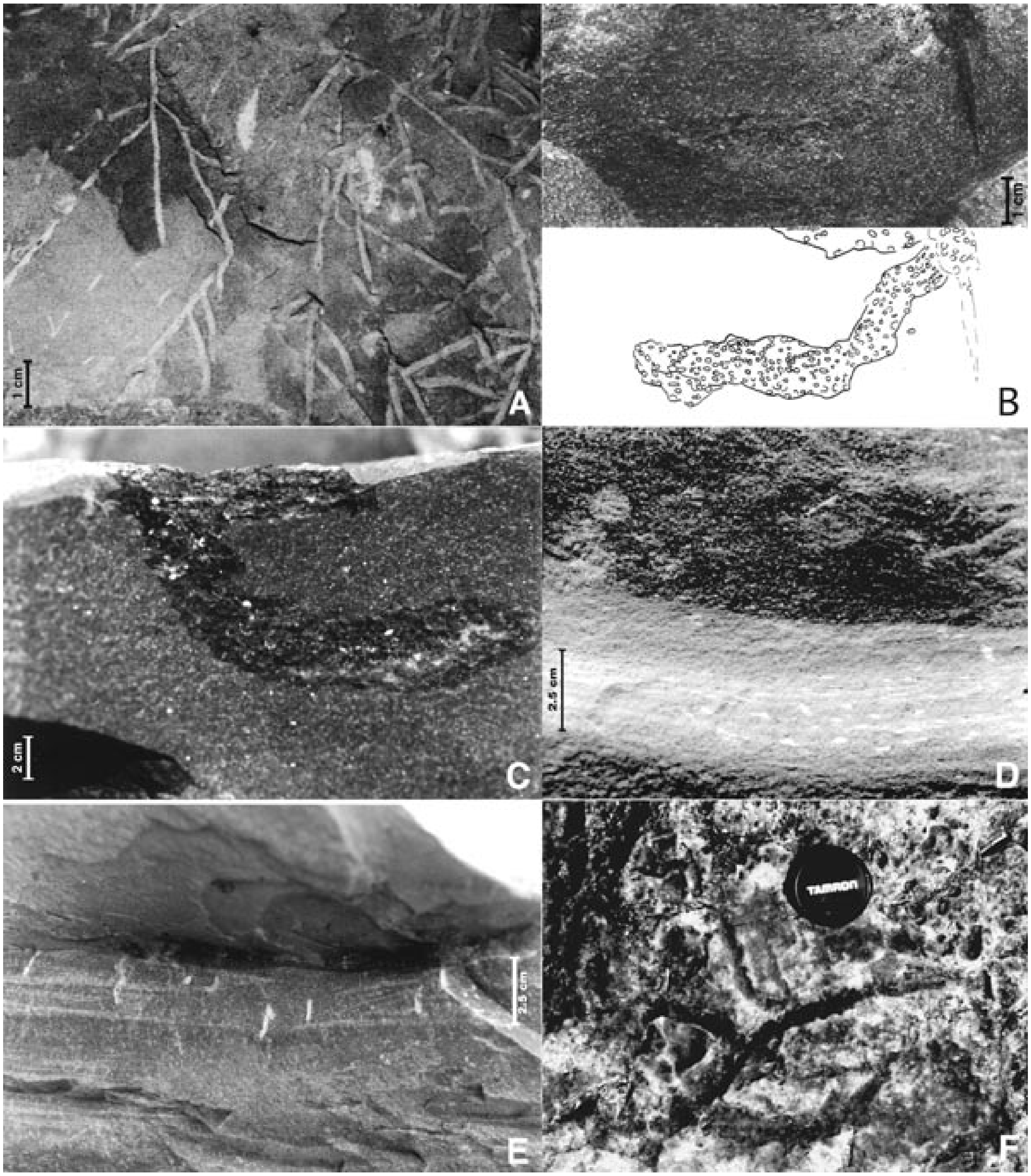

Figure 4. A: *Chondrites* burrows exposed on bedding planes of fine sandstone within unit 3 at El Peñon. These deep deposit-feeding burrows consist of branching and dominantly horizontal tunnels. Scale bar is 1 cm (from Ekdale and Stinnesbeck, 1998). B, C: Spherule-filled burrows in sandstone near base of unit 2 at El Peñon and Rancho Canales, and outline of burrow in photograph of B. Note that burrows are filled with dark colored, unbroken, calcite spherules and truncated at top by scour and overlying sand. Burrows of this nature are 0.5–1.5 cm in diameter and 6–10 cm long. D: *Chondrites* burrows exposed on bedding planes of fine silt in unit 3. Such burrows are common in fine-grained silt or shale layers of unit 3 in many outcrops. E: Vertical shafts of Chondrites burrows; some are truncated by scour and overlying sand. Such burrows are common in fine-grained silt and shale layers of unit 3 in many outcrops. F: *Ophiomorpha* burrows exposed on bedding planes within sandstone near top of unit 3 at La Sierrita. Such burrows are abundant within unit 3 and also at top of unit 3 in many outcrops Lens cap, 50 mm, for scale.

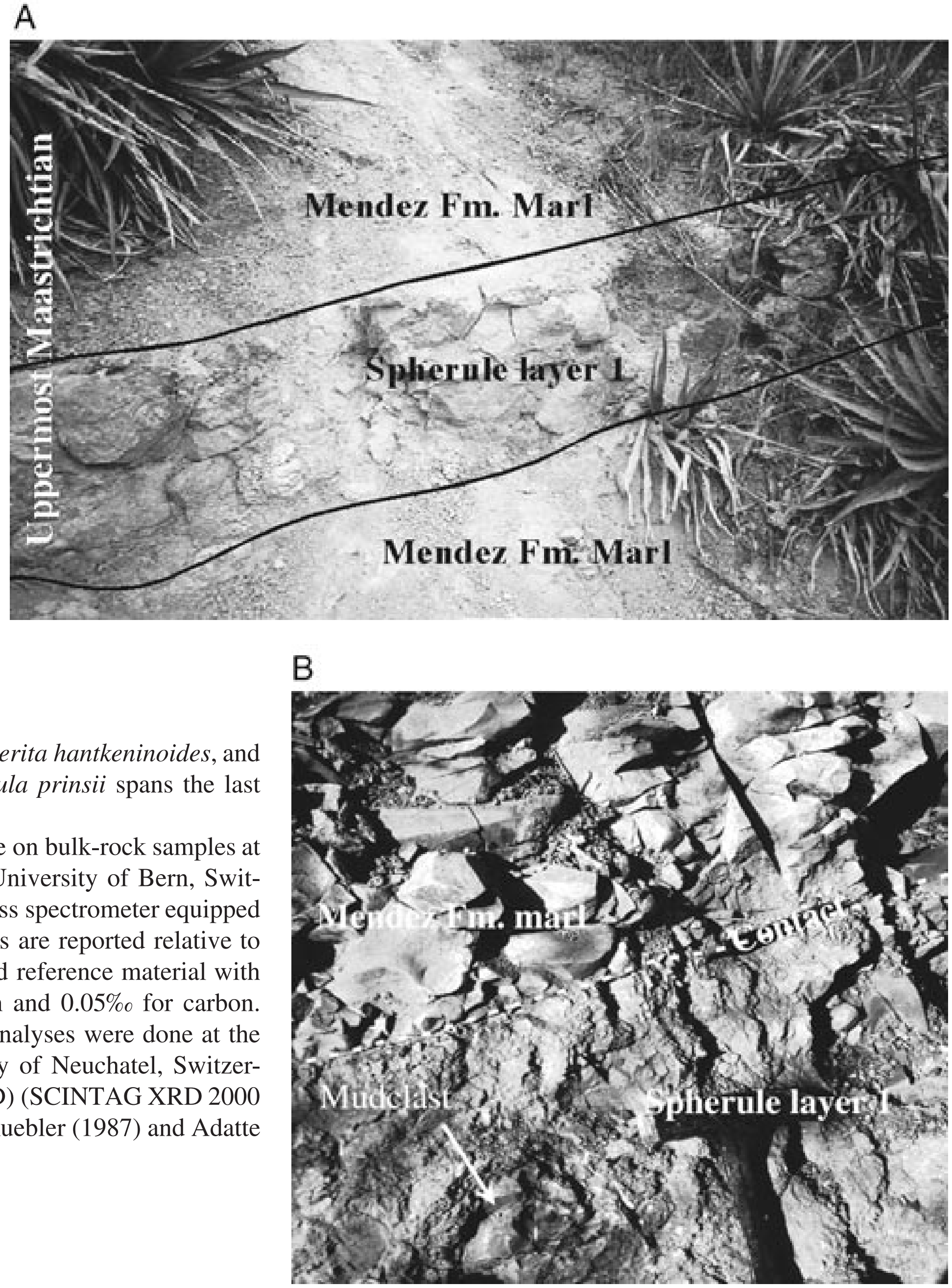

Figure 5. A: Spherule layer 1 at Loma Cerca B is within marls of Mendez Formation and 10 m below sandstone-siltstone complex. This spherule layer is nearly 1 m thick and was deposited within *Micula prinsii* zone and near base of *Plummerita hantkeninoides* zone (CF1); latter spans last 300 k.y. of Maastrichtian. Sediment accumulation rates suggest that this spherule layer was deposited ~270 k.y. before Cretaceous-Tertiary boundary. B: Spherule layer 1 showing sharp upper contact with overlying marl. This suggests gradational transition. Mud clasts are rare in spherule layer 1 and there is generally no upward fining of spherules. Fm.—Formation.

identified by the total range of *Plummerita hantkeninoides*, and the calcareous nannofossil zone *Micula prinsii* spans the last 450 k.y. of the Maastrichtian.

Stable isotope analyses were done on bulk-rock samples at the stable isotope laboratory of the University of Bern, Switzerland, using a VG Prism II ratio mass spectrometer equipped with a common acid bath. The results are reported relative to the Vienna Peedee belemnite standard reference material with a standard error of 0.1‰ for oxygen and 0.05‰ for carbon. Clay and whole-rock mineralogical analyses were done at the Geological Institute of the University of Neuchatel, Switzerland, based on X-ray diffraction (XRD) (SCINTAG XRD 2000 diffractometer) using the method of Kuebler (1987) and Adatte et al. (1996).

RESULTS

Age of spherule layers

Biostratigraphic investigations based on planktic foraminifera indicate that the top 10 m of marls in the Mendez Formation at Loma Cerca B were deposited within the latest Maastrichtian *Plummerita hantkeninoides* zone CF1, which spans the last 300 k.y. of the Maastrichtian (Pardo et al., 1996). This age is supported by the presence of the *Micula prinsii* zone calcareous nannofossil assemblage that marks the last 450 k.y. of the Maastrichtian. Faunal assemblages within the CF1 interval are diverse and typical of the latest Maastrichtian low-latitude Tethys, as characterized by the presence of *P. hantkeninoides* (fragile apical spines frequently broken), the dominance of biserial species, and generally low abundance of globotruncanids (Fig. 6). Species populations within the marls show no evidence of transport and reworking, repetition due to slumps, or missing intervals due to major erosion at the base of the spherule layers within the marls. However, there are occasional outcrops in the La Sierrita area where there are minor local slumps, a few meters in lateral extent. At Loma Cerca B, a short interval may be missing at the unconformity at the base of the sandstone-siltstone complex, as indicated by the undulating erosional surface, the spherules filling the troughs, and the presence of common

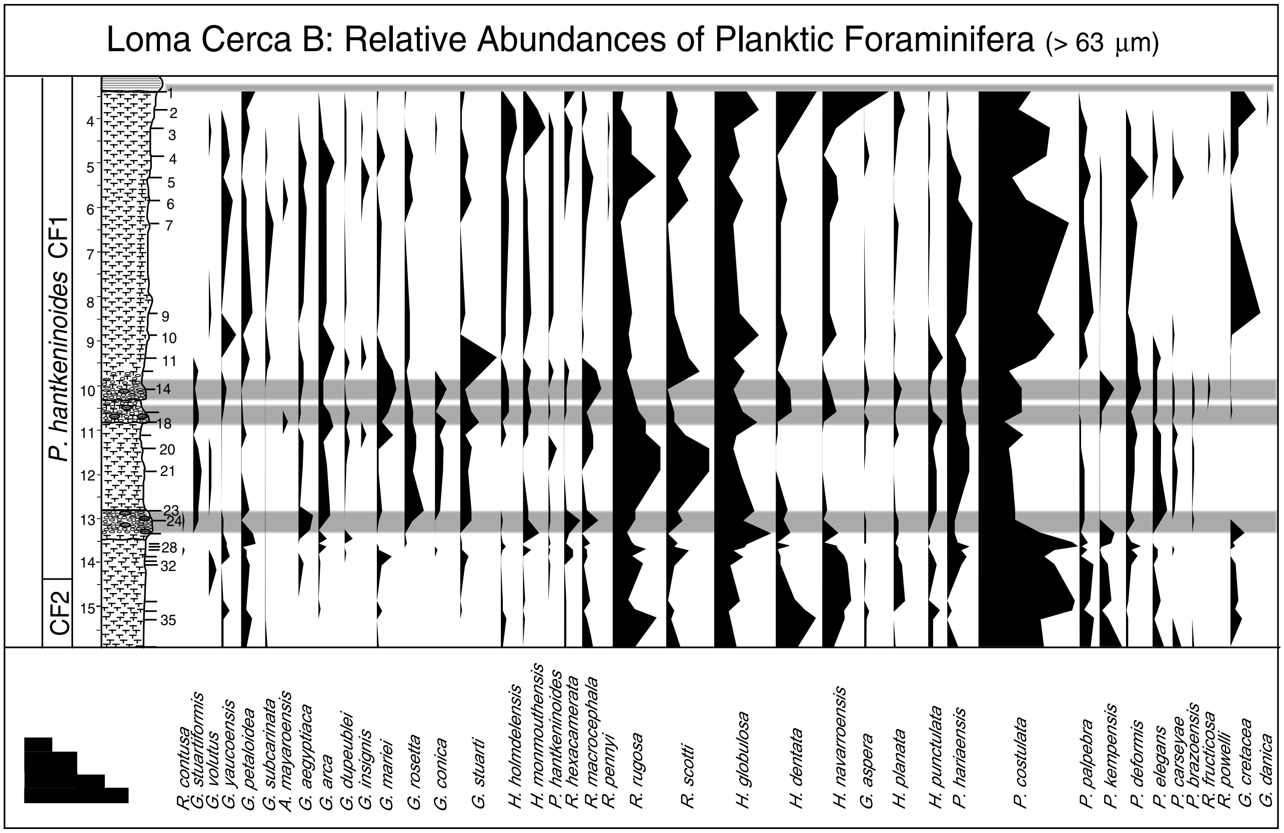

Figure 6. Relative abundances of late Maastrichtian planktic foraminifera in Mendez marls below sandstone-siltstone complex. Note that species diversity and relative abundances are characteristic of Tethyan assemblages and that there is no indication of chaotic deposition or major reworking in Mendez marls. However, anomalous abundance peaks in globotruncanids at bases of spherule layers 2 and 3 indicate influx of reworked specimens. Deposition of Mendez marls from 1 m below spherule layer 1 to top occurred within latest Maastrichtian *Plummerita hantkeninoides* (CF1) zone that was deposited during last 300 k.y. of Maastrichtian.

clasts. Erosion of the uppermost Maastrichtian is also suggested by the absence of the characteristic end-Maastrichtian increase in biserial species. However, the missing interval appears to be minor, as indicated by the lithological variations of more than 12 sections in the region (Fig. 2). In addition, the presence of common *Guembelitria cretacea* in the upper 4 m of the Mendez Formation marl (Fig. 6) is characteristic of the latest Maastrichtian in the Tethys (Abramovich et al., 1998).

The CF1-CF2 boundary is 11 m below the sandstone-siltstone complex and 1 m below the first spherule layer. On the basis of paleomagnetic and biostratigraphic correlations at Agost, Spain, the base of zone CF1 is about 300 k.y. below the K-T boundary (Pardo et al., 1996). Assuming that most of the CF1 zone interval is present at Loma Cerca B, the average sediment accumulation rate of the marl was 3 cm/k.y. This compares favorably with 2 cm/k.y. at El Kef and 4 cm/k.y. for marls at Elles, Tunisia, for the same interval (Li et al., 1999; Abramovich and Keller, in press) and suggests relatively continuous sedimentation at Loma Cerca B. On the basis of these sediment accumulation rates, the oldest spherule layer was deposited about 270 k.y. before the K-T boundary. The second and third layers were deposited ~215 k.y. and ~210 k.y. before the K-T boundary, respectively, assuming that there was little erosion prior to deposition. Although these are approximate ages with uncertainties due to possibly discontinuous sedimentation, they provide the best age estimates consistent with biostratigraphy at this time.

Estimating the depositional age of spherule layer 4 has additional uncertainty due to the unknown length of time it took to deposit the sandstone-siltstone complex. This deposit must predate the K-T boundary by an unknown, although short, interval, as indicated by the multiple horizons of trace fossils in units 2 and 3. Each renewed colonization of the ocean floor could have taken place within a few years. If we assume that no significant erosion and time lapses occurred between repeated influxes of siliciclastic sediments alternating with pelagic sedimentation, then spherule layer 4 could have been deposited only a few thousand years before the K-T boundary.

Evidence for original deposition of late Maastrichtian marls

Until the discovery of multiple spherule layers within the late Maastrichtian Mendez marls in sections throughout northeastern Mexico, there was no question that these marls represented original pelagic sedimentation (Smit et al., 1992, 1996; Stinnesbeck et al., 1996; Keller et al., 1994, 1997). However, the age and origin of these multiple spherule deposits within the marls and the far-reaching implications of a late Maastrichtian age for the current impact–mass-extinction scenario require thorough evaluation of all possible depositional scenarios. In particular, it has been suggested that the multiple spherule layers may be due to slumping and repeated sections as a result of seismic activity induced by the Chicxulub impact at the K-T boundary (Soria et al., 2001). Although we find no evidence to support this scenario in our survey of numerous outcrops over more than 50 km, we detail our observations in the following.

Faunal evidence: planktic foraminifera. Biostratigraphic and quantitative planktic foraminiferal analyses reveal normal pelagic deposition within a subtropical to tropical Tethyan ocean with late Maastrichtian faunal assemblages similar to those documented throughout the Tethys (Li and Keller, 1998b; Luciani, 1997; Abramovich et al., 1998). There is no faunal evidence of significant reworking within the marls of Loma Cerca (Fig. 3), or any of the other numerous sections examined. There is no faunal evidence of large-scale slumps, repeated sections due to slumping, or chaotic deposition as a result of storm deposits (e.g., impact tsunami, Stinnesbeck et al., 2001). Whether the faunal and biostratigraphic data of Loma Cerca B is viewed alone, or within the context of more than 24 northeastern Mexico sections, or even within the context of the larger Tethyan ocean from the Negev of Israel to Mexico, these data can not be interpreted as having been compromised by slumps, repetition of sections, or major reworking within the marls. This is indicated by the overall similarity of the fossil assemblages, the similarity in the relative abundances of most species, and the relative abundance changes within species populations (e.g., globotruncanids, guembelirids, roguglobigerinids, and heterohelicids) at Loma Cerca B. All of these proxies reflect similar environmental changes in other Tethys sections with known undisturbed and continuous sedimentation records of the last 500 k.y. of the late Maastrichtian (Pardo et al., 1996; Abramovich et al., 1998; Abramovich and Keller, in press; Luciani, 1997).

Faunal evidence: benthic foraminifera. The relative abundance of benthic species is an index of paleodepth. In neritic environments, benthic species are abundant and diverse, and dominate foraminiferal assemblages. At bathyal depths benthic species are less diverse and decrease to <5% with planktic foraminifera dominating (95%). Peak abundances at bathyal depths are therefore generally due to downslope transport, reworking, or dissolution. In addition, many benthic species are specific in their depth habitats, neritic species generally being restricted to shelf areas and bathyal species being restricted to slope areas at depths deeper than 300 m (Morkhoven et al., 1986; Keller, 1992). At Loma Cerca B, benthic species average between 2% and 5% in the Mendez Formation marls, which indicates normal pelagic deposition in a relatively deep water environment (Fig. 7). They thus provide no evidence for significant reworking during marl deposition. However, peak increases in benthic abundances to 10% and 23% at the bases of spherule layers 2 and 3, respectively, indicate that significant reworking occurred in these intervals. Apparently no significant reworking was associated with deposition of spherule layer 1. Earlier studies have shown that spherule layer 4 at the base of the sandstone-siltstone complex also contains common transported shallower shelf species, indicating reworking (Keller et al., 1994, 1997).

Most of the benthic species present at Loma Cerca B and other Sierrita sections examined are known to live in upper bathyal and outer neritic environments (Table 1), and there are no shallower neritic species in any of the samples examined. This indicates that deposition occurred in an upper bathyal environment at depths of ~300–500 m. All of the species present in the Mendez Formation are also commonly present in outer neritic to upper bathyal depths in late Maastrichtian to early Danian sections at Caravaca, Spain, the Negev, Israel, and El Kef in Tunisia (Keller, 1992). However, in the Mexican sections benthic species are very rare (2%–5% relative to planktic species), which indicates that the Mexican sections were deposited in a deeper upper bathyal environment than those in Spain, the Negev, or Tunisia.

Lithological evidence. More than 48 K-T boundary transitions have been examined in Mexico spanning a distance of more than 300 km. More than 24 of these sections are in the La Sierrita area (Fig. 1), where the late Maastrichtian was examined in detail and where individual spherule layers are exposed for several tens of meters along the hillslopes without evidence of major slumps and faults. However, in some isolated sections minor local slumps spanning a few meters were observed. In general, the various spherule layers can be observed in many outcrops spanning an area of more than 50 km (Fig. 2). That not all four spherule layers are present in all sections indicates a variable degree of erosion and reworking, and it may reflect the topographic relief of the seafloor. This is also indicated by the variable thickness or occasional absence of the sandstone-siltstone complex (Lindenmaier, 1999; Schulte, 1999; Affolter, 2000; Schilli, 2000). The regional continuity of pelagic marls and presence of spherule layers within the last 300 k.y. of the Maastrichtian zone CF1 rules out the possibility that deposition occurred as a result of slump deposits, or any other type of significantly disturbed deposition. However, it does not rule out the possibility that spherule layers 2, 3, and 4 derived from a single spherule-producing event in the late Maastrichtian (spherule layer 1) via periodic reworking and redeposition.

Mineralogic evidence. X-ray diffraction (XRD) and granulometric analyses of the insoluble size fraction provide further

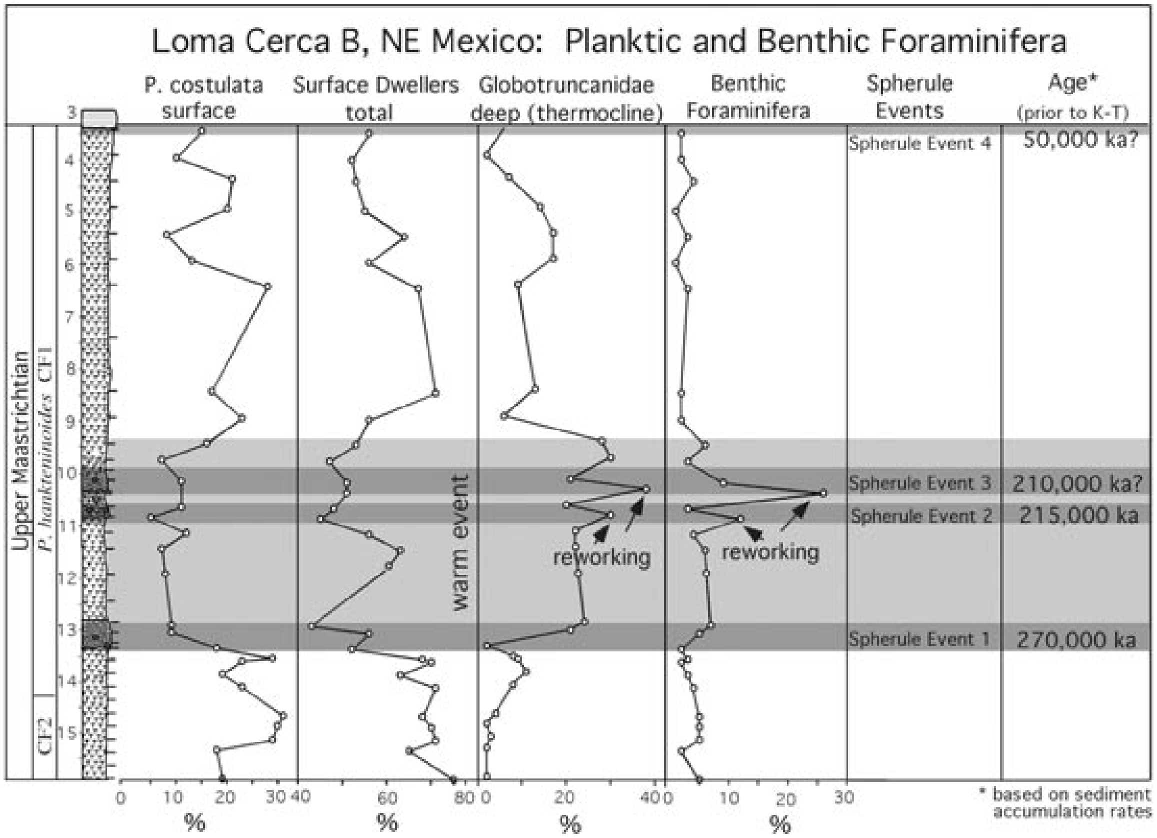

Figure 7. Foraminiferal proxies as indicators of climate change and reworking. Note that reworked sediments are restricted to short anomalous peaks in globotruncanids and benthic foraminifera at bases of spherule layers 2 and 3. Planktic foraminifera are depth ranked based on carbon and oxygen isotopes (see Li and Keller, 1998b). At Loma Cerca B, as well as Tethys ocean in general, late Maastrichtian surface mixed layer is characterized by common to abundant surface dwellers (e.g., rugoglobigerinids and heterohelicids), whereas subsurface (thermocline) dwellers are dominated by globotruncanids (Abramovich et al., 1998; Li and Keller, 1998a, 1998b; Luciani, 1998). At Loma Cerca B, increased abundance of globotruncanids indicates climate warming beginning with deposition of spherule layer 1 and ending ~1.5 m above spherule layer 3. Age of this warming coincides with major warm pulse in stable isotope record of middle latitude Deep Sea Drilling Project Site 525 (Li and Keller, 1998a), and also with major Deccan volcanism between 65.4 and 65.2 Ma (Hoffman et al., 2000).

evidence for normal pelagic sedimentation. Pelagic marls tend to be uniformly fine grained (<16 µm); calcite and phyllosilicates are the most abundant components. This reflects normal pelagic sedimentation under weak hydrodynamic conditions. At Loma Cerca B, insoluble grain-size fractions average ~50% in the 0–4 µm range and 50% in the 4–16 µm range (Fig. 8). Just below the sandstone-siltstone complex and spherule layer 4 a fine-grained interval marks a bentonite layer that has not yet been dated. XRD analyses of whole-rock marls indicate the same average compositions (45%–50% calcite, 12%–18% quartz, 5%–10% plagioclase, 25%–30% phyllosilicates) for the entire marl sequence at Loma Cerca B, as well as Mesa Juan Perez, 10 km to the northeast (Stinnesbeck et al., 2001). Similar values were previously reported for the Mendez marls at other northeastern Mexico sections where no additional spherule layers were observed (Adatte et al., 1996). Only the insoluble residue of the spherule-rich layers has a larger (16–150 µm) grain size present due to the spherules. In addition, there is a small (~10%) peak in the larger (16–150 µm) grain size apparent at the CF1-CF2 boundary that marks the presence of a bioturbated interval with trace fossils at Loma Cerca B and may represent a short hiatus. These uniform mineralogical values, either within the marls of the Loma Cerca B section or within the marls across the region (Stinnesbeck et al., 2001), do not support a scenario of slumps, reworking, and sliding movements induced by seismic waves as a result of a K-T boundary impact, as suggested by Soria et al. (2001).

Stable isotopes. Marls of the Mendez Formation are diagenetically altered and therefore measured stable isotopes do not represent original $\delta^{18}O$ values. In contrast, $\delta^{13}C$ values are little affected by recrystallization processes because pore waters have low concentrations of carbon (Magaritz, 1975; Brand and

TABLE 1. BENTHIC FORAMINIFERA FROM MARLS AND SPHERULE LAYERS AT LOMA CERCA B, MEXICO

Species	Depositional environment
Cibicicoides dayi (White)	Primarily bathyal
Cibicidoides succedens	Outer neritic and upper bathyal
Coryphostoma midwayensis (Cushman)	Outer neritic and upper bathyal
Bolivinoides draco (Marsson)	Outer neritic and upper bathyal
Coryphostoma incrassata (Reuss)	Outer neritic and upper bathyal
Bolivina incrassata gigantea (Wicker)	Outer neritic and upper bathyal
Bulimina faragraensis Le Roy	Outer neritic and upper bathyal
Prebulimina cushmani (Sandidgei)	Outer neritic and upper bathyal
Praebulimina reussi	Outer neritic and upper bathyal
Dorothia oxycona (Reuss)	Outer neritic and upper bathyal
Gaudryina pyramidata Cushman	Outer neritic and upper bathyal
Gyroidinoides planulata	Outer neritic and upper bathyal
Gyroidinioides subangulataus (Plummer)	Outer neritic and upper bathyal
Gyroidinoides globulosus	Outer neritic and upper bathyal
Cassidulina globosa	Outer neritic and upper bathyal
Uvigerina maqfiensis Le Roy	Outer neritic and upper bathyal
Trifarina esnaensis Le Roy	Outer neritic and upper bathyal
Spiroplectamina dentata	Outer neritic and upper bathyal
Stensioina beccariiformis	Outer neritic and upper bathyal
Lenticulina muensteri	Neritic to bathyal
Anomalinoides welleri	Outer neritic and upper bathyal
Anomalinoides acuta	Outer neritic and upper bathyal

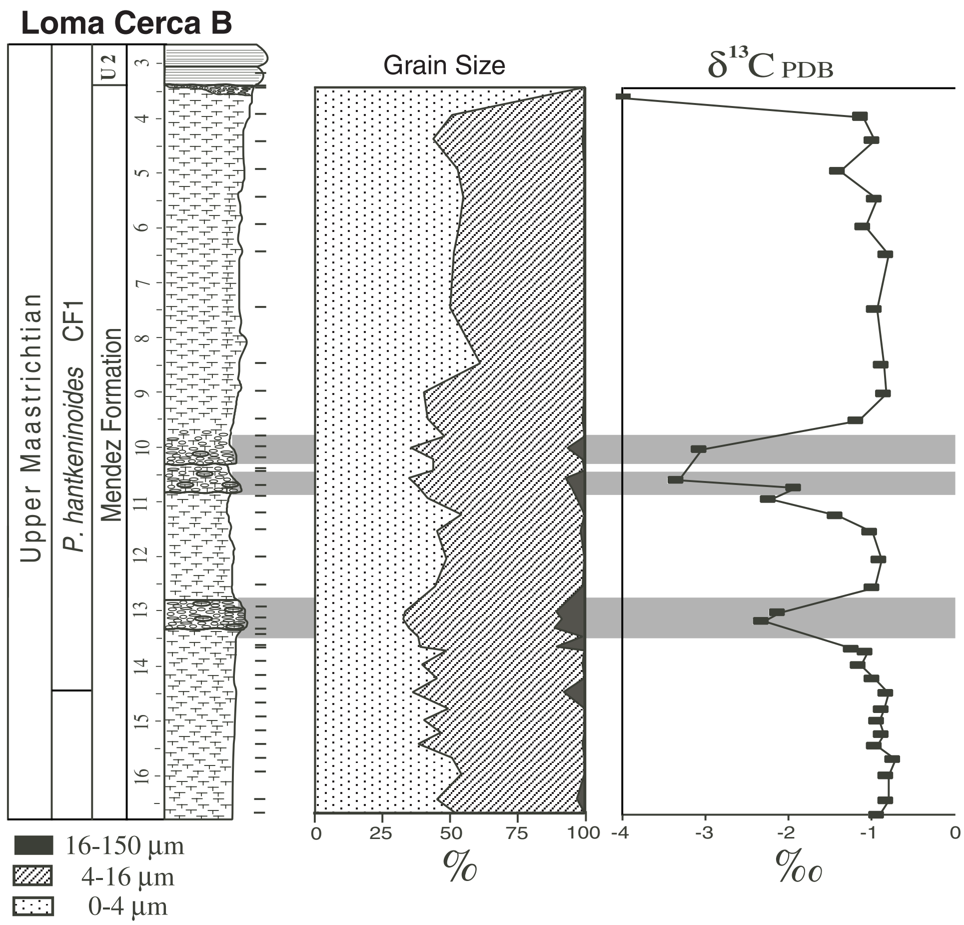

Figure 8. Grain-size distribution and $\delta^{13}C$ record at Loma Cerca B. Note that marly sediments are uniform; no major changes are apparent in lithology or stable isotopes. Only variations in these patterns are seen in spherule layers that differ by their larger grain sizes and lighter $\delta^{13}C$ values as result of nonbiogenic calcite infilling of spherule voids. PDB is Peedee belemnite.

Veizer, 1980; Schrag et al., 1995). In this study, $\delta^{13}C$ values of bulk carbonate were analyzed in order to test whether sediments show major isotopic trends that would indicate the presence of K-T sediments, or chaotic values due to mixing of sediments. No such trends are observed. Bulk-rock $\delta^{13}C$ data show relatively uniform values of 1‰ throughout the Maastrichtian marls (Fig. 8). These values and stable trends are comparable to other low-latitude sections with late Maastrichtian marls (e.g., Zachos et al., 1989, 1994; Keller and Lindinger, 1989), and suggest pelagic deposition. Lower $\delta^{13}C$ values are only observed in the spherule layers and the bentonite at the top of the section. These highly negative values are likely due to the presence of significant quantities of nonbiogenic calcite that now infills most of the original spherule cavities (Fig. 9A). Although these $\delta^{13}C$ data provide no firm evidence for normal pelagic deposition of the Mendez marls, they provide no evidence against such an interpretation in the form of chaotic or random fluctuations.

Evidence for original spherule-producing event

Although the arguments presented here show that we can rule out the multiple spherule layers within the marls being due to slumps or repeated stacking of sections with each containing the original spherule layer, questions remain of when, where, and how the original spherule deposition occurred. One of the most challenging tasks is to determine whether one or more of the spherule layers represent the original spherule-producing event(s). Alternatively, all or some of the spherule layers may be redeposited from an earlier, unknown, spherule-producing event. Although none of the four spherule layers at Loma Cerca B or any of the other localities (Schilli, 2000; Affolter, 2000) is associated with an Ir anomaly, there is strong evidence that the oldest late Maastrichtian spherule layer 1 at Loma Cerca B, as well as at several other northeastern Mexico sections (e.g., Mesa Juan Perez, Las Ruisas B, Fig. 2), represents the original spherule-producing event, whereas others may have been re-

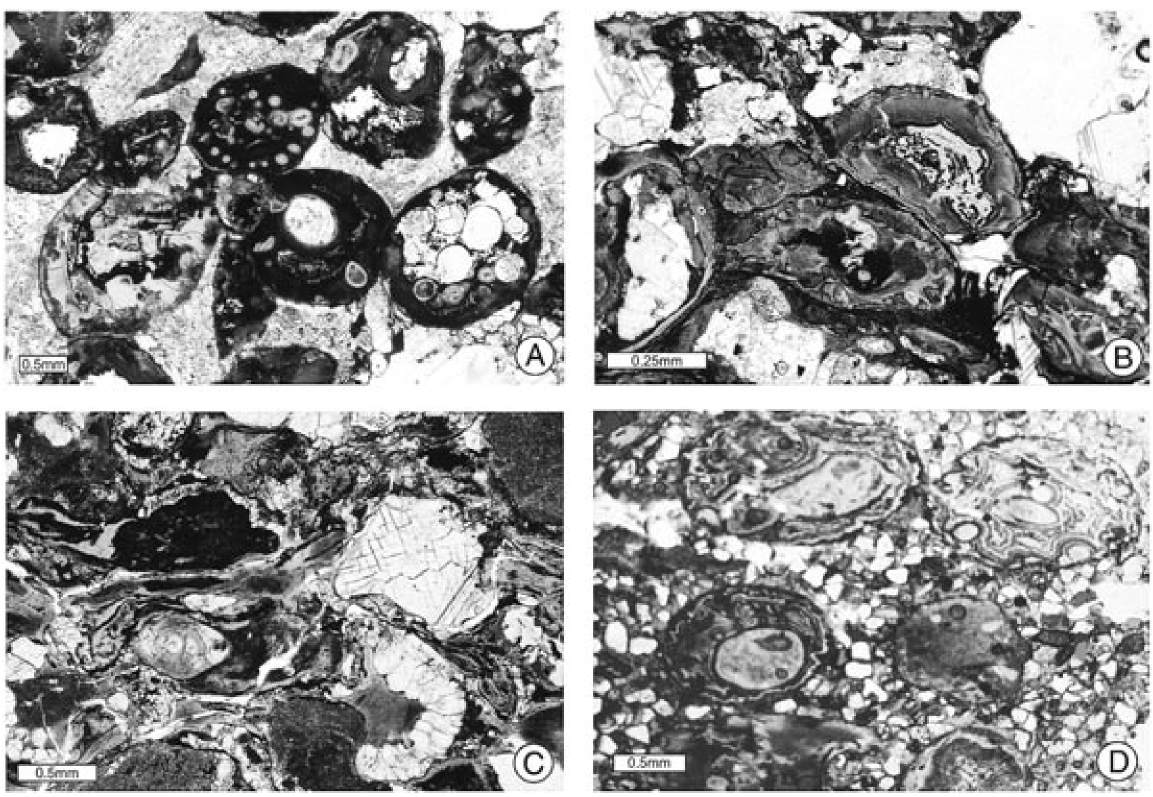

Figure 9. A–D: Stratigraphically oldest spherule layer 1 consists almost entirely of closely packed devitrified vesicular spherules and glass fragments to 5 mm and 7 mm, respectively, in diameter within matrix of blocky calcite (A). Spherules are often compressed and welded together with concave-convex contacts and dark schlieren features (B). Another feature of spherule layer 1 resembles polymict microbreccia where dominant component consists of angular to flaser-like shards and welding or plastic deformation of glass around more rigid constituents, such as carbonate clasts and occasional shells of benthic foraminifera (C). These features suggest that deposition of glass spherules occurred while glass was still hot and ductile during transport and primary deposition. In contrast, matrix of spherule layers 2–4 consists largely of marl clasts, and in spherule layer 4 of terrigenous influx (sand; D).

worked. There are several lines of evidence that lead us to this conclusion.

Nature of spherule layer 1. Thin sections of the spherule layers indicate that the oldest spherule layer 1 (shown in Fig. 5, A and B) consists almost entirely of closely packed devitrified vesicular spherules and altered glass fragments to 5 mm and 7 mm in diameter, respectively, with a blocky calcite matrix (Fig. 9A). There are very few broken spherules. Spherules are often compressed and welded together with concave-convex contacts and dark schlieren features (Fig. 9B). In some sections, spherule layer 1 resembles a polymict microbreccia, the dominant component of which consists of angular to flaser-like shards with welding or plastic deformation of glass around more rigid constituents, such as carbonate clasts and occasional shells of benthic foraminifera (Fig. 9C). These features suggest that deposition of the glass spherules occurred while the glass was still hot and ductile during transport and primary deposition.

Faunal evidence against major reworking in spherule layer 1. Most benthic foraminifera, as well as the planktic foraminifers (e.g., globotruncanids) have robust, thick-shelled tests that preferentially survive carbonate dissolution, transport, and reworking. Therefore, sharp anomalous abundance peaks in these species groups are proxies for poor preservation (dissolution) or transport and sediment redeposition. At Loma Cerca B there is no evidence of carbonate dissolution, and no significant reworking of species was observed in either benthic or planktic foraminifera in spherule layer 1. Quantitative faunal analysis indicates that benthic foraminifera in the Mendez marls average between 2% and 5%, and there is no increase at the base or within spherule layer 1 (Fig. 7). In addition, there are no transported shallower neritic species present that would indicate downslope transport. Globotruncanids are only 2% of the total foraminiferal population near the base of the section and rise to 11% prior to the first spherule layer. However, they decreased to 1% at the base of spherule layer 1 and abruptly increased to 20% at the top of spherule layer 1 (Fig. 7).

This abundance increase is sustained and long term, continuing through the 2 m of marls between spherule layers 1 and 2, through spherule layers 2 and 3, and well into the marls above. There is no evidence of test abrasion, breakage of specimens, elimination of fragile planktic species, and increase of benthic species that would suggest that the increased abundance of globotruncanids in spherule layer 1, or throughout the interval of globotruncanid dominance, is due to reworking and transport. These faunal data are in agreement with observations based on grain-size analyses, mineralogy, and lithology. The reason for the globotruncanid abundance may be found in the other constituents of the planktic foraminiferal assemblage. Relative abundance changes indicate that the increase in globotruncanids is coupled with a significant increase in warm-water surface dwellers (e.g., *Rugoglobigerina rugosa* and *R. scotti*, Fig. 6) that suggests climate warming. Similar peaks in warm-water species in the latest Maastrichtian are observed in sections across latitudes (e.g., Keller, 1993; Schmitz et al., 1992; Luciani, 1997; Nederbragt, 1998; Li and Keller, 1998a, 1998b; Pardo et al., 1999). We conclude that (1) the welded nature of spherules in spherule layer 1, (2) the near absence of benthic and planktic foraminifera, clasts, and terrigenous influx in the spherule matrix, and (3) the absence of peak abundance in transported benthic species and globotruncanids all point toward spherule layer 1 as the time of deposition of the original spherule-producing event. The presence of this spherule layer near the base of zone CF1, which has been dated as 65.3 Ma, and extrapolation based on sediment accumulation rates suggest that deposition of spherule layer 1 occurred ~270 k.y. prior to the K-T boundary and that deposition of this spherule layer coincided with the onset of the global warm event between that documented between 65.4 and 65.2 Ma (Li and Keller, 1998a).

Evidence for reworked spherule layers 2–4

It is easier to argue that spherule layers are reworked because we generally assume that deposition of impact or volcanic spherules is likely to be accompanied by seismic disturbance, slumping, or tsunami waves. A significant transported component would be expected if, as a result of a sea-level lowstand, a shallow-water spherule deposit is reworked and transported into deeper waters. Spherule layers 2, 3, and 4 appear to fall within the latter category for the following reasons.

Nature of spherule layers 2–4. These spherule layers contain abundant devitrified glass spherules and fragments, and occasional welded or agglutinated spherules with fluidal textures similar to spherule layer 1. However, they differ in that the matrix contains a chaotic mixture of irregularly shaped marl clasts to several centimeters in size, lithic fragments, and benthic and planktic foraminifera. Terrigenous input (sand) is most abundant in spherule layer 4 (Fig. 9D). This indicates transport, albeit over a relatively short distance as suggested by the size and angularity of marl clasts and sand grains. The strongest evidence for transport and redeposition of spherule layers 2–4 comes from planktic and benthic foraminiferal assemblages.

Faunal evidence for redeposition. Spherule layers 2 and 3 show anomalous peaks in globotruncanids of 10% and 18% above background values at the base of these spherule layers (Fig. 5). Benthic foraminifera also show anomalous peaks 10% and 23% above background values at the base of spherule layers 2 and 3, respectively. Because these abundance peaks are due to concentration of large, robust species that readily survived transport, they most likely mark intervals of transport, reworking, and redeposition associated with spherule layers 2 and 3. The absence of shallower neritic species within these spherule layers suggests that reworking and transport occurred from outer shelf to upper bathyal depths. Insufficient material was available from spherule layer 4 for a quantitative estimate. However, previous investigations of this spherule layer revealed the presence of abundant transported benthic foraminifera and marl clasts (Keller et al., 1994, 1997).

Paleoclimate at Loma Cerca during the last 300 k.y. of the Maastrichtian

During the latest Maastrichtian, sediment deposition in northeastern Mexico occurred in a tectonically active region (Laramide event), as indicated by the clay mineralogy and the high detrital content. The climate was probably arid, although active tectonism that caused increased erosion from uplifted areas overprinted climate signals. However, planktic foraminiferal assemblages indicate that a typical subtropical to tropical Tethyan environment prevailed.

Maastrichtian climate changes are well documented based on high-resolution stable isotope records from low and middle latitudes. In the southern middle to high latitudes, temperature records based on stable isotopes indicate that climate cooled by ~7–8°C during the Maastrichtian and had reached a minimum 500 k.y. before the K-T boundary (Barrera, 1994; Li and Keller, 1998a). Beginning at 65.45 Ma the climate rapidly warmed, resulting in a 3–4°C increase in bottom and surface waters in middle to high latitudes, and reached a maximum by 65.30 Ma. During the last 100 k.y. of the Maastrichtian, climate cooled gradually by 3°C (Fig. 10). These strong climate changes are evident in faunal assemblages across latitudes. In middle and high latitudes, there is a brief incursion of subtropical and tropical species (e.g., rugoglobigerinids) during the maximum warming (Schmitz et al., 1992; Pardo et al., 1999). At the same time, globotruncanids that lived at thermocline depth doubled their populations in low latitudes. However, by K-T boundary time a more temperate cool climate prevailed again. Globotruncanids responded to this cooling by decreased abundance

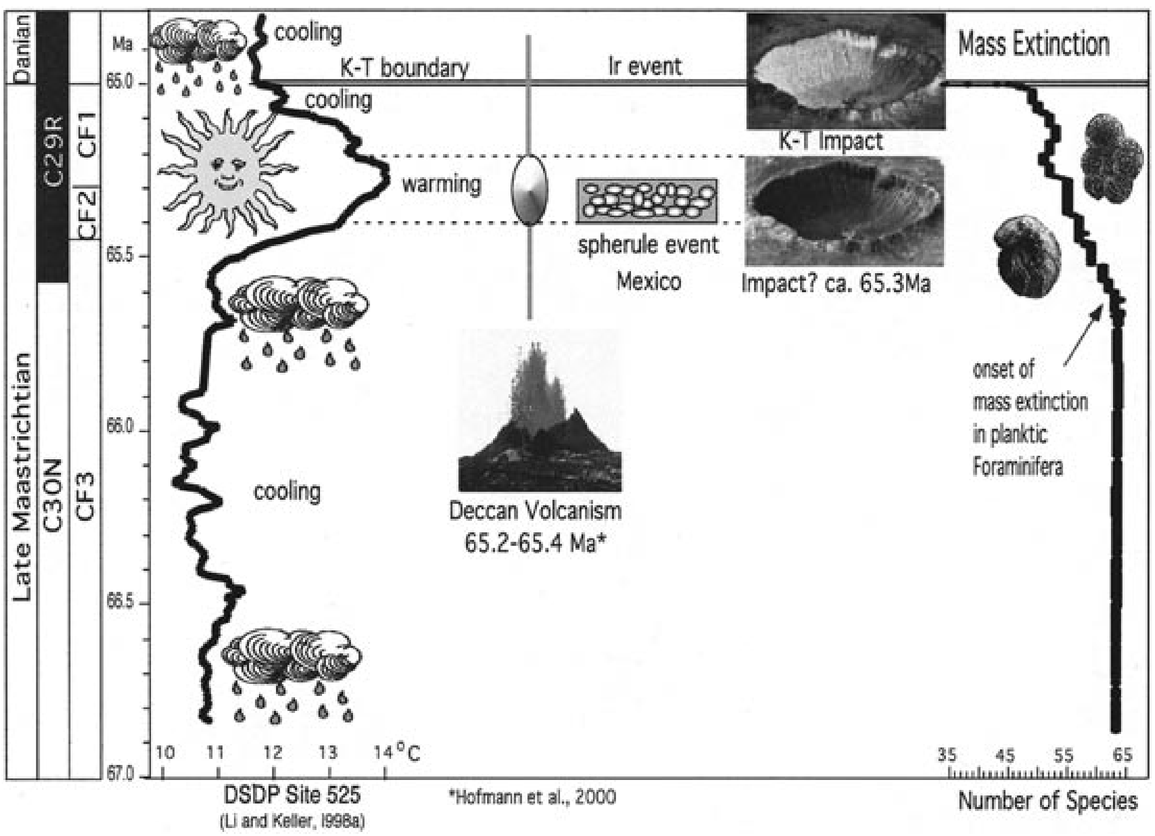

Figure 10. Sequence of climatic, volcanic, and impact events plotted next to deep-water temperature curve of Deep Sea Drilling Project (DSDP) Site 525 (data from Li and Keller, 1998a). Note that global warming of 3–4°C occurred between 65.4 and 65.2 Ma, coincident with latest estimates of major Deccan volcanism (Hoffman et al., 2000). New discovery of spherule layers in late Maastrichtian Mendez marls indicates that original spherule deposition event occurred ~270 k.y. before Cretaceous-Tertiary (K-T) boundary and is also associated with major warming. These data indicate that latest Maastrichtian global climate warming was triggered by Deccan volcanism, and at least locally (in Central and North America) exacerbated by impact (spherule layer 1). Spherules from Mexico and Haiti were originally been linked to Chicxulub impact based on chemical evidence of glass spherules. If this conclusion still holds in view of present multiple spherule layers, then Chicxulub impact predates K-T boundary by ~270 k.y. Regardless of age of Chicxulub, there is now strong evidence for multiple impacts, one at K-T boundary and one in late Maastrichtian ca. 65.3 Ma. Extinctions in planktic foraminifera began during maximum cooling at 65.5 Ma and gradually continued through last 0.5 m.y. of Maastrichtian, ending with rapid extinction of all tropical and subtropical species at or near K-T boundary.

to <5% of the foraminiferal assemblage in the >63 µm size fraction, and to <10% in the >150 µm size fraction (Nederbragt, 1991, 1998; Schmitz et al., 1992; Keller et al., 1995, 2001; Abramovich et al., 1998; Abramovich and Keller, 2001). Relative abundance fluctuations in planktic foraminiferal species are thus excellent environmental proxies for changes in water-mass stratification and climate.

At Loma Cerca faunal assemblages show clear indications of major climate changes during the last 300–400 k.y. of the Maastrichtian, as seen in the relative abundance changes of surface and thermocline dwellers (Fig. 7). For example, the relative abundance changes of the dominant surface dweller, *Pseudoguembelina costulata*, and those of globotruncanids show opposite trends. The same trends are amplified by the strong relative abundance changes in the overall population of surface dwellers that reflect major climate fluctuations.

Prior to deposition of the first spherule layer, *P. costulate* dominated, averaging 30%, and the total group of surface dwellers averaged 70% of the planktic foraminiferal population. At the same time, tropical and subtropical intermediate dwellers (globotruncanids) averaged 2% and rose to 10% near the base of CF1. The remainder consisted of intermediate-dwelling heterohelicids (e.g., *Heterohelix globulosa*, *H. dentata, H. planata*) that were ecological generalists able to thrive in variable conditions across latitudes. The extremely low abundance of species restricted to the tropical-subtropical environment (2%) in zone CF2 reflects high-stress conditions as a result of cool temperatures and correlates with the global cooling trend that reached a maximum ca. 65.5 Ma (Li and Keller, 1998a).

Spherule layer 1 coincides with a major faunal change that continued through spherule layers 2 and 3. During this interval, globotruncanids averaged a constant 20%–25%, except for two brief peaks of nearly 30% and 40% at the bases of spherule layers 2 and 3, respectively. Although it is tempting to dismiss this long-term abundance maximum in tropical and subtropical globotruncanid species as being due to reworking, there is little support for this interpretation. As noted herein, only the anomalous peaks in globotruncanids and benthic foraminifera at the bases of spherule layers 2 and 3 indicate reworking. The remainder of the spherule samples, including the samples from the marls and marly limestone between the spherule layers, contain typical warm-climate, low-latitude Tethyan assemblages dominated by globorotalids, rugoglobigerinids, and low-oxygen-tolerant heterohelicids. This strongly suggests that the spherule-producing event near the base of zone CF1 coincides with, or is causally related to, the onset of the short-term rapid global warming that has been dated as occurring between 65.4 to 65.3 Ma (Li and Keller, 1998a). This intriguing possibility must be explored further in additional sections in Mexico. Oxygen isotope analyses of Loma Cerca and another nearby section have proved useless because carbonate is strongly diagenetically altered.

In the 6 m of marls between spherule layers 3 and 4 at the base of the sandstone-siltstone complex, planktic foraminiferal assemblages suggest climate cooling with increasing abundance of ecological generalists (heterohelicids) near the top of the section (Fig. 3). Increasing dominance of heterohelicids (e.g., *H. globulosa*, *H. dentata*, *H. planata*, *H. navarroensis*) generally characterizes Tethyan assemblages during the last 100–200 k.y. of the Maastrichtian (Keller et al., 1995, 2001; Abramovich et al., 1998; Luciani, 2001). That this increase begins only near the top of the section just below the sandstone-siltstone complex at Loma Cerca indicates that deposition of the sandstone-siltstone complex occurred near the end of the Maastrichtian.

K-T extinction scenario revised

The new discovery of an older late Maastrichtian spherule layer deposited in pelagic marls about 270 k.y. prior to the K-T boundary in northeastern Mexico, and the associated faunal evidence of significant climate warming correlates well with the global warming of 3–4°C in surface and deep waters between 65.4 and 65.2 Ma (Li and Keller, 1998a), a major pulse in Deccan volcanism between 65.4 and 65.2 Ma (Hofmann et al., 2000), and the onset of mass extinctions in planktic foraminifera ca. 65.5 Ma (Fig. 10; Abramovich et al., 1998; Abramovich and Keller, 2001). These data indicate a complex interplay of climate change, volcanism, and impacts that caused the end-Cretaceous mass extinction.

This multievent mass-extinction scenario began ~400–500 k.y. before the K-T boundary at the transition that marks the end of the long-term Maastrichtian global cooling and onset of rapid global warming (Fig. 10). Maximum global warming between 65.4 and 65.2 Ma was probably linked to increased atmospheric CO_2 due to volcanic eruptions (Hoffman et al., 2000). The spherule event documented in Central America coincided with this warm event and exacerbated the already extreme climatic and environmental changes. During the last 100 k.y. of the Maastrichtian, climate cooled rapidly by 2–3°C across latitudes. The K-T boundary event coincided with a relatively cool climate that continued through the early Danian (Fig. 10). These extreme climatic fluctuations resulted in severe biotic stresses for tropical and subtropical planktic foraminifera. A gradual decrease in diversity began ca. 65.5 Ma, their combined relative abundance dropped to ~5%–10% of the total population, and their demise was met at or near the K-T boundary.

Chixculub impact or multiple impact events?

Glass spherules in Cretaceous-Tertiary boundary sections in Central America and the Caribbean are generally interpreted as melt droplets of target rocks dispersed by the Chicxulub impact in Yucatan, Mexico. The critical supporting evidence is based on the stratigraphic position of the glass spherules near the K-T boundary, their chemical similarity with melt rock in subsurface cores at Chicxulub, and an $^{40}Ar/^{39}Ar$ age of ca. 65 Ma of the spherules and melt rock (Izett et al., 1990; Swisher et al., 1992; Dalrymple et al., 1993). However, at the time these conclusions were reached only one spherule layer was known at the base of the sandstone-siltstone complex in northeastern Mexico. Four new discoveries have since been made that challenge this interpretation. (1) As many as 4 spherule layers within 10 m of pelagic marls below the sandstone-siltstone complex and K-T boundary in northeastern Mexico have been discovered (this study; Stinnesbeck et al., 2001). (2) At Beloc, Haiti, the spherule layer and Ir anomaly above it are within early Danian shales of the *P. eugubina* zone (Stinnesbeck et al., 2000; Keller et al., 2001; Stüben et al., this volume). (3) At Coxquihui, east-central Mexico, a thick spherule deposit and Ir anomaly above it also occur in the early Danian *P. eugubina* zone (Stinnesbeck et al., in press). (4) Above a thick breccia deposit at El Caribe in Guatemala, spherules and an Ir anomaly occur in shales of the early Danian *P. eugubina* zone (Fourcade et al., 1998, 1999; Keller and Stinnesbeck, 1999).

In view of these discoveries, it remains to be determined whether the Chicxulub crater is the source of all of these glass spherules, as previously concluded on the basis of chemical similarity of the glass spherules and melt rock from Chicxulub cores. If this conclusion stands, then the Chicxulub event must predate the K-T boundary by ~270–300 k.y. Regardless of the age of Chicxulub, current spherule data from late Maastrichtian marls and the K-T iridium anomaly worldwide strongly support a multiple impact scenario with a spherule-producing event (but no iridium anomaly) in the latest Maastrichtian (65.3 Ma), and an impact event at the K-T boundary (65.0 Ma). Accumulating data of spherules and Ir anomaly in the *P. eugubina* zone of Mexico, Haiti, and Guatemala indicates that there may have been a third impact event in the early Danian.

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