Late Maastrichtian age of spherule deposits in northeastern Mexico: implication for Chicxulub scenario

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Abstract: In the La Sierrita area of Nuevo Leon, Mexico, three spherule layers are present and separated from the overlying siliciclastic deposits by up to 6 m of pelagic marls. The marls are of latest Maastrichtian age (*Plummerita hantkeninoides* (CF1) Zone, *Micula prinsii* Zone) and deposited under normal pelagic conditions with no significant evidence of reworking or slumping. Original deposition of the spherule layers occurred during the last 300 ka of the Maastrichtian and well prior to the Cretaceous–Tertiary (K–T) boundary event. Thus, if the spherules in northeastern Mexico provide critical evidence of an impact at Chicxulub, this impact predates the K–T boundary.

Résumé : Dans la région de La Sierrita de Nuevo Leon, au Mexique, on retrouve trois couches de sphérules et jusqu'à 6 m de marnes pélagiques les séparent des dépôts silicoclastiques sus-jacents. Les marnes sont du Maastrichtien terminal (zone *Plummerita hantkeninoides* (CF1), zone *Micula prinsii*) et elles ont été déposées sous des conditions pélagiques normales sans évidence significative de reprise ni de glissement. La déposition originale des couches de sphérules a eu lieu au cours des derniers 300 ka du Maastrichtien et bien avant l'événement limite K–T. Ainsi, si les sphérules au nord-est du Mexique fournissent une évidence critique pour un impact à Chicxulub, cet impact a eu lieu avant la limite K–T.

[Traduit par la Rédaction]

Introduction

It is widely accepted that a bolide impact occurred at the Cretaceous–Tertiary (K–T) boundary near Chicxulub, on the Yucatan Peninsula, Mexico, although discussions about its biological consequences continue. In this scenario, spherule-rich, siliciclastic, and limestone breccia deposits in sections around the Gulf of Mexico and the Caribbean are interpreted as impact ejecta and impact-generated megatsunami deposits (e.g., Bourgeois et al. 1988; Hildebrand and Boynton 1990; Alvarez et al. 1992; Smit et al. 1992, 1996; Bralower et al. 1998; Smit 1999). Alternatively, these deposits have been interpreted as the result of long-term multi-event environmental changes related to volcanism, impact, climate and sea-level fluctuations (e.g., Keller and Stinnesbeck 1996*a*, 1996*b*; Keller et al. 1997, 1998). The placement of the K–T boundary is fundamentally different in these two scenarios. In the impact scenario, the spherule layer is thought to mark the K–T boundary, whereas in the multi-event scenario the K–T boundary is placed above the siliciclastic deposits at a small iridium anomaly and the mass extinction of tropical and subtropical planktic foraminifera.

Northeastern Mexico is of critical importance in evaluating the impact- and multi-event hypotheses, as well as the stratigraphic age of the Chicxulub event (e.g., Smit et al. 1992, 1996; Smit 1999; Stinnesbeck et al. 1993, 1996; Bohor 1996; Keller et al. 1997). In this area, sections containing spherule-rich deposits and a complex sandstone–siltstone sequence have been recognized over a distance of 500–600 km, from Los Ramones, near Monterrey to the north, to Tlaxcalantongo and Coxquihui near Poza Rica to the south (Fig. 1). The newly discovered sections in the La Sierrita area east of Montemorelos (State of Nuevo Leon, Fig. 1) differ from these in the presence of up to three

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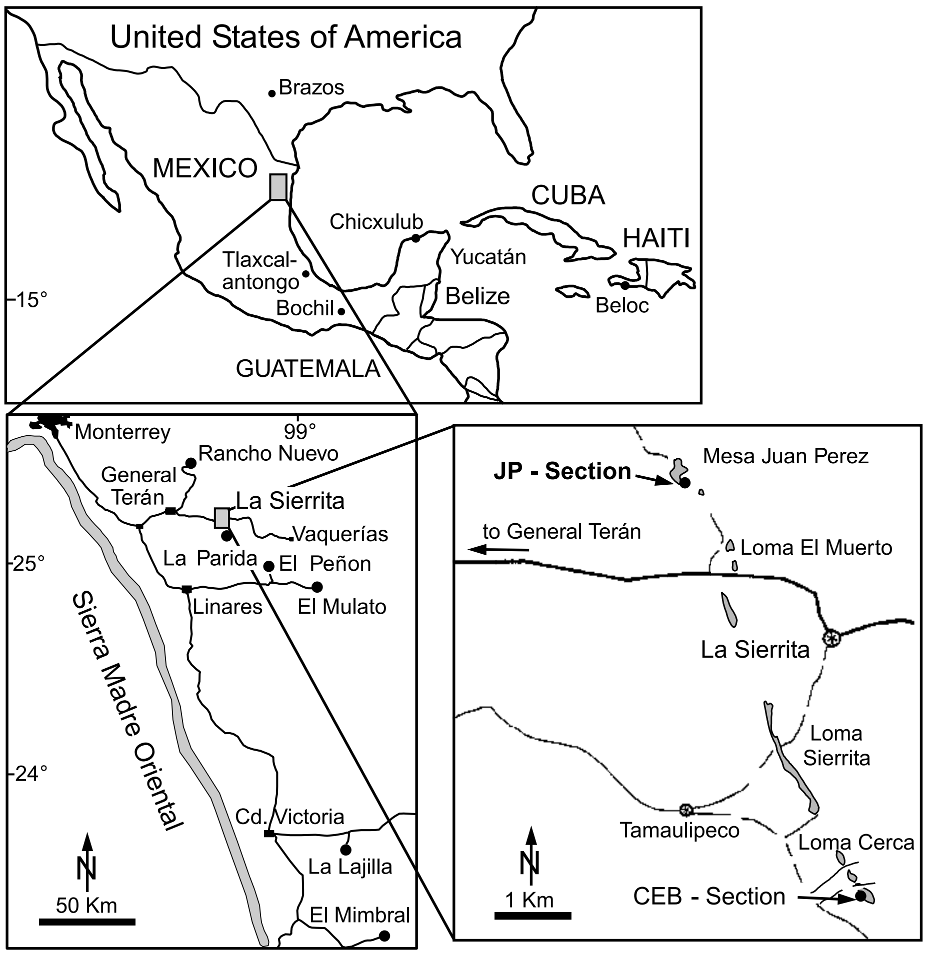
Fig. 2. Stratigraphic and lithologic correlation of two K–T boundary sequences in the La Sierrita area. Sections at Loma Cerca and Mesa Juan Perez are located at about 10 km from each other. Note that three spherule-rich layers are interlayered in pelagic marls of the Mendez Formation. 1.5 m (at Mesa Juan Perez) and 6 m (at Loma Cerca) of late Maastrichtian (Zone CF1) marls separate the spherule-rich layers from the fourth and topmost spherule layer at the base of the siliciclastic deposits, which are well known from many K–T boundary sections in northeastern Mexico.

Fig. 1. Location map of K–T boundary sections with siliciclastic or breccia deposits from Texas, Mexico, and the Caribbean. Lower map to the left shows locations of northeastern Mexico sections; lower map to the right shows locations of Mesa Juan Perez (JP) and Loma Cerca (CEB) sections. Note that in the La Sierrita area K–T outcrops align in a northwest–southeast-trending series of low-lying, flat-topped hills.



spherule-rich layers within pelagic sediments of latest Maastrichtian age. The stratigraphic position of these spherule layers, well below the siliciclastic deposit and the K–T boundary, calls for reevaluation of the K–T impact scenario and of the age of the Chicxulub K–T impact crater.

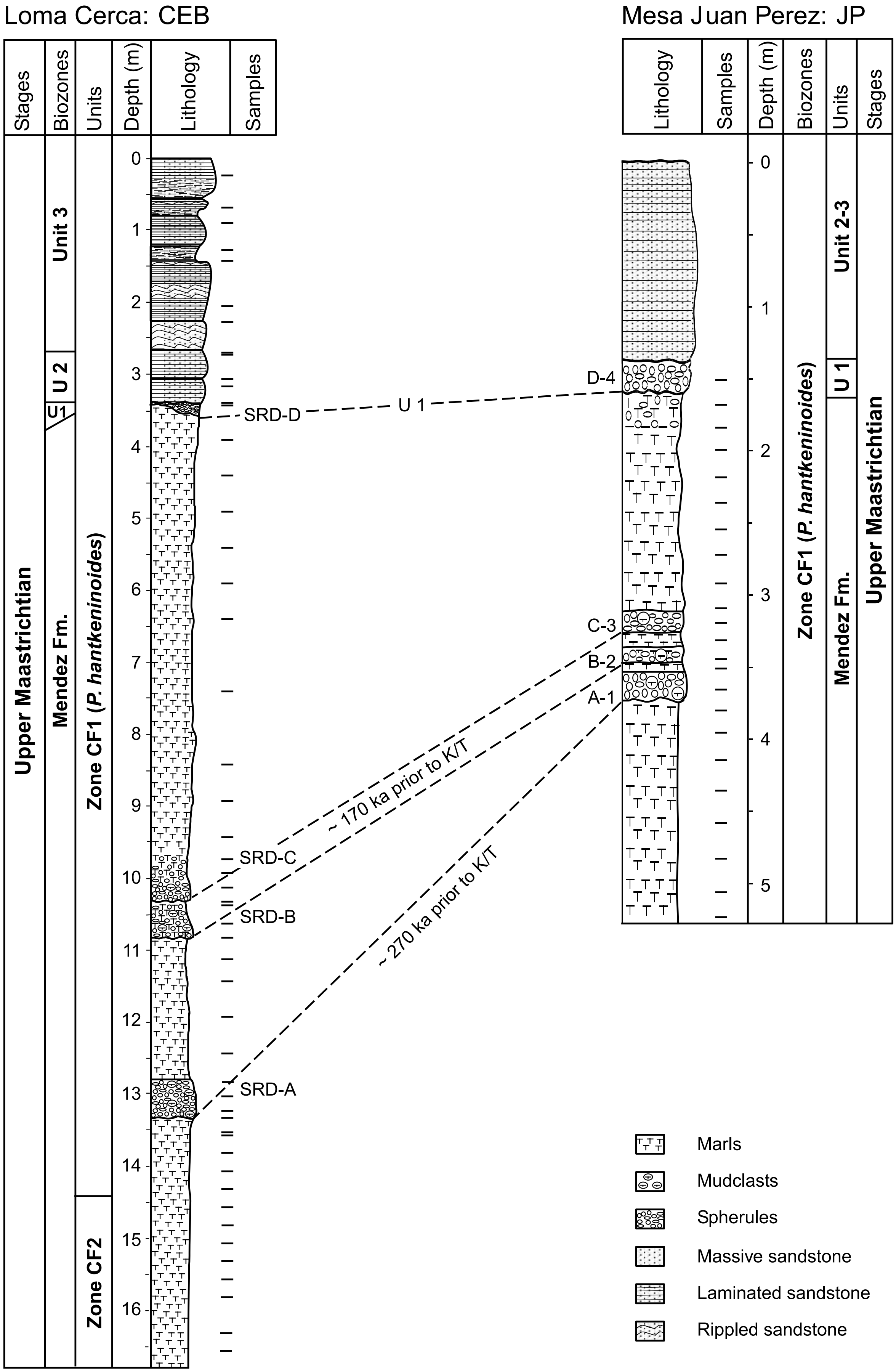
Geologic setting

The La Sierrita area is characterized by a northwest–southeast-trending series of low-lying hills, which consist of marls with the top formed by the resistant layers of the sandstone–siltstone complex and the uppermost of four spherule layers (Fig. 1). We report on two outcrops, the Loma Cerca (CEB) and Mesa Juan Perez (JP) sections, which are separated by 10 km and located about 40 km east of Montemorelos and 25 km east of General Teran, respectively.

Mesa Juan Perez section

The Mesa Juan Perez section outcrops along the southern hillside of the Mesa Juan Perez. The top of the hill is formed by a 1.2 m thick fine-grained homogenous sandstone with some horizontal laminations (Fig. 2), which overlies a 5–10 cm thick spherule-rich deposit (SRD). These two lithologies are correlated with units II and I, respectively, of the siliciclastic deposit in other sections (e.g., Mimbral, La Lajilla, Peñon; Stinnesbeck et al. 1993, 1996; Keller et al. 1997). The contact between units I and II is characterized by an undulose surface and probably represents a disconformity. A second disconformity is present between the base of unit I and the underlying marls of the Mendez Formation.

A continuous sequence of over 10 m of grey marls is exposed below the spherule layer (SRD-D4; Fig. 2). Within


Loma Cerca: CEB
Stages
Biozones
Units
Depth (m)
Lithology
Samples
Upper Maastrichtian
Unit 3
U 2
U1
Mendez Fm.
Zone CF1 (P. hantkeninoides)
Zone CF2
SRD-D
SRD-C
SRD-B
SRD-A
U 1
~ 170 ka prior to K/T
~ 270 ka prior to K/T
Mesa Juan Perez: JP
Lithology
Samples
Depth (m)
Biozones
Units
Stages
D-4
C-3
B-2
A-1
Zone CF1 (P. hantkeninoides)
Unit 2-3
U 1
Mendez Fm.
Upper Maastrichtian
Marls
Mudclasts
Spherules
Massive sandstone
Laminated sandstone
Rippled sandstone

this interval three additional spherule-rich layers are present between 240 and 180 cm below the base of unit I (SRD-A1, SRD-B2, SRD-C3; Fig. 2). The lowermost spherule layer, SRD-A1, is 15 cm thick and contains rare marl clasts. A 5 cm thick marl, which is devoid of spherules, separates SRD-A1 from the second 8 cm thick spherule layer SRD-B2. This spherule layer contains large (up to 0.5 cm) composite spherules and mud clasts in a marl matrix. A 10 cm thick marl layer separates the second and third spherule layers. The third spherule layer, SRD-C3, is 20 cm thick and contains mudclasts, spherule lenses, and clusters. No spherules were observed in the 1.2 m of marls that overlie SRD-C3. Though a few isolated spherules were observed in the white marls about 20 cm below the fourth spherule layer (SRD-D4, Fig. 2).

Loma Cerca section

This section is located on the western flank of the Loma Cerca hill, approximately 10 km south of Mesa Juan Perez (Figs. 1, 2). As at Mesa Juan Perez, the top of the hill is marked by the siliciclastic deposit, which is 3.5 m thick at Loma Cerca. A resistant fine-grained sandstone with horizontal laminations marks unit II. The overlying unit III is marked by cross-bedded, bioturbated layers. The contact between unit II and the underlying marls is an undulating, erosive surface. The troughs of this surface are up to 5 cm thick and infilled with spherules, and isolated spherules are present in the basal 5–10 cm of the overlying unit II sandstone. Stratigraphically, these spherules are relics of unit I (SRD-D) and correlate to SRD-D4 of the Mesa Juan Perez section.

Over 15 m of grey marls of the Mendez Formation are exposed below the siliciclastic deposit. In these marls, two well-separated spherule layers are present at 6 and 10 m below the siliciclastic deposit (Fig. 2). The lowermost spherule-rich deposit, SRD-A, is about 50 cm thick and has an undulating lower contact, but gradual upper contact with occasional mudclasts and spherule clusters at the base of the overlying marls. Two metres of grey marls separate this spherule layer from the overlying spherule layers (SRD-B and SRD-C; Fig. 2). SRD-B/C is about 1 m thick and consists of at least 2 individual layers of spherules that are marked by undulating and erosive lower surfaces with upward decreasing abundances of spherules and increasing mud content. About 6 m of pelagic marls separate the top of SRD-C and the base of units I and II of the siliciclastic deposit.

Age of spherule-rich layers

Fifty samples were analysed from the Mesa Juan Perez and Loma Cerca sections. Planktic foraminifera are abundant, though generally recrystallized and sometimes poorly preserved, similar to other sections in northeastern Mexico (Keller et al. 1994, 1997; Lopez Oliva and Keller 1996). All marl samples examined contain diverse and abundant late Maastrichtian assemblages, including diverse globotruncanids (e.g., *Globotruncana arca, G. aegyptiaca, G. rosetta, G. conica, G. dupeublei, G. insignis*), rugoglobigerinids (e.g., *Rugoglobigerina rugosa, R. hexacamerata, R. scotti*), heterohelicids (e.g., *Heterohelix globulosa, H. dentata, H. navarroensis, Pseudoguembelina costulata, P. kempensis, P. costata, Pseudotextularia elegans, P. deformis*), hedbergellids and globotruncanellids. The presence of *Plummerita hantkeninoides* and absence of Danian species indicates deposition during Zone CF1, which marks the latest Maastrichtian. Zone CF1 is equivalent to the latest Maastrichtian calcareous nannofossil zone *Micula prinsii*. Analysis of calcareous nannofossil assemblages of the two sections reveals a latest Maastrichtian age and deposition within the *Micula prinsii* Zone. A relative age difference within *M. prinsii* Zone is observed between samples from below the basal spherule layer and those above spherule layers 2 and 3 (SRD-B–C, SRD-B2, SRD-C3). Below the basal spherule layer *Thoracosphaera* is rare, as is characteristic of the lower part of the *M. prinsii* Zone. However, above spherule layers 2 and 3, *Thoracosphaera* is common, as is characteristic of the upper part of the *M. prinsii* Zone (A. Tantawy, unpublished data, 1999). Thus, both planktic foraminifera and calcareous nannofossils indicate that deposition of the spherule-rich layers occurred within the latest Maastrichtian biozone and well before the K–T boundary. Carbon isotopes also support a Maastrichtian age of these marls by their high values and absence of the characteristic negative excursion that mark the K–T boundary.

The actual age of spherule deposition can be estimated based on the stratigraphic correlation of Zone CF1 (*Plummerita hantkeninoides* Zone) with the paleomagnetic record at Agost, Spain, where this zone spans the last 300 ka of the Maastrichtian (Pardo et al. 1996). An average sediment accumulation rate can be estimated for Zone CF1 at Loma Cerca based on the following assumptions**:** (1) the spherule layers represent geologically instantaneous deposits, (2) marl deposition is pelagic without significant transported material, and (3) essentially the entire Zone CF1 is present. Based on these assumptions, the 9 m of marls that mark Zone CF1 at Loma Cerca represent average sediment deposition of 3 cm/1000 years, which compares favorably with 2 cm/1000 years at El Kef and 3 cm/1000 years at Elles, Tunisia, for the same interval (Li et al. 2000; Abramovich and Keller, in press). Based on these sediment accumulation rates, spherule layers SRD-A and SRD-B/C were deposited approximately 270 ka and 170 ka prior to the K–T boundary, respectively.

The previously known single spherule layer at the base of the siliciclastic deposit in many northeastern Mexico sections and elsewhere around the Gulf of Mexico and the Caribbean is frequently considered to be of K–T boundary age based on the assumption that the spherules are of impact origin and that the impact occurred at Chicxulub at the K–T boundary (e.g., Bralower et al. 1998; Smit 1999). However, we have previously documented that these deposits are stratigraphically below the K–T boundary, as defined globally by the mass extinction of tropical and subtropical planktic foraminifera, the Ir anomaly, and above it the first appearance of Danian species (Keller et al. 1994, l997; Lopez and Keller 1996). Furthermore, it has been convincingly demonstrated that the siliciclastic deposits between the K–T boundary and the spherule layer can not be due to a short-term depositional event, such as impact-related megatsunami deposits, as frequently argued (e.g., Smit et al. 1992, 1996; Smit l999; Bralower et al. l998), because they contain multiple horizons of repeated invertebrate colonization of the ocean floor (see Keller et al. l997; Ekdale and Stinnesbeck 1998). Clearly, the repeated establishing of invertebrate communities on the ocean floor could not have taken place within the hours or days of a tsunami event, but required an extended time period. Therefore, the unit I spherule layer that lies below the siliciclastic deposit with the multiple biohorizons can not be the same age as the Ir anomaly and first appearance of Danian species, which are above the siliciclastic deposit. The spherule-rich layer must, therefore, be older and of latest Maastrichtian age. The discovery of three additional spherule-rich layers below the original unit I layer and their presence within the latest Maastrichtian *M. prinsii* and *P. hantkeninoides* zones further confirms a pre-K–T age for these deposits.

Slumps, reworking, or multi-event spherule deposition?

The four spherule-rich layers either represent four spherule-producing events or one event and subsequent redistribution due to episodes of reworking, slumping, or tectonic faulting. The sections provide little evidence for either scenario. The marls are lithologically uniform, and show no structural features of either slumps or repeated faulting, although this remains a possibility. Multiple spherule-producing events, over a period of about 200–300 ka, either due to multiple impacts or volcanic events, also appear unlikely. This leaves us with the reworking hypothesis with a single spherule-producing event originating in the latest Maastrichtian *M. prinsii* and *P. hantkeninoides* zones and subsequent repeated reworking and redistribution of the original deposit within a normal pelagic environment. There are several reasons why the reworking hypothesis seems the more likely scenario.

(1) At Loma Cerca granulometric analyses of the insoluble residues were carried out by a laser particle counter Galai CIS system, using the method described in Jantschick et al. (1992; Fig. 3). Marls and the spherule-rich deposits from below the siliciclastic deposit were analysed to test possible reworking by a single catastrophic event that would have resulted in coarser grain sizes. As expected, the SRDs differ by their coarser grain sizes (16–150 μm), but the marls show uniformly smaller grain sizes (<16 μm), except for a short interval at the CF1–CF2 boundary, and suggest normal pelagic deposition (Fig. 3).

(2) Normal pelagic sedimentation, rather than slump deposits, is also suggested by the generally mottled character of the marls, where individual trace fossils (e.g., *Chondrites, Planolites*) are still recognizable in an apparently undisturbed configuration. No erosional surfaces, layers with mudclasts, or other evident changes in the lithology were observed within the marls in the field or during thin section studies.

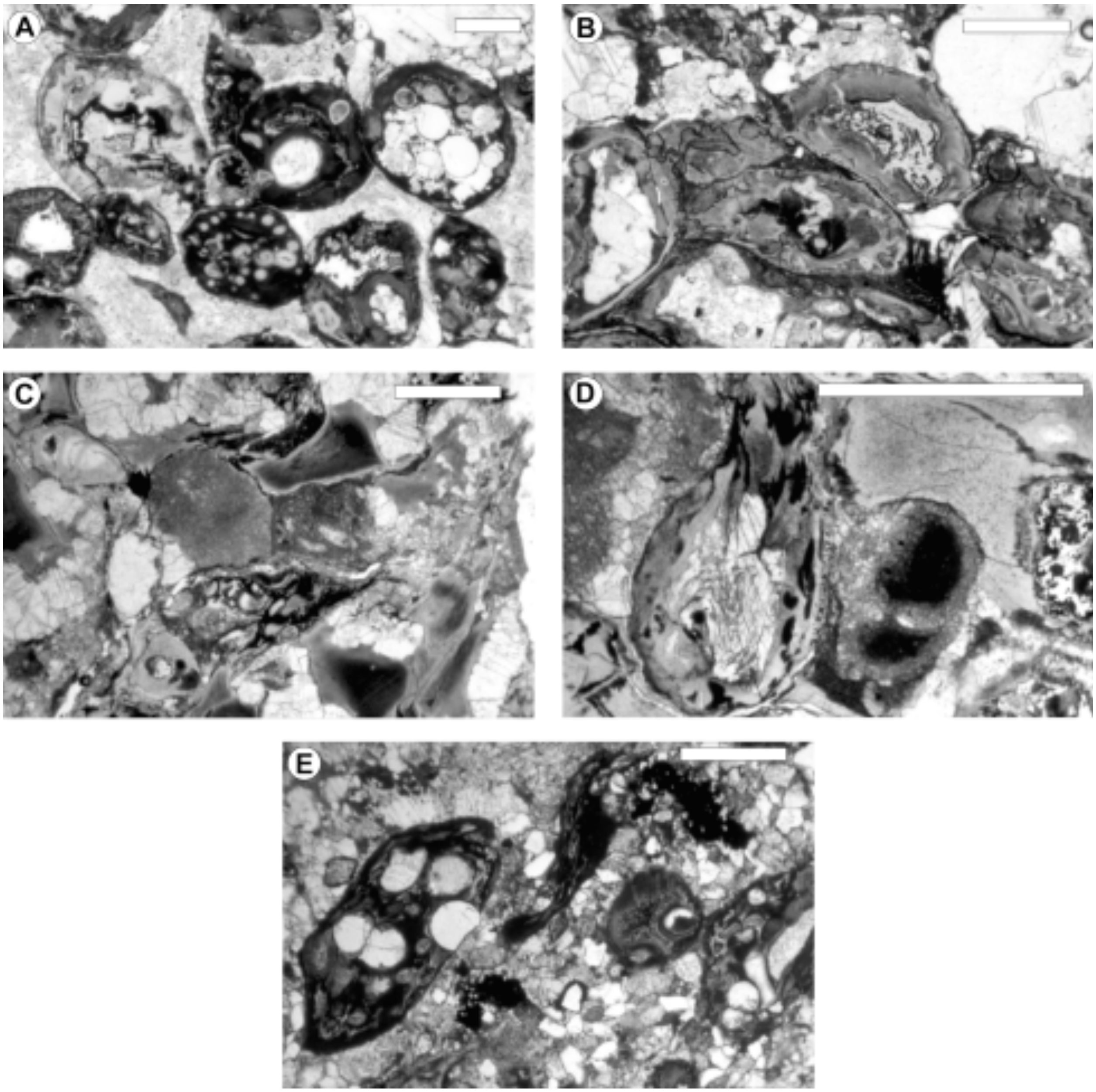
(3) X-ray diffractometer (XRD) analyses of whole-rock marls at Loma Cerca and Mesa Juan Perez indicate average compositions of 45–50% calcite, 12–18% quartz, 5–10% plagioclase, and 25–30% phyllosilicates. There is no difference between marls below, between, or above the SRDs. These whole-rock compositions are almost identical to coeval Mendez marls at El Peñon and Mimbral (Adatte et al. 1996). Calcite and phyllosilicates are the most abundant components and suggest normal pelagic sedimentation and weak hydrodynamic conditions. XRD analysis indicates that the clay fraction is almost identical in all marl layers. Fine-grained mixed layers of illite–smectite and chlorite–smectite (<2 μm) are dominant when compared to mica and chlorite, similar to other coeval Mendez marls in the region. The abundance of these clay minerals implies normal and quiet pelagic sedimentation (Adatte et al. 1996). Reworking, slumping, or sliding movements induced by seismic waves could not have settled these fine-grained marly deposits within the hours required prior to the backwash of coarser tsunami sediments, assuming that the spherules are impact derived (Fisher 1965).

(4) Stable isotopes of bulk-rock samples show relatively uniform signals with major variations restricted to the SRDs. Values for δ^{18}O are very negative ranging from –8.7‰ to –7.4‰ and indicate strong diagenetic alteration and recrystallization of carbonate in the presence of meteoric water depleted in δ^{18}O. The δ^{13}C values range from –5.2‰ to –0.7‰ and are slightly more negative than in coeval sections (El Kef and Elles) in Tunisia or Site 525 in the South Atlantic (Li and Keller 1998; Li et al. 2000). These δ^{13}C values of the SRDs are systematically lower than in the marls (Fig. 3), probably due to diagenesis. The δ^{13}C values of marls are uniform throughout the section, similar to the grain-size distribution and whole-rock composition, all of which suggest normal pelagic deposition and absence of significant reworking. However, δ^{13}C values are more variable in the spherule layers and suggests higher amounts of reworked and redeposited sediments.

(5) Thin section and XRD analyses indicate that SRD-A–C and SRD-A1–C3 at Loma Cerca and Mesa Juan Perez differ from unit I spherule layers (including SRD-D, SRD-D4) by the low amount of coarse terrigenous minerals (Figs. 3A–D). Quartz and plagioclase are lowest in SRD-A1 and increase in SRD-B2 and SRD-C3. This may reflect an increase in detrital flux in the SRD's upsection, which may represent a progressive dilution of a source spherule deposit by terrigenous sediment. Significantly higher amounts of quartz and lithic fragments were detected in the unit I spherule layers (SRD-D and SRD-D4), similar to all other northeastern Mexico deposits (Stinnesbeck et al. 1993, l996; Smit et al. 1996; Fig. 3E). This lithological difference suggests that SRD-A–C and SRD-A1–C3 are not associated with the siliciclastic sediments and represent depositional events different from unit I. They, thus, do not result from a repetition of the unit I SRD upsection by postdepositional faults, slides, or slumps.

(6) Outcrop exposures in the La Sierrita area are excellent. Individual spherule layers were traced for several tens of metres along the hillslope at Loma Cerca and Mesa Juan Perez. Numerous sections similar to Mesa Juan Perez and Loma Cerca were mapped in the area that give evidence for continuity of the multiple spherule layers in this area. Recently, the outcrop area was extended by as much as 30 km to the south of Loma Cerca. At El Peñón II (Stinnesbeck et al. 1996, for de-

Fig. 3. Microphotographs of thin sections showing characteristics of spherule-rich deposits at Loma Cerca and Mesa Juan Perez. (A–B) SRD-A1, spherulithic variety: aggregates of devitrified vesicular spherules in a matrix of blocky calcite. Note that some spherules exhibit concave–convex contacts, which indicate primary deposition while still hot and ductile. No marly sediments are present as matrix between spherules, which indicates there was little mixing with marls of the Mendez Formation. (C–D) SRD-A1, agglutinated variety: welded spherules, hyaline fragments, marl clasts, and foraminifers. Note that marl clasts and foraminifers are enclosed by devitrified fragments and spherules, which indicates that deposition occurred while the glass was still hot and ductile. (E) SRD-D4, spherule layer of unit I at Mesa Juan Perez. Note the abundance of coarse-grained terrigenous detritus that suggests reworking of spherules at the base of the siliciclastic deposit. Scale bars = 0.5mm.



tailed description of the section), a 30 cm thick spherule-rich layer has been detected 1 m below the spherule-rich layer of unit I at the base of the siliciclastic deposit. The marly sediments between these two spherule-rich layers contain diverse latest Maastrichtian planktic foraminiferal assemblages of Maastrichtian Zone CF1 age.

(7) Microfossil assemblages present in the basal spherule-rich layer differ markedly from those in the overlying SRD layers at both Loma Cerca and Mesa Juan Perez. The basal SRD contains rich assemblages of planktic foraminifera and calcareous nannofossils. But the upper spherule-rich layers, including the topmost SRD, contain common fragments of break-resistant benthic and planktic foraminifera, but no calcarous nannofossils. This suggests that the upper SRD layers are reworked with fine-grained sediments, including most planktic foraminifera and calcareous nannofossils, winnowed

out. Another possibility is that microfossils in the upper SRDs are dissolved due to diagenetic alteration, though this interpretation is suspect, since diagenesis would equally have affected calcareous microfossils within the stratigraphically lowermost SRD.

(8) Marl clasts present in the spherule-rich deposits suggest the presence of reworking and redeposition of at least some material, though the clasts could also have been part of the original deposit. However, the presence of common benthic foraminiferal fragments and enrichment of break-resistant foraminiferal species (e.g., globotruncanids, rugoglobigerinids, benthic species) suggest reworking. On the other hand, sediment transport on the sea floor can not have been over a long distance, because fragile components, such as vesicular spherules, clusters of spherules, and needlelike spherule shards, remained unfragmented and mudclasts are often angular.

These data suggest that the presence of multiple spherule-rich layers of late Maastrichtian age (Zone CF1) in the La Sierrita area are not artifacts caused by slumps or repeated faulting. Rather it suggests that times of pelagic marl deposition alternated with spherule and spherule-rich marl deposition, which was probably accompanied by higher energy conditions and possibly reworking of the original spherule deposit.

Uniqueness of spherule layer

La Sierrita sections are not unique in either the presence of multiple spherule layers or biostratigraphic position that indicates a non-K–T age. For example, although glass spherules from Mexico, Haiti, and Guatemala are similar in their chemical composition and likely originated from the same (?impact) event, their stratigraphic positions differ significantly. In the Beloc sections of Haiti, there are several spherule-rich layers intercalated with bioclastic limestones that contain rare altered spherules. Diverse assemblages of in situ foraminiferal faunas of early Danian Zone P1a (*P. eugubina*) age are present from the base of the SRD upsection (Stinnesbeck et al. 2000; Keller et al. 2001). These faunas indicate that deposition, or redeposition from the original deposit, occurred well after the K–T boundary. At El Caribe in Guatemala, altered spherules are present in the uppermost layers of a limeclast breccia that also contains Zone P1a faunal elements (Fourcade et al. 1998, 1999; Keller and Stinnesbeck 2000). This also suggests that deposition or redeposition may have continued into the early Danian. In contrast, the multiple spherule-rich layers in the La Sierrita sections are stratigraphically below the K–T boundary within the latest Maastrichtian Zone CF1 or *M. prinsii* Zone. Assuming that there is a single origin for these glass spherules, the stratigraphically oldest layer must represent the original event from which all younger spherule-rich layers were redeposited. We, therefore, interpret the age discrepancy in the stratigraphic position of the spherule layers between Mexico, Haiti, and Guatemala as the result of reworking and redeposition of the original SRD, which was deposited during the latest Maastrichtian Zone CF1 or *M. prinsii* Zone.

Platinum group elements

At Loma Cerca, a total of 18 samples of spherule-rich sediments and marls below, between, and above the SRDs were analysed for platinum group elements to establish a possible relationship to the global K–T boundary iridium event. Methods for preconcentration and matrix eliminiation (by fire assay with nickel sulfide collection) follow Cubelic et al. (1997). The analysis was carried out with a high-resolution AXIOM inductively coupled plasma – mass spectrometer. Measured values are close to the detection limits (Ru, 0.1 μg/kg; Rh, 0.05 μg/kg; Ir, 0.07 μg/kg; Pt, 0.4 μg/kg). No significant platinum group element anomalies were detected in the SRDs or marls of the Loma Cerca section, and hence no correlation can be shown with the K–T boundary event.

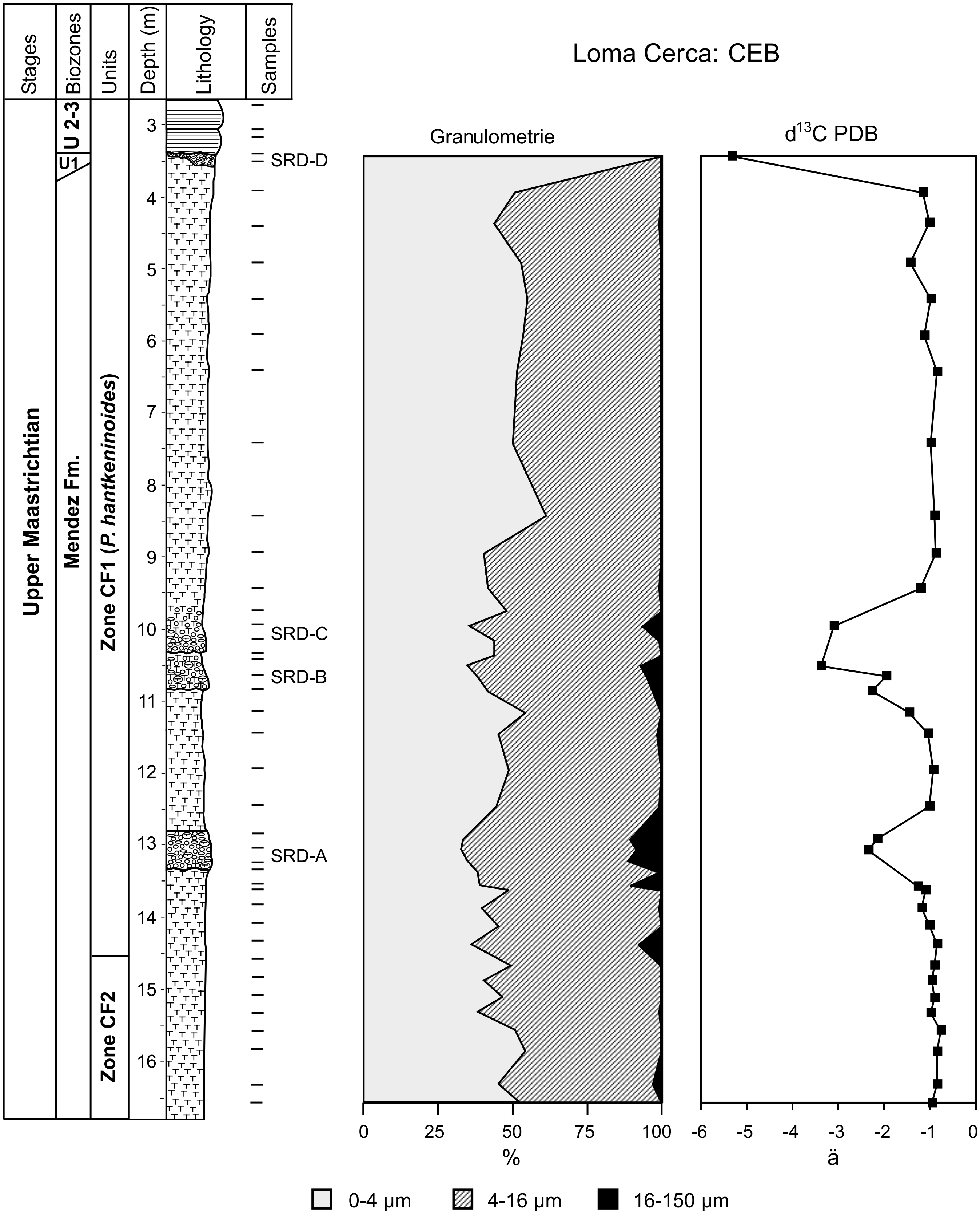
Characteristics of spherules and of spherule-rich deposits

The SRDs at Loma Cerca and Mesa Juan Perez contain abundant light to dark brown and some green devitrified spherules and devitrified fragments, though original morphologies are well preserved. The spherules are up to 5 mm in diameter and round, oval to tear-drop, or elliptical in shape. The devitrified fragments are up to 6 mm in diameter, angular, and of irregular elongated shape. Most are composite spherules which contain vesicles up to 75% of the overall spherule volume. Vesicles are generally spherical and usually infilled with blocky calcite or siliceous material (opaline, tridymite). Devitrification appears to be complete (no glass residues after processing), though most spherules are dark under crossed nicols or show high-interference colors at the edges, which suggests alteration to amorphous palagonite and clay minerals. XRD analysis identifies these clay minerals as smectite, chlorite–smectite and illite–smectite mixed layers. This points to a basaltic to intermediate composition, which is also suggested by the dark color of spherules and devitrified fragments and the presence of euhedral feldspar microliths in some massive spherules.

Two types of SRDs are differentiated in the basal spherule layer based on textural characteristics. Type 1 is characterized by a grain-supported texture with abundant spherules (spherulithic variety; Figs. 4A, 4B). Devitrified fragments, marl, terrigenous input, foraminifers, and marl clasts are rare to absent. Spherules are often oriented parallel to their elongate axis. The frequency of eutaxitic spherule textures, their convex–concave contacts and the agglutination between spherules suggest that they were still hot and ductile during transport and primary deposition Figs. 4A, 4B). This welding is not a diagenetic effect as indicated by high pore volume (>40%) and pores filled with blocky calcite, and the excellent preservation of fragile details, such as dark “schlieren,” vesicles, and inclusions. In addition, there is no indication of low-grade metamorphism.

The second variety presents chaotic grain-supported textures of devitrified spherules; abundant devitrified fragments, which are flaserlike, frequently welded; and show fluidal textures (hyaline agglutinated variety; Figs. 4C, 4D). The devitrified fragments often enclose lithic fragments, irregular-shaped marl clasts, foraminifers, and spherules. Many of

Fig. 4. Grain-size distribution and $\delta^{13}C$ record at Loma Cerca. Note that the marly sediments are very uniform and no major changes are apparent in lithology or in stable isotopes. This suggests normal pelagic deposition and the absence of significant reworking. Spherule-rich layers differ by coarser grain sizes and stronger diagenetic alteration of isotope values.



the spherules are strongly elongated and show infillings of dark marl. Marl clasts up to several cm in size are present. Terrigenous minerals are rare and the cement consists of blocky calcite.

Origin of spherules

Spherule layers in the La Sierrita area differ from SRDs previously reported from northeastern Mexico by the excellent preservation of spherules and scarcity of marl or terrigenous detritus (quartz, feldspar, mica) in the sediment matrix. No size gradation of spherules appears to be present within individual layers or between layers. The absence of size gradation either suggests immediate cooling and sinking of hot pyroclastic or impact ejecta, or sinking of cool “rafts” of spherule clusters or agglutinated fragments. In a descriptive sense, the spherulitic variety resembles fallout deposits with minimal redepositional transport, whereas the devitrified agglutinated variety shows characteristics of a proximal pyroclastic flow. However, the textural characteristics alone of the La Sierrita SRDs do not provide unequivocal evidence of their origin, whether volcanic or impact; other parameters have to be considered as well. Several research groups have argued for an impact-glass origin of the northeastern Mexico and Haiti spherules based on the glass geochemistry and inhomogeneity with lechatelierite and other mineral inclusions (Koeberl and Sigurdsson 1992), the oxygen isotope values (Blum and Chamberlain 1992), Rb–Sr and Sm–Nd isotopic data (Blum et al. 1993), the presence of sulfate (Chaussidon et al. 1994), and very low water content (Koeberl 1994). They argue that these data advocate against a volcanic origin of the Haiti and Mexico glass and link it to melt rock from the Chicxulub impact crater.

Implication for Chicxulub impact hypothesis

Spherule deposition in the Caribbean is widely considered to be a single event that originated with the K–T boundary impact at Chicxulub. This view is strongly supported by chemical similarities of spherules in Haiti and northeastern Mexico and andesitic glass from the Chicxulub cores (e.g., Izett 1991; Blum and Chamberlain 1992; Smit et al. 1992; Koeberl 1994). Assuming that this spherule origin interpretation is correct, then the multiple spherule layers observed in the La Sierrita sections must be explained by reworking of the original layer. However, this does not solve the problem of the original age of the spherule layer which appears to predate the K–T boundary in the La Sierrita sections.

Although our data from Loma Cerca and Mesa Juan Perez do not provide conclusive evidence for either impact or volcanic origin of the Mexican spherules, they provide strong evidence that places the onset of spherule deposition in the latest Maastrichtian *P. hantkeninoides* Zone (CF1) or *Micula prinsii* Zone. Two metres of latest Maastrichtian marls at Mesa Juan Perez and almost 6 m at Loma Cerca overlie and stratigraphically separate the spherule-producing event(s) from the siliciclastic-event deposition (units I to III). If the spherules are melt glass of the Chicxulub impact, then the lowermost spherule layer (SRD-A resp. A1) represents the original ejecta deposit, whereas all overlying layers (SRD-B–D and SRD-B2–D4) are likely redeposited. This would suggest that the Chicxulub impact is a latest Maastrichtian event and predates the K–T boundary by about 270 ka.

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