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Discussion

Comment on the paper "Chicxulub impact predates K-T boundary: New evidence from Brazos, Texas" by Keller et al. (2007)

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of the earlier studies.

outlined in Molina et al. (2006) are:

Keller et al. (2007) interpret their findings from the Brazos River area in Central Texas as evidence of two impacts at the close of the Cretaceous with the Chicxulub impact predating the Cretaceous—Paleogene (K–P) boundary by 300 ky, followed by another — yet not documented — impact at the boundary. Specifically, Keller et al. correlate the K–P boundary to a level about 20–40 cm above the well-known spherule-rich (Chicxulub) event bed at the concurrent lowest occurrence (LO) of several Paleocene microfossils. In addition, the authors report on a cm-thick yellow clay layer 40 cm below this event deposit and suggest that the yellow clay is the original Chicxulub ejecta deposit that formed 300 ky before the K–P boundary. Subsequently, they present a highly complex depositional and sealevel scenario to explain the extensive reworking of Chicxulub ejecta 200 ky following original deposition.

In our view, the data and interpretations presented to warrant the staggering conclusions of this paper are insufficient, contradictory, and in part erroneous. In brief, our major points at issue in the paper by Keller et al. (2007) are: (i) the misplacement of the K–P boundary, (ii) the untenable reworking and sea-level scenario, (iii) the lack of impact evidence in the

Stratigraphic Commission (ICS, www.stratigraphy.org) and

yellow clay layer, and (iv) the exclusion of nearly all overwhelming evidence in support of the genetic link between the

Chicxulub crater and the K-P boundary clay from numerous

K-P sections within and beyond the Gulf of Mexico. A much

more extensive discussion of the data from these K-P sections

would be required to seriously contradict the general outcome

- (1) evidence for asteroid impact (Iridium anomaly, Ni-rich spinels, shocked quartz, spherules etc.) and
- (2) major extinction horizon, including planktic foraminifers and calcareous nannofossils.

Numerous previous studies reported iridium anomalies up 0.5 ppb in Brazos K–P sections and cores starting in the top of the spherule-rich event bed and peaking with up to 1.5 ppb about 10–20 cm above it, though the exact level and magnitude

^{1.} Misplacement of the K–P boundary

The "golden spike" of the global boundary stratotype section and point (GSSP) of the basal Danian (= basal Paleocene and basal Paleogene) is located at the base of the (black) boundary clay at El Kef, Tunisia. The primary criteria for correlation of the base of the Danian (i.e. the K–P boundary) by the International

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of the iridium peaks varies between sections and cores (see Fig. 1 and Hansen et al., 1987, 1993). The onset of the multiple iridium anomalies on top of the spherule-rich event bed at Brazos is explained by the ejecta spherules at proximal locations to Chicxulub comprising rapid, ballistically-transported target rocks, whereas the Ir-rich extraterrestrial material was lofted by the hot ejecta plume well-above the atmosphere and settled considerably later (e.g., Smit, 1999; Claeys et al., 2002; Kring, 2007). At regions distal to Chicxulub, e.g., at El Kef, Tunisia, these two distinct impact layers merge to one layer rich in ejecta spherules, shocked minerals, and iridium (see Fig. 1). However, by discussing the iridium enrichments at the Brazos Riverbed section, Keller et al. aligned all plots in their Fig. 8 giving the false expression that the three major iridium peaks are at the same level well-above the spherule-rich event bed (see a comparison from Keller et al.'s Fig. 8 with the original iridium data in our Fig. 1).

Moreover, Keller et al. state on page 352 that "...the sudden mass extinction of all tropical-subtropical planktic foraminifera is diminished in the Brazos region...". The absence of a sudden mass extinction event at Brazos is, however, in stark contrast to the observations in numerous K-P sections, where the mass

extinction of tropical planktic foraminifera is abrupt (e.g., Keller et al., 2002) and coincident with a sharp drop of the calcareous nannofossil abundance (e.g., Pospichal, 1996; Gardin and Monechi, 1998).

Therefore, we criticize Keller et al. principally on the fact that they (a) fail to provide the characteristics in support of a clear K–P boundary position according to the official primary criteria as shown above and (b) instead of employing the primary criteria (evidence for asteroid impact, planktic extinctions, see Fig. 1) to correlate the base of the Danian, Keller et al. rely exclusively on secondary – at best – and poor stratigraphic markers to position this level at Brazos as outlined in the following.

Keller et al. place the K–P boundary at the level of the lowest occurrence (LO) of several Paleocene microfossils (planktic foraminifera and organic-walled dinocysts) at 40–80 cm above the top of the spherule-rich event bed. Additional support for this K–P boundary level is thought to be provided by a δ^{13} C minimum observed in the coarse silt fraction (38–63 μ m; i.e. small and juvenile planktic and benthic foraminifera) and in *Lenticulina* spp. (benthic foraminifera). This approach for positioning the K–P boundary is tentative at best and can only

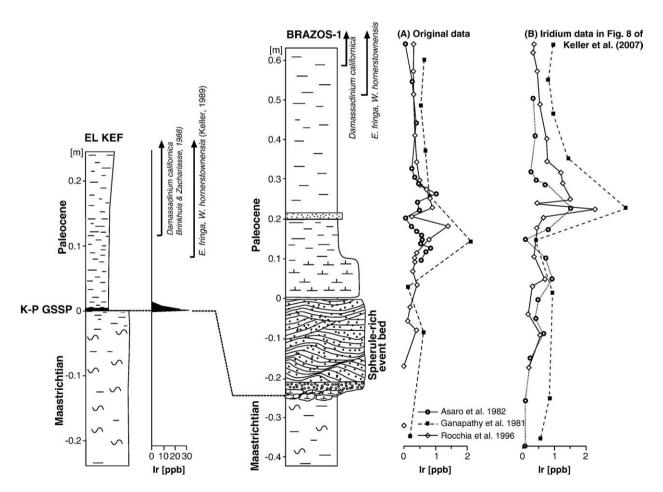


Fig. 1. Lithology, LO *Damassadinium californicum* (Brinkhuis et al., 1998), LO Paleogene planktic foraminifers and iridium (unpublished data, JS) of the El Kef K–P Global Stratotype and Point (GSSP) section compared to the Brazos-1 Riverbed section across the K–P boundary. Ir Brazos: (A) our compilation following Ganapathy et al. (1981), Asaro et al. (1982), and Rocchia et al. (1996). Note that the maximum at each of the analyses is at a different level, and not at the thin sandstone layer as compiled in (B) from Fig. 8 by Keller et al. (2007). LO Brazos: Smit, Brinkhuis, Hoof and Galeotti in prep. Note that the LO of the Paleocene taxa is consistently well-above the K–P boundary level.

be useful in discontinuous sequences or low-resolution pilot studies. The beds overlying the spherule-rich event bed, however, are not discontinuous and the sequence is quite expanded compared to the majority of K-P boundary sequences worldwide. Many studies have provided evidence that the LOs of Paleocene microfossils are irrelevant in determining the precise placement of the K-P boundary (see Fig. 1 and Brinkhuis and Zachariasse, 1988; Odin, 1992; Olsson and Liu, 1993; Bown, 2005; Molina et al., 2006; Schulte et al., 2006). As yet, there is not a single stratigraphic marker species within any biotic group, which LO coincides with the base of the Danian in an expanded continuous sequence. Instead, among planktic foraminifera the basal Danian is usually characterized by survivors. often associated with specimens that are likely to have been reworked, as found at El Kef and at Brazos River too (e.g., Speijer and Van der Zwaan, 1996; Arenillas et al., 2000; Schulte et al., 2006).

The planktic foraminiferal biozonation applied by Keller et al. (2007) does not follow internationally accepted definitions. Biozone P0 is defined as the biostratigraphic interval characterized by the partial range of Guembelitria cretacea between the highest occurrence of large Cretaceous taxa and the lowest occurrence of Parvularugoglobigerina eugubina (Keller, 1988; Berggren et al., 1995). Since Keller et al. do not record the simultaneous extinction of Cretaceous taxa (see page 352) the base of Biozone P0 cannot be established based on these data. It is also quite surprising that Keller et al. use the simultaneous LOs of W. hornerstownensis, G. daubjergensis, and P. extensa as a K-P marker since the same pattern has been used before as evidence for stratigraphic incompleteness by Keller et al. (2002). These taxa, in fact, show a discrete succession of first evolutionary appearances in the lowermost Danian. According to Keller et al. (2002), the youngest one of these is the LO of G. daubjergensis as high up as subzone P1a. Clearly, this reconfirms that the LO of Paleocene planktic foraminifera is not suitable for accurately correlating in this or any other K-P boundary sequence (Fig. 1).

Keller et al. (page 348) also claim that the LO of the dinocyst Damassadinium californicum (=Danea californica) is a "global K-T marker". Global distribution patterns of *D. californicum*, however, provide no support for this claim. This species first occurs at 15 cm above the K-P boundary in the El Kef GSSP section, near the top of the G. cretacea (P0) planktonic foraminiferal zone (see Fig. 1 and Brinkhuis et al., 1998). In the Seymour Island K-P sections, Antarctica, D. californicum has its LO about 20 cm above the Ir peak (Elliot et al., 1994). Closer to Brazos, at Moscow Landing in Alabama, D. californicum first occurs 129 cm above the K-P boundary (Habib et al., 1996). Even in condensed K-P sections such as Caravaca, Spain, the LO of *D. californicum* is still situated above the K–P boundary (Brinkhuis et al., 1998). Hence, in relatively expanded K-P sections - as Brazos is - there is always a significant stratigraphic interval of yet uncertain duration between the K-P boundary and the LO of D. californicum (cf. Fig. 1). This "global K-T marker" is therefore merely a lower Danian marker, just like the planktonic foraminifera discussed above.

Furthermore, Keller et al. show a complex δ^{13} C curve with minima in both the coarse silt fraction, and in *Lenticulina* spp., at the event deposit, followed by sharp recovery to pre-event values and a subsequent gradual decline to a minimum 0.4-0.8 m above the event deposit. In contrast, a sharp drop in planktic foraminifera and fine fraction δ^{13} C values characterizes the K-P boundary level in more distal K-P sections (Keller et al., 1995; D'Hondt et al., 1998; Molina et al., 2006). Moreover, Fig. 3 of Keller et al. also reveals a strong correlation between δ^{13} C values and calcite contents. Such a correlation may be taken to indicate strong diagenetic overprint (Marshall, 1992). Keller et al. provide neither an explanation for the unusual and gradual nature of the δ^{13} C anomaly at Brazos, nor do they discuss the potential of diagenetic artifacts or reworking on the δ^{13} C record of *Lenticulina* spp. It is also not clear why Keller et al. chose the coarse silt fraction of 38-63 µm for their study — this is an unusual size fraction for stable isotope bulk analyses, excluding calcareous nannofossils as well as micrite. Although Keller et al. do not indicate this, the studied size fraction is probably dominated by small-sized benthic and planktic foraminifera. It is well-established that benthic foraminifera normally have lighter δ^{13} C values than planktic foraminifera (e.g., D'Hondt et al., 1998). Since data on the relative proportions of benthic and planktic specimens are lacking – but are known to vary in the study area (Schulte et al., 2006) inferring any relation to a global δ^{13} C signal based on the 38– 63 um size fraction is unwarranted. The anomalous patterns and the choice of using an unknown mix of foraminifera for stable isotope analysis undermine the claim that these δ^{13} C records provide supporting evidence for the position of the K-P boundary. The patterns would rather support the idea of significant reworking of Cretaceous microfossils into deposits overlying the spherule-rich event bed (see next paragraph).

2. An untenable reworking and sea-level scenario

The identification of a cm-thick yellow clay layer, 40 cm below the well-known spherule-rich event deposit, as the original Chicxulub ejecta layer is an extraordinary conclusion. Extraordinary conclusions demand extraordinary evidence. Yet, the authors fail to provide this in any aspect. According to the interpretation presented by Keller et al., the ejecta spherules in the spherule-rich event bed are the result of repeated reworking of the original spherule deposit about 200,000 years (!) after the Chicxulub event.

The long-term reworking scenario outlined by Keller et al. strongly contrasts with observations on resedimented volcanic clasts, which always show a significant sorting, abrasion, dispersal and dilution by background sedimentation during reworking (Clayton et al., 1996; Nakayama and Yoshikawa, 1997; d'Atri et al., 1999; Schneider et al., 2001). Yet, Keller et al. propose that, more than 200,000 years after initial deposition, the reworking of a cm-thick original ejecta spherule layer would have lead to a secondary coherent dm-thick spherule deposit without any dilution by background sedimentation. The reverse process could make sense, this one not. In fact, it is sedimentologically impossible. To aggravate the situation,

Keller et al. seem to consider it irrelevant for their hypothesis that the reworked spherules are unbroken and in a much better state of preservation than in the assumed "original" yellow clay layer.

In order to justify the enigmatic long-term reworking of Chicxulub ejecta spherules, Keller et al. (2007) provide a rather complex sea-level scenario with a sea-level lowstand and incised valley fill at the base of the event bed, followed by a transgressive interval in the 0.4-0.8 m above the event bed, peaking in a maximum flooding surface exactly at the level where the authors place the K-P boundary. We do not agree with this complex sea-level scenario since supporting data is not presented in the paper and Keller's interpretation evidently violates well-established sequence stratigraphic concepts. For instance, Keller et al. suggest that the event deposit infills a scoured channel or incised valley without providing any paleorelief or outcrop-data in support of this hypothesis. Incised valley fills result from fluvial downcutting into the subaerially exposed shelf during sea-level lowstand (e.g., Catuneanu, 2002). However, Keller et al. show no evidence of subaerial exposure, nor do they show the large, hundreds of meter- to kilometer-wide valley associated with "incised valley" formation by fluvial incision (Dalrymple et al., 1994).

Fig. 9 of Keller et al. shows that the highstand systems tract (HST) starts immediately with the claystone above the spherulerich event deposit, whereas in the text it is suggested that this interval is part of the transgressive systems tract (TST). In addition, the level of the K–P boundary in Keller et al. is assigned as "maximum flooding surface" (mfs), which is in conflict with a position within the HST as shown in their Fig. 9. Note that the maximum flooding surface generally separates the TST from the HST, as proposed by the seminal work of Baum and Vail (1988) and many other sequence stratigraphic studies.

We are really puzzled by what Keller et al. mean with "sealevel transgression (HST)" in their Fig. 9. In the first place, the sea or rather the shoreline or facies-belts may transgress or regress in response to relative sea-level change. Sea-level, however, rises, falls, or remains stable. Since regressions and transgressions result from the interplay between eustasy, subsidence/ uplift and sediment input, a rising sea-level does not necessarily lead to transgression and neither does falling sea-level automatically lead to regression (e.g., Coe et al., 2003). Second, following Baum and Vail (1988), the maximum flooding surface separates the HST from the TST and is characterized by maximum transgression. Subsequently, at the onset of the HST the shoreline is shifting basin-ward and thus the HST is regressive, not transgressive. However, the sand/silt ratios shown in Fig. 3 of Keller et al. remain surprisingly constant during the suggested change from the highstand to the transgressive systems tract. Hence, granulometric data reveal no evidence for changes in the detrital input that may be related to a position shift of the shoreline.

3. Lack of impact evidence for the yellow clay layer

Keller et al. (2007) refer to a cm-thick yellow clay layer in the Brazos succession as "...original impact spherule layer..." or as "...original ejecta layer with relic glass spherules mostly altered to clay." (page 349 and Fig. 9 of Keller et al., respectively). However, nowhere in the paper it is clarified whether the authors have found the remnants of true Chicxulub ejecta spherules, i.e. round- or drop-shaped spherules with internal cavities and vesicles. The micrograph in their Fig. 9 from the yellow clay only shows some vaguely round structures (recent rootlets?) in a reddish matrix whereas clear evidence for the presence of true ejecta spherules is lacking. Without further supporting evidence for an impact event (Ir anomaly, shocked minerals, etc.), a volcanic origin for the yellow clay layer is more plausible (see Ewing and Caran, 1982, for details on late Cretaceous volcanism in Texas).

Besides the lack of evidence for an impact origin for the yellow clay layer, the clay and ejecta spherule mineralogy and geochemistry presented by Keller et al. (2007) exposes considerable shortcomings and inconsistencies. First, the heading "impact glass spherules" on page 349 and in Table 1 is not appropriate since Keller et al. have not reported data from true glass spherules. Second, on page 349 Brazos spherules are described as having 48–50% SiO₂, 15–18% FeO etc. with some variations for the different spherule layers. Yet, on the next page 350, the authors summarize that all three layers are similar and reveal "...typical Mg-enriched cheto-type smectite high in SiO₂ (66–71%), Al₂O₃ (19–20%) and low in FeO (4.4–4.8%)." Which, if any, of the data is the reader supposed to consider correct?

Furthermore, the spherule geochemistry provided by Keller et al. in Table 1 shows very high potassium content (>5% K_2O) for the "smectite" of the yellow clay layer and the "smectite" spherules. This high amount of potassium is, however, incompatible with pure smectite mineralogy but rather suggests the presence of considerable illite interstratification (Newman and Brown, 1987). Also, when normalized to $O_{20}(OH)_4$, Keller et al.'s spherule data reveal a total octahedral occupancy of 4.5-4.65 significantly exceeding the normal value of <4 for smectites giving further evidence for the presence of illite interstratification.

According to Keller et al. (page 342), "cheto smectite clay is characterized by a high percentage of expandable layers (>95%), excellent crystallinity, very high intensity of the 001 reflection, and a webby morphology. Keller et al. however, nowhere document these characteristics for the Brazos sections and they apply also to other smectites than the cheto-type (see Chipera and Bish, 2001). The proof of the presence of true "cheto-type smectite" can only be made by a careful combination of XRD, geochemical thermal, and morphological analysis (Grim and Kulbicki, 1961; Landgraf, 1979). Furthermore, the use of ternary FeO+MgO, K₂O+Na₂O, and CaO diagrams in Fig. 7 of Keller et al. (2007) to characterize and correlate Chicxulub spherules is inappropriate in mineralogical terms since Ca, K, and Na are exchangeable cations. Hence, the amount of these cations within the interlayers may vary considerably depending on the clay provenance, the depositional environment, and the diagenetic history (Moore and Revnolds, 1997).

It is also not clear why Keller et al. use the spherule geochemistry for correlation with other spherule layers exclusively in the Gulf of Mexico area, but do not show the excellent correlation with K–P Chicxulub ejecta spherules from the Caribbean, the Atlantic, and the Tethyan realm as revealed by the detailed clay mineralogical studies of Martínez-Ruiz et al. (2002, 2006), Ortega-Huertas et al. (2002), and Schulte et al. (2006).

4. Omission of evidence from K-P sections inside and outside the Gulf of Mexico

Various independent proxy data (e.g., concentric ejecta grainsize distribution, similar isotopic ages, and distinct compositional range of ejecta phases) from many continental and marine K-P boundary sections as well as from more than 24 recent Ocean Drilling Program (ODP) K-P drillcores all provide strong support for the genetic relationship between the Chicxulub impact event and the worldwide distributed K-P boundary ejecta layer (Sigurdsson et al., 1997; Olsson et al., 1997; Smit, 1999; Sweet and Braman, 2001; Martínez-Ruiz et al., 2002; Bralower et al., 2002; Erbacher et al., 2004; Zachos et al., 2004; Schulte and Kontny, 2005; Arenillas et al., 2006; MacLeod et al., 2007; Kring, 2007). In fact, the grain-size distribution of spherules and shocked minerals in the K-P boundary beds actually predicted the site of the Chicxulub crater structure in southern Mexico in the late 80s (Hildebrand and Boynton, 1988), well before (!) this impact structure had been identified as such in 1991 (see also Alvarez et al., 1995; Kring and Durda, 2002; Morgan et al., 2006). The thickness of the ejecta layer and the grain-size of spherules and shocked quartz increase as one approaches Chicxulub (Claevs et al., 2002; Kring, 2007). Moreover, the specific geochemical compositional range ("fingerprint") found in proximal Chicxulub ejecta and distal K-P clay layers reflects the igneous and metamorphic Pan-African Yucatan basement as well as the overlying carbonate platform. For instance, ejecta spherules show frequently a distinct Ca-S-enrichment. In addition, dolomite and carbonate spherules are found in the K-P boundary clay besides unshocked and shocked silicic mineral phases (e.g., Bohor and Glass, 1995; Martínez-Ruiz et al., 2002; Griscom et al., 2003).

To conclude, none of the studies outlined above provided evidence in support of a multi-impact scenario. All boundary layers that are generally agreed to be stratigraphically complete contain only one horizon rich in impact debris and that layer is intimately associated with faunal and floral evidence for the mass extinction at the K–P boundary. The vast amount of data linking Chicxulub to the K–P boundary has become overwhelming. Yet, Keller and her co-workers prefer to keep ignoring nearly all of it.

5. Conclusions

Based on the following major points of criticism, we suggest that Keller et al. (2007) have not made any case for Chicxulub as a pre-K-P boundary impact:

i. The Brazos K-P boundary level suggested by Keller et al.
 is misplaced since they rely exclusively on secondary – at
 best – and poor stratigraphic markers. Therefore, it does
 not fit the primary criteria of the International Commission of Stratigraphy (ICS) and the Cretaceous-Paleogene

- Working Group for positioning the K-P boundary (Molina et al., 2006).
- ii. The scenario of long-term reworking of the original Chicxulub ejecta layer into a coherent, thicker, and better-preserved ejecta *layer* after several hundred thousand years is sedimentologically impossible. Also, the sequence stratigraphic interpretation of the Brazos K–P transition presented by Keller et al. is in conflict with well-defined sequence stratigraphic concepts (e.g., "sea-level transgression (HST)" and "mfs within HST").
- iii. The paper provides no evidence for an impact origin of the late Maastrichtian yellow clay layer that the authors consider as original Chicxulub ejecta layer. Moreover, Keller et al. present erroneous and misleading data on Chicxulub ejecta spherule geochemistry and mineralogy: Keller et al.'s "cheto smectite" is actually an interstratified illite-smectite, they provide no evidence for impact glass, and the spherule geochemistry is not consistent between text, tables, and figures.
- iv. It remains unclear why Keller et al. develop their multiimpact scenario strictly on data of some Gulf of Mexico K–P sections, where sedimentology and stratigraphy are inherently complex due to the proximity to the high-energy Chicxulub impact event. Keller et al. consistently ignore further data from proximal (e.g., El Guayal) and from numerous distal Western Interior and Atlantic K–P sites that include a sharp iridium anomaly and a graded Chicxulub ejecta deposit exactly at the K–P boundary level, clearly supporting a genetic link between the Chicxulub impact and the K–P boundary clay.

Note added in proof

Each ODP Leg (e.g., Leg 207) drills at up to four sites (e.g., ODP Leg 207 Sites 1258, 1259, 1260, and 1261) and at each site, up to three single cores are drilled (e.g., 1259a, b, and c). Therefore, an ODP Leg may provide multiple records of the K–P boundary. For a detailed list of more than 48 DSDP and ODP K–P boundary cores please visit the ODP website at http://www-odp.tamu.edu/database/.

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