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Global bioevents and the Cretaceous/Paleogene boundary in Texas and Alabama: stratigraphy, correlation and ocean acidification.

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ABSTRACT

With increasing levels of atmospheric \( p\text{CO}_2 \) the oceans are becoming progressively more acidic, with the impact of a lowered pH beginning to affect the calcification of numerous invertebrate groups, including foraminifers, pteropods, heteropods and calcareous nannoplankton. Research on the ecology of foraminifera in the Mediterranean Sea, Gulf of California, Caribbean Sea and elsewhere has shown how modern assemblages are responding to acidification. Experimental work in mesocosms and laboratory cultures are also adding to our knowledge of the response to pH changes. Near Ischia (Italy), natural CO\(_2\) vents amongst sea grass meadows are creating low pH environments in which it is possible to observe the response of benthic foraminifera. At a pH of 7.8 the foraminiferal assemblages are already becoming less diverse and below pH 7.6 there are often no calcite-secreting benthic foraminifera. In the Gulf of California, in a deeper-water setting, natural CO\(_2\) (and methane) vents are also lowering sea floor pH. The foraminifera show the impact of this change, although the relatively high carbonate saturation ensures that calcite-secreting foraminifers are able to live and reproduce in these relatively low pH environments, only becoming impacted by dissolution effects once dead. Using data from the Cretaceous–Paleogene boundary in Texas, Alabama and north-west Europe it is clear that the plankton was severely impacted by surface water acidification.
while the relatively shallow water benthic foraminifera show little change and no visible signs of post-mortem dissolution due to ocean acidification.

1. Introduction
In recent years there have been major advances in the understanding of the cause(s) of major extinction events in Earth history. Despite this massive literature base (e.g., Bond and Grasby, 2017, and references therein) there remains little consensus over some of the mechanisms involved, timing (see Schulte et al., 2010; Deenen et al., 2010) and the intensity or duration of such events (Koeberl, 2017). Almost every scientific meeting shows that these events are still controversial, especially as the extinctions at the Cretaceous/Paleogene (K/Pg) boundary cover such a range of organisms (e.g., non-avian dinosaurs, ammonites, planktic foraminifera and calcareous nannofossils). Bond and Grasby (2017, p. 3) list the usual extinction-causing ‘suspects’, including anoxia, global warming, changes in atmospheric $pCO_2$ and, more recently, ocean acidification. Many of the Phanerozoic extinction events are now being related to either the eruption or weathering of large igneous provinces (LIPs), but – again – this links back to the problems of timing both of the eruptions and the ensuing bioevents. Adjacent to, and at, the K/Pg boundary the eruption of the Deccan volcanics certainly had an environmental effect but the impact at Chixculub is precisely coincident with the main extinction events as can be seen in the Gulf Coast region of the USA (and elsewhere). Here we attempt to assess the role of ocean acidification in the K/Pg boundary successions in Texas, Alabama and elsewhere.

2. Global bioevents
The Phanerozoic contains a number of significant bioevents, many of which have been described as mass extinctions (Bond and Grasby, 2017). As recognized by Sepkoski’s (2002) and earlier (Sepkoski et al., 1981; Raup and Sepkoski, 1982, 1984) compilations the ‘big five’ extinction events can be identified (Alroy, 2008; Alroy et al., 2008) as well as a number of other significant bioevents (Bambach, 2006). The data associated with these extinction events are being constantly revised and updated (e.g., Aberhan and Kiessling, 2012; Brett, 2012; Bond and Grasby, 2017; Erlykin et al., 2017; Melott and Bambach, 2017) by those interested in global patterns of evolution and diversification. In many cases so-called single events (e.g.,
end-Permian and end-Triassic) are, in fact, multiple events that are often separated by several million years. This does not appear to be the case for the K/Pg boundary where there appears to be a single event as will be demonstrated later. Between the ‘big five’ are a number of lesser, though still significant, biotic turnovers (e.g., Pliensbachian-early Toarcian, end-Cenomanian) caused by a variety of global, or local, phenomena.

The end-Permian and end-Triassic events have been attributed to major volcanic episodes: the eruption of the Siberian Flood Basalts (Campi, 2012, and references therein) and the Central Atlantic Magmatic Province (CAMP) (Wignall, 2001; Hesselbo et al., 2002; Corso et al., 2014) respectively. There are other extinction events where significant volcanic activity is known to have played a part, if not the sole cause of the extinctions. Amongst the most discussed are the eruptions of the Caribbean Large Igneous Province near the Cenomanian/Turonian boundary (Sinton and Duncan, 1997; Kerr, 1998; Wignall, 2001; Turgeon and Creaser, 2008; Jenkyns et al., 2017) and the eruptions of the Deccan Plateau around the end of the Cretaceous (Courtillot et al., 1986, 1988; Keller, 2012, and references therein). The latter are, of course, partly coincident with the major bolide impact on the Yucatan Peninsula (Mexico) at Chixculub. Two of these major events (end-Triassic and end-Cretaceous) have been suggested as periods influenced by ocean acidification (Hautmann et al., 2008; Martindale et al., 2012; Alegret et al., 2012). While such bioevents may be attributed to a range of causes, the impact of any variables (e.g., increasing atmospheric pCO$_2$) will have changed through geological time as both the oceanic and terrestrial biota has evolved.

In the Palaeozoic, the oceanic plankton was dominated by organic-walled (e.g., acritarchs, chitinozoa, etc.) and siliceous (e.g., radiolaria) groups, with ammonoids and nautiloids representing the only calcifiers inhabiting the water column (Fig. 1). The ‘carbonate factories’ of the Palaeozoic were, as a result, restricted to shallow-water environments where benthic calcifiers thrived (e.g., the Silurian and Middle Devonian limestones of the Welsh Borders and of New York State, Devonshire and other parts of north-west Europe). As all of these were formed in neritic environments, this situation has been described as the ‘Neritan Ocean’ by Zeebe and Westbroek (2003) and Ridgwell (2005).

In the Mesozoic and Cenozoic, neritic carbonate factories continued (e.g., the Urgonian Limestones of the French Alps, the Lower to mid-Cretaceous limestones of
the Oman Mountains (Wohlwend et al., 2016) and the Asmari Limestone of Iran) but were gradually overtaken in importance by the pelagic environment as the carbonate-producing plankton (e.g., calcareous nannofossils, planktic foraminifera, calpionellids, calcareous dinocysts and pteropods/heteropods) gradually evolved. Ridgwell (2005, his fig. 1) appears to indicate that this ‘Neritan’–‘Cretan’ transition was close to the Permo-Triassic boundary, even though the various taxa comprising the calcareous plankton do not appear until the latest Triassic, or even later. While the calcareous nannofossils appeared in the Triassic, they did not colonise the open ocean in large numbers until the post-Toarcian (Bown et al., 2004; Bown, 2005). This is almost the same time that the planktic foraminifers appeared in the Tethys Ocean (Wernli, 1995; Wernli and Görög, 1999; Hart et al., 2003, 2012a; Hudson et al., 2009). The planktic foraminifers did not, however, become diverse and abundant until the Early Cretaceous (Premoli Silva and Sliter, 1999; Hart, 1999; Hart et al., 2002). All of the Jurassic planktic foraminifers appear to have been relatively simple ‘globigerine’ forms with aragonitic tests (Hart et al., 2012a). The earliest planktic ooze, with a ~99:1 planktic:benthic ratio has been reported from the mid–Upper Jurassic of Southern Poland (Wierzbowski et al., 1999; Hudson et al., 2005) where these sediments were deposited above the Aragonite Compensation Depth (ACD). The switch from a ‘Neritan Ocean’ to the ‘Cretan Ocean’ of the present day was, therefore, a gradual process encompassing the mid-Jurassic to earliest Cretaceous. Other important calcifying plankton, including the calpionellids, calcareous dinocysts and pteropods/heteropods, appeared in the latest Jurassic, mid-Cretaceous and latest Cretaceous respectively.

In the mid–Late Jurassic, the diversity of planktic foraminifera remained low with only 2–3 genera and relatively few species (Gradstein et al., 2017a, b). In the earliest Cretaceous there were, effectively, only one or two genera (i.e., Conoglobigerina and Favusella) and it is almost impossible to determine a plausible evolutionary link to the newly-appearing Cretaceous assemblage (Banner and Desai, 1988; BouDagher-Fadel et al., 1997), with taxa characterized by calcitic, rather than aragonitic, tests. Segev and Erez (2006) have suggested that the planktic foraminifers were probably incapable of switching between aragonite and calcite (or between high- and low-Mg calcite) and that the appearance of the calcite-secreting planktic foraminifers in the earliest Cretaceous (in the Calcite II Ocean of Stanley (2006), Stanley et al. (2005a, b), Stanley and Hardie (1998) and van Dijk et al., 2016)
reflected a different ocean chemistry as well as an unrelated phylogeny. This hypothesis suggests that the aragonitic Jurassic planktic foraminifers (which appeared in the Aragonite II Ocean) did not evolve directly into the in-coming Cretaceous–Cenozoic lineages, probably evolved from another benthic ancestor. This may explain why the later forms developed a much wider range of morphologies than their Jurassic precursors (Leckie, 2009). It is important to note that the Jurassic genus *Favusella* continues into the Cretaceous but does not give rise to any further lineages, becoming rare in the mid-Albian (Hart and Harris, 2012) and, eventually, extinct in the mid-Cenomanian (Carter and Hart, 1977). In terms of the development of the ‘Cretan Ocean’ the timing is not that suggested by Zeebe and Westbroek (2003) and taken forward in their analysis by Hönisch et al. (2012). The responses to the end-Triassic and end-Cretaceous bioevents took place, therefore, in two very different oceans. Also in the bioevents debate are the ‘Strangelove Ocean’ where (almost) everything was killed (Kump, 1991; Adams and Mann, 2004; Zeebe and Westbroek, 2003; Alegret et al., 2012) and the ‘Living Ocean’ where this was not the case (D’Hondt et al., 1998; D’Hondt, 2005; Alegret and Thomas, 2007; Sepúlveda et al., 2009; Alegret et al., 2012).

Using information from modern work on acidification (changes in pH) and an understanding of changes resulting from hypoxia/anoxia (see Hart, 2018 for discussion) it is possible to re-visit the Cretaceous/Paleogene boundary succession in Texas and Alabama and their correlation elsewhere.

### 3. Cretaceous/Paleogene boundary

The Cretaceous/Paleogene (K/Pg) boundary and the possible causes of the associated extinctions is one of the most contentious issues in the geosciences (e.g., Archibald et al., 2010; Courtillot and Fluteau, 2010; Keller et al., 2010; Schulte et al., 2010). Our recent work in Texas and Alabama (Hart et al., 2012b, 2013) has yet again confirmed that the extinctions are coincident with the formally accepted K/Pg boundary (Molina et al., 2006), although it must be recognized that with the GSSP definition tied to the “moment of the meteorite impact, which implies that all the sediments generated by the impact belong to the Danian” (Molina et al., 2006, p. 263), there is a degree of circularity in the argument. The alternative view is summarized by Adatte et al. (2011), Keller and Adatte (2011) and Keller (2012). Their
interpretations, however, were partly, based on an incorrect interpretation of a ‘yellow clay’ which is seen in Cottonmouth Creek, Brazos River area (Fig. 2), 30–40 cm below the K/Pg boundary: for a full discussion see Hart et al. (2012b).

The K/Pg extinctions in the Gulf Coast and elsewhere have been attributed to a range of causes, including global darkness (caused by dust), ozone destruction, cooling/warming and – more recently – ocean acidification (Alegret et al., 2012). The interval between the timing of the impact and recovery – which is here taken as the onset of the planktic foraminiferal zone P1a – is approximately 80–100 kyrs based on the interpretation of precession cycles (Leighton et al., 2017). In Denmark (Stevns Klint), Hart et al. (2005) have documented the $\delta^{13}$C record in a much-expanded thickness of the Fiskeler Member (= Fish Clay of authors) in which there were approximately four isotopic excursions, with the lowest excursion, characterized by the largest negative $\delta^{13}$C excursion, being the most commonly reported elsewhere (e.g., Alegret et al., 2012, their fig. 2). In the River Bank South (RBS) section (Figs 2, 3) on the Brazos River (Hart et al., 2012b; Leighton et al., 2017) a comparable number of $\delta^{13}$C excursions are recorded in the lowest part of the Littig Member (Kincaid Formation). The large, negative excursion of the Stevns Klint succession is not recorded in Texas, probably because of the effects of the tsunami and ‘Event Bed’ deposition which is not recorded in Denmark and other distal K/Pg sites. The Danish succession (Hart et al., 2005, their fig. 10) appears to be reasonably complete, preserving the $\delta^{13}$C excursions, the iridium layer (Damholt and Surlyk, 2012 and references therein), a sharp ‘spike’ in Mo and Mo/Al ratios (Vellekoop et al., 2018, their figs 3, 4) and the short-lived presence of disaster taxa (mainly calcareous dinocysts): see Leighton et al. (2011).

If foraminiferal zones P0 and Pα represent approximately 80–100 kyrs (Leighton et al., 2017), then any extinction-causing events must be over within this time interval. In their chronology of the K/Pg boundary on Demerara Rise (North Atlantic Ocean, ODP Leg 207, Site 1259), MacLeod et al. (2007) indicate that P0 was ~30,000 years and this agrees with Leighton et al. (2017) who recorded slightly more than one precession cycle in that zone. This gives an outline indication of the time-scale across the boundary interval in which to identify the various near-instantaneous events (hours/days/months) which may have left little or no geological record; e.g., the 30 years cited by Brugger et al. (2017) or the short-term cooling postulated by Vellekoop et al. (2014).
The micropalaeontological investigations of the Brazos River area extend back to Plummer (1926, 1931), who described the ‘Event Bed’ exposed at River Bank South on the Falls/Milam county boundary as a ‘pair of anticlines’. She also noted the presence of large (mainly nodosarid) benthic foraminifera that were visible in the field; an occurrence confirmed by more recent fieldwork (Hart et al., 2012b). The history of the investigation of the area (Brazos River, Cottonmouth and Darting Minnow creeks, Mullinax boreholes, etc.) has been documented by a number of workers as indicated in Hart et al. (2012b). Many of these investigations (e.g., Gale, 2006) used the exposures on the bed of the Brazos River downstream of the Rt. 413 bridge (Fig. 4a). It should be noted that access to these locations is governed by the release of water from an upstream dam, rather than local rainfall and that visiting the outcrops at a ‘dry time’ does not guarantee access to the succession. In these outcrops the eroded top of the Maastrichtian mudstones can be seen, overlain by a conglomerate of calcareous nodules (Fig. 4b, c) derived from the underlying mudstones.

3.1. K/Pg boundary events in the Gulf of Mexico and Gulf Coast Region

The impact of the end-Cretaceous bolide into the Yucatan Peninsula would have generated a seismic shock, followed closely by the tsunami. The magnitude 10–11 earthquake (e.g., Day and Maslin, 2005) would have disturbed the Cretaceous mudstones and calcareous mudstones of the Gulf Coast, stirring up the unconsolidated sediment and, perhaps, shaking the semi-consolidated mudstones into blocks that would have settled back with the mud in suspension. The massive sub-sea slumping events in the Gulf of Mexico reported by Alvarez et al. (1992), Bralower et al. (1998), Grajales-Nishimura et al. (2000), Norris et al. (2000), Dohmen (2002), Denne and Blanchard (2013), Denne et al. (2013) and Sanford et al. (2016) would also be over quite quickly, although some instability may have continued for a longer period of time. Some of the faulting seen in the Brazos River area (Yancey, 1996) and in Alabama (Olsson et al., 1996; Smit et al., 1996; Hart et al., 2013) may have originated at this time, but some of these structures can also be seen cutting overlying strata and are either later or were subsequently re-activated.

This seismic activity would have been quickly overtaken by the arrival of the impact-induced tsunami. Using evidence derived from the Indian Ocean earthquake
(26th December 2004), the tsunami – and reflected waves – from the Chicxulub impact would have dissipated over 2–4 hours. The reflected waves would have gradually diminished in intensity over time, accompanied by a reduction in their sedimentological effects (G. Shapiro, pers. comm., 2012). The ‘Event Bed’ of the Brazos River area (Fig. 5) contains a series of sediment packages of comparable intensity and the inter-bedded, thin mudstone layers (with undamaged large benthic foraminifera and scaphopods) must have been deposited during periods of quiescence and cannot have been re-deposited by the tsunami event (Hart et al., 2012b). The uppermost Cretaceous surface in both the Brazos River area (Hart et al., 2012b) and in mid-Alabama (Olsson et al., 1996; Hart et al., 2013, their figs. 5, 8-10) consists of a generally smooth, undulating surface which has an amplitude of ~1 m (Hart et al., 2012b, their fig. 4). This is, perhaps, best seen in the three-dimensional views photographed during the Miller’s Ferry construction works (Olsson et al., 1996). There, the E–W trend of the axes is at right angles to the direction of the path of the Chixculub tsunami. This surface, following the definition of the K/Pg boundary (Molina et al., 2006, p. 263), was created by the tsunami and, as close as possible, marks the time of impact. The overlying spherule-rich horizons, sandstone beds, etc. are, therefore, lowermost Paleocene. On the Demerara Rise (ODP Site 1259), MacLeod et al. (2007, their fig. 2) show the presence of a thin, white, disturbed layer, which may also mark the passing of the tsunami: given the hypothesized wavelength of the tsunami wave, it would have disturbed sediments to a considerable depth (G. Shapiro, pers. comm., 2012). In the Gulf Coast area the tsunami would have, almost certainly, removed almost all of the seismically disturbed sediments. The amount removed, however, may not have been that great, as the uppermost Corsicana Mudstones in the Brazos River area still contain the very uppermost Cretaceous zone of *P. hantkeninoides*. In the Brazos River area, blocky mudstone ‘conglomerates’ are seen below the spherule-rich horizon at the base of the ‘Event Bed’. Near the RT 413 bridge spanning the Brazos River (Fig. 4a, b, c) these mudstone conglomerates contain calcareous nodules that are reworked from the Corsicana Formation, but the disturbed strata below the Cottonmouth Creek waterfall does not contain such nodules. It is possible, as postulated by Yancey and Liu (2013), that these mudstone conglomerates were either formed by the tsunami or its backwash (Vellekoop et al., 2018). The overlying sandstones of the ‘Event Bed’ contain abundant, and often quite large, *Thalassinoides*-like burrow systems (Fig. 6)
that confirm that all of these sandstones and mudstone interbeds could not have just been deposited by a short-lived tsunami event. The presence of intense bioturbation in the sandstones and abundant gastropods, bivalves, scaphopods, large delicate benthic foraminifera and ostracods does not indicate reduced levels of \( \text{O}_2 \) (Vellekoop et al., 2018). Calcareous nannofossil analysis of the basal Paleocene mudstones shows the presence of abundant reworked material from both Maastrichtian and even Campanian strata, indicating that there had been considerable erosion of the underlying mudstones in the local area.

Direct evidence of acidification is provided by this analysis of the calcareous nannofossils. In the RBS section (Figs 2, 3) the uppermost sample (A) of the Corsicana Formation (Maastrichtian) contains, as would be expected, an assemblage of latest Maastrichtian taxa (Fig. 7) with rare *Braarudosphaera* spp. and *Thoracosphaera* spp. The overlying ‘Event Bed’ and basal claystones (Sample F) of the Kincaid Formation (Zone P0) contain only rare microfossils, with some foraminifera and calcareous nannofossils, almost all of which are reworked Maastrichtian taxa. Only in the lower levels of Zone Pα are the first calcareous nannofossils of the Paleocene (*F. petalosa* and *C. intermedia*) recorded. Just above this level there is a distinct reduction in the percentage of reworked Cretaceous material. If the *in-situ* Maastrichtian calcareous nannofossils (Fig. 7) are compared to the reworked Maastrichtian specimens from P0 and the lower levels of Pα, there is a significant difference in the quality of preservation. The reworked Maastrichtian individuals from the Paleocene claystones are clearly etched, the majority of specimens showing signs of dissolution and fragmentation. It is postulated that these reworked Maastrichtian taxa were lifted into suspension by the tsunami (and its backwash) and, prior to re-deposition in the lowermost Paleocene claystones, etched and dissolved by the reduced pH in the surface waters. The same dissolution features are not visible in the *in-situ*, and reworked, foraminifera which presumably were only moved close to the sediment/water interface.

It has recently been suggested (Gibbs et al., 2016) that ocean warming and not acidification controlled coccolithophore responses during past greenhouse climates. While this may be the case, the features we describe here would not be caused by warm temperatures alone and the damage to the nannofossils requires quite significant dissolution (but see Tyrrell et al., 2015).

Following the impact, there were two other events that must have occurred
very rapidly: the thermal pulse (Vellekoop et al., 2014; Brugger et al., 2017) and the fallout of the spherules. There have been many suggestions that the thermal radiation from the impact would have been sufficient to ignite wildfires (Melosh et al., 1990; Kring and Durda, 2002; Belcher, 2009). There would also be the heat generated by the ejecta particles (spherules) as they fell back to Earth. There are various estimates of the thermal pulse, and the affects that it may have generated (Wolbach et al., 1990; Hildebrand, 1993; Shuvalov and Artemieva, 2002), including the view that the majority of trees may have been killed before being, subsequently, ignited. The field evidence from the Gulf Coast is minimal, and the only location in which it is possible to observe in-situ charcoal is in the Clayton Basal Sands of the Mussell Creek locality (Fig. 8). In a series of multi-method and multi-proxy analyses Belcher et al. (2003, 2005, 2009) concluded that extensive K/Pg wildfires were unlikely, and that the K/Pg-derived soot and PAHs have a signature derived from combustion at the impact site (see also Harvey et al., 2008).

The spherules provide the first direct evidence of the impact, likely arriving in many areas surrounding the Gulf Coast and the Atlantic Ocean (e.g., Demerara Rise) within about one hour of the impact (Alvarez et al., 1995; MacLeod et al., 2007). In almost all shallower-water successions where spherules are recorded (e.g., New Jersey (Olsson et al., 1997), Colombia (Bermúdez et al., 2016) and Brazil (Gertsch et al., 2013)) they are reworked and mixed with sediment clasts, fossils and other debris. The succession (MacLeod et al., 2007, their fig. 2) on the Demerara Rise records an in-situ, graded bed that may have taken approximately one month to accumulate (allowing for the time to settle through the water column). Belcher (2009) indicates that the heat provided by the spherules to the surface was <325°C, lasting only for a very short period of time. As indicated by Hart et al. (2012b, 2013) the spherule-rich horizons in the Brazos River area and in Alabama are clearly re-worked, the spherules being associated with sediment grains, ichthyoliths (fish teeth and bone fragments), re-worked foraminifers and other clasts (Hart, 2016, his fig. 4).

The impact, following the definition of the K/Pg boundary by Molina et al. (2006), is also associated with the mass extinction (including calcareous nanofossils, planktic foraminifers, ostracods, ammonites, etc.). The limitations for our understanding of the order, and timing, of events in the very earliest Paleocene is what is actually preserved in the rock record. In the Stevns Klint succession (Hart et al., 2005, figs. 7, 10) the relatively flat end-Cretaceous surface is overlain by a thin,
mineral rich, Fe-stained layer that contains the iridium anomaly (Damholt and Surlyk, 2012). This is almost coincident with the large negative $\delta^{13}C$ stable isotope anomaly, which is itself coincident with a flood of calcareous dinoflagellates (Leighton et al., 2011), a disaster taxon. In many locations (e.g., RBS, Brazos River area), this stable isotope anomaly is missing, probably indicating that the sedimentary record did not preserve this earliest Paleocene event or that it is obscured by re-worked sediment. The data from Miller’s Ferry are equivocal, and one is uncertain if this large negative $\delta^{13}C$ stable isotope anomaly is preserved (Hart et al., 2014, fig. 7), even though some excursions are recorded in the Clayton Basal Sands (Olsson et al., 1996).

In the Brazos River area, and in the Stevns Klint succession there is no evidence of a total productivity collapse (= Strangelove Ocean model), unless it was of such short duration as to be undetected. Dinocyst productivity appears to continue across the K/Pg boundary in a number of locations (Molina et al., 2006; Prauss, 2009; Hull and Norris, 2011; Hull et al., 2011; FitzPatrick et al., 2013, 2018; Tuba Aydin, pers. comm., 2013). In Denmark, the $P$. grallator/$D$. californicum zonal boundary coincides with the K/Pg boundary, with a flood of calcareous dinocysts (e.g., $Pithonella$ spp. and $Orthopithonella$ colaris) being located only a centimeter above the base of the Fiskeler Member and within the interval of iridium enrichment (Leighton et al., 2011). The iridium ‘marker’ is missing in the Brazos River area and there is no recorded flood of calcareous dinocysts comparable to those recorded at Stevns Klint.

In the RBS succession, the calcareous nannofossil data show a significant disturbance, with the base of Zone NP1 being located at the base of the Littig Member. Associated with this is evidence of major re-working of Maastrichtian (and even Campanian) nannofossils, together with ‘disaster taxa’ such as $Braarudosphaera$ spp. and $Thoracosphaera$ spp. The benthic foraminifers (Hart et al., 2011; Leighton, 2014) are only marginally affected, with some evidence of possible re-working. This reworking of some benthic foraminifera has also been reported by Alegret and Thomas (2001) in northeast Mexico. In the mudstone horizons within the ‘Event Bed’ in Texas (Fig. 5) and in the Clayton Basal Sands of mid-Alabama (Fig. 8), there are large, beautifully-preserved lenticulinids and very long, uniserial nodosariids (Hart et al., 2012b; Leighton et al., 2017, fig. 3). These show very little evidence of systematic breakage, reduced calcification or post-mortem dissolution. In the Wagner Basin (Canet et al., 2010), Pettit et al. (2013)
have showed that living benthic foraminifers can exist in quite low pH environments (7.88 – 7.55), but often suffer some post-mortem dissolution (expansion of pores, loss of smooth test surfaces, etc.) prior to final burial. This taphonomic effect is not recorded in the Brazos River material, even though the water depth (50–100 m) may have been within the potential range of surface water acidification. In the lower levels of the Fiskeler Member in Denmark (Hart et al., 2005, figs. 10, 11) some benthic foraminifers (e.g., *Stensioeina pommerana* and *Cibicidoides succedens*) have lost their chamber walls (apparently by dissolution), being reduced to ‘skeletons’ formed by the keels and sutures. As this is recorded in a relatively deeper-water setting it is thought to have been the result of taphonomic processes (or even modern weathering), rather than problems associated with calcification in acidified waters.

In the studies of modern environments in which pH is reduced by sub-sea CO$_2$ vents, both Dias et al. (2010) and Pettit et al. (2015) have shown that below pH 7.8 the assemblage becomes progressively dominated by agglutinated foraminifers as the calcareous component of the assemblage finds it more difficult calcify new chambers, as indicated by the experimental work of de Nooijer et al. (2009a, b). The benthic assemblages of the lowermost Paleocene in Texas and Alabama are dominated by calcareous taxa, with no evidence of any pH-limiting control. In the K/Pg boundary interval Ridgwell (2005) and Hönisch et al., 2012) have predicted a pH of ~7.8 (Fig. 2), which is comparable to that reported by Pettit et al. (2013) in the modern Wagner Basin.

The ‘background’ level of pH 7.8 was abruptly altered by the Chicxulub impact, which is thought to have vaporized gypsum and carbonates at the impact site, creating acid rain and the rapid acidification of the ocean surface waters (Sigurdsson et al., 1991; D’Hondt et al., 1994; Schulte et al., 2010; Hönisch et al., 2012; Alegret et al., 2012). Whereas Hönisch et al. (2012, p. 1060) indicate that a single driver (e.g., ocean acidification) may not have been the sole cause of the end-Cretaceous plankton extinctions, Alegret et al. (2012) suggest that a brief, rapid, but severe, acidification event may have been the primary cause. Lasting only months to years, Alegret et al. (2012) suggest that this may have caused the extinctions in the calcareous nannofossils and planktic foraminifers. Using the Caldeira and Wickett (2003, 2005) models a very brief pulse of increased CO$_2$ would only reduce the pH of the surface waters. This may have been enough to damage the calcareous nannofossil assemblages significantly, although modern experimental work has
shown a very mixed response by the nannoflora to reduced pH (Langer et al., 2006; Stoll, 2009; Beaufort et al., 2011; Smith et al., 2012). In some cases the impact is species-specific and even limited to a single taxon, where some heavily-calcified morphotypes dominate the most acidic waters. In the case of the planktic foraminifers it is the more massive, deeper-dwelling morphotypes that became extinct, perhaps indicating that it was the surface-dwelling juveniles that were affected the most, leaving only tiny *Hedbergella* spp. and *Guembelitria* spp. to re-colonize the Paleocene. The calcareous dinocysts presumably survived along with the organic-walled dinoflagellates, returning in floods (Leighton et al., 2011) within the first (20 ka) precession cycle of the Paleocene.

The ammonites could also have suffered in this surface-water acidification ‘event’. Their small, floating eggs and aragonitic protoconchs may have been more prone to calcification problems than the larger, more-protected, eggs of the deeper living nautiloids (Landman et al., 1996) although recent work on the feeding habits and jaw structures of ammonites (Kruta et al., 2011; Tanabe, 2011) have suggested that it was the disappearance of the plankton that had the greatest effect. Loss of the ammonites would have had implications for the higher levels in the oceanic food web, including the marine reptiles. There are, of course, continuing records of surviving, Paleocene, ammonites (Landman et al., 2012; Stilwell and Håkansson, 2012), but whether these occurrences are the result of reworking or taphonomic biases is yet to be resolved.

3.2. *K*/*Pg* boundary events in the Brazos River area (Texas)

In the latest Maastrichtian, the Brazos River area was in an open marine setting with near-continuous mudstone deposition. This is only interrupted by heterolithic horizons, often on a mm-to-cm scale. The mudstones display lamination and indicate that they were deposited in a quiet, low energy setting, below storm wave base in a mid-outer shelf environment (~ 50–100 m). Some thin sandstone horizons are present within the Upper Maastrichtian, one of which can be seen following the regional strike across the Brazos River immediately to the north of Rt. 413 bridge in an area we refer to as River Bank North (*Fig. 2*). This particular sandstone was also recorded in the Mullinax-1 core, which was drilled on the flood plain just west of the river. These horizons represent the transport of siliciclastic material off-shore, probably as a result of storm events. Bivalves and gastropods are present
throughout, although not abundant within the uppermost Maastrichtian. Towards the end of the Maastrichtian, Hart et al. (2012b) record the presence of a volcanic ash, which was dated (Hart et al., 2012b, pp. 75–77) as being 65.95 ± 0.04 Ma. This is exposed 30–40 cm below the Event Bed in Cottonmouth Creek. *Baculites* spp. and other ammonites are present in the Corsicana Formation and confirm that the sediments are latest Maastrichtian in age (Witts et al., 2017); this supports the data from a study of the planktic foraminifera and calcareous nannofossils (Leighton et al., 2017).

There is an ash-fall deposit recorded immediately north of the Rt. 413 bridge at River Bank North and while this looks to be identical in both appearance and thickness it is almost impossible to confirm if it is the same ash. Yancey (1996, fig. 4) has shown that the K/Pg boundary in the Brazos River at this point is both faulted and gently folded and, while the ash appears to be lower in the Maastrichtian succession than the one exposed in Cottonmouth Creek, it is probably the same marker bed and points to differential erosion of the end-Maastrichtian mudstones.

The absence of the Event Bed that was recorded in the core Mullinax-3 sited near to Darting Minnow Creek was reported by Adatte et al. (2011) to indicate that the Event Bed seen in other locations had been eroded away by a period of subaerial exposure and that the presence of a palaeosol and rootlets near the top of the core was evidence of a mangrove environment in the earliest Danian. Our field work has shown that Mullinax-3 was probably drilled through a positive area of the end-Cretaceous sea floor and, therefore, did not contain the Event Bed, which is only present in the sea floor lows. This was different to the Mullinax-1 core site which was located in the area of a trough and, as a result, cored the ‘Event Bed’. The rootlets within the postulated palaeosol described by Adatte et al. (2011) can clearly be attributed to the Pleistocene river deposits which blanket the area. The pedogenic features (gypsum-filled fractures and wide oxidation margins on mudstone blocks) in the Mullinax-3 core illustrated by Adatte et al. (2011, fig. 17) and Keller et al. (2011, fig. 27) directly underlie Pleistocene terrace sediments and are the products of Pleistocene weathering processes. Yancey and Liu (2013) also indicate that these are not related to K/Pg boundary environments and that there is no evidence for subaerial exposure in the end-Maastrichtian or earliest Danian.

**Figure 9** shows the ‘Event Bed’ at River Bank South, with a close up of the spherule bed that rests on the eroded Maastrichtian mudstones. The ‘Event Bed’
sandstones and underlying spherule bed are present within the troughs and absent on the ‘highs’ which in one case (at River Bank South) preserves a shell pavement (Hart et al., 2012b, fig. 4A, 4B). The various successions of the Brazos River area can be interpreted and used to construct a sequence of events (Fig. 10) that includes Maastrichtian mudstone deposition, arrival of a volcanic ash, the erosion caused by the tsunami, and the subsequent deposition of the ‘Event Bed’ and overlying Paleocene mudstones. The large, earliest Paleocene, $\delta^{13}$C excursion and the iridium layer are not recorded as the area was affected by too many other sedimentological events at that time. How this interpretation of the geological history of the Brazos River area compares to other important K/Pg boundary successions (Demerara Rise, Stevns Klint and El Kef) is shown in Figure 11. If the time-scale proposed by Leighton et al. (2017) is approximately correct, the time from surface-water acidification and extinction to the onset of recovery was very short, being in the order of 30,000 years, with significant biotic recovery in around 80,000–100,000 years. The well-preserved benthic foraminifera point to only a surface water effect, before water column mixing allowed the onset of recovery.

4. Summary

The current stratigraphy of the Cretaceous/Paleogene boundary provides a robust framework for international correlation and the documentation of the events associated with both the Deccan volcanism and the Chicxulub impact. Certain features, such as disturbed strata, erosion surfaces, presence of spherules (in-situ or reworked), the iridium anomaly, presence/absence of charcoal and the biotic extinctions and/or turnover, all point to a series of events that can be located in relative time. It is clear, however, that within one precession cycle of ~20,000 years there are a number of events (e.g., ocean acidification, possible fires, etc.) that were over very quickly and remain beyond our present resolution in the geologic record. The evidence of where such events fit into the overall time-scale are often indirect and, in places, vague at best. As more work on the Gulf Coast successions is undertaken, this resolution will undoubtedly improve, especially with a detailed analysis of the cyclostratigraphy, but still will undoubtedly lack the ability to discern events that may have occurred over intervals of less than a few years. The extinctions of the calcareous nannofossils and the planktic foraminifers may have been caused by a brief acidification event, but the impact of this was never more
than in the very near-surface waters as the preservation and taxonomic composition of benthic foraminifera and their assemblages recovered from the Gulf Coast successions show no evidence of a calcification crisis or even post-mortem dissolution.

While there are other events happening as a result of the Deccan volcanism, the extinction events at the K/Pg boundary appear to be a single event, very closely aligned to the Chicxulub impact.

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Figure Captions

Figure 1. The changing nature of the plankton through time and the changes in ocean chemistry (modified after Ridgwell, 2005). The timing of the Neritan and Cretan oceans has been altered from the original proposals of Ridgwell (2005). The distribution of the calcitic/aragonitic oceans is based on Stanley (2006).

Figure 2. Map of the Brazos River area, Falls County, Texas, showing the location of the various creeks, boreholes and other sections mentioned in the text. After Hart et al. (2012b)

Figure 3. View across the Brazos River to the Riverbank South succession. The Pleistocene valley gravels, which are pink in colour, overlie the lowermost Paleocene succession that rests on the ‘Event Bed’ and the Corsicana Mudstone Formation of the Maastrichtian. The letters along the succession refer to the lithological markers identified by Yancey (1996).

Figure 4. (a) View of Brazos River immediately south of the RT 413 bridge, showing the general nature of the exposures at a time when river flow is low. The rippled surface is the top of the Event Bed; (b) The spherule-rich mudstones and the overlying cross-bedded sandstones of the ‘Event Bed’ are seen resting on conglomeratic mudstones (derived from the Corsicana Mudstone Formation) which (c) include small, rounded carbonate-rich concretions (also derived from the underlying succession).

Figure 5. The ‘Event Bed’ at the K/Pg boundary in Darting Minnow Creek, Brazos River area, Texas. The irregular surface below the ‘Event Bed’ is indicated and the mudstone interbeds are clearly visible. These contain quite large benthic foraminifers (mainly Lenticulina spp. and Nodosaria spp.) as well as macrofossils, including scaphopods.

Figure 6. Exceptionally long Thalassinoides-style burrow system within one of the sandstone units of the ‘Event Bed’.
Figure 7. Impact of acidification on *in-situ* and re-worked calcareous nannofossils at the K/Pg boundary. Scanning electron micrograph images A–D are from sample F, basal Paleocene claystones, while E–G are from sample A in the uppermost Maastrichtian mudstones. Sample locations are shown in Hart et al. (2012b their fig. x). A, *Retecapsa crenulata* (Bramlette and Martini), basal Paleocene, scale bar 1 μm; B, *Kamptnerius magnificus* Delandre, basal Paleocene, scale bar 2 μm; C, arkangelskiellid, probably *Gamerago obliquum*, basal Paleocene, scale bar 1 μm; D, *Retecapsa crenulata* (Bramlette and Martini), basal Paleocene, scale bar 2 μm; E, *Micula staurophora* (Gardet) Stradner, uppermost Maastrichtian, scale bar 1 μm; F, *Prediscophaera cretacea* (Arkangelskey) Gartner, uppermost Maastrichtian, scale bar 2 μm; G, *Arkangelskiella cymbiformis* Vekshina, uppermost Maastrichtian, scale bar 1 μm.

Figure 8. The Clayton Basal Sands in the Mussell Creek section, Alabama. The inset images show (left) the re-worked clast of Prairie Bluff Chalk within the yellow, charcoal-rich, yellow sands and (right) a large charcoal fragment that is ~5 cm in diameter. This is the section that was described in detail by Savrda (1993) and previously discussed by Hart et al. (2013).

Figure 9. The ‘Event Bed’ at River Bank South with (inset) a close-up of the sandstones overlying the re-deposited bed of spherules, shell fragments, bone fragments and foraminifera.

Figure 10. Sequence of events across the K/Pg boundary, including the deposition of the volcanic ash (2), arrival of the tsunami (4, 5), deposition of the spherule bed (6), deposition of the ‘Event Bed’ (7, 8, 9) and the subsequent deposition of the Litig Formation mudstones (10). A summary of these events is presented (11), which can also be seen in Figure 11.

Figure 11. Schematic correlation of the Brazos River succession (from Figure 10), with the Demerara Rise, El Kef (Tunisia) and Stevns Klint (Denmark).
HIGHLIGHTS

This paper discusses the K/Pg in terms of surface water acidification caused by the K/Pg impact event. This is coupled with a new model for, and correlation of, the events recorded in a number of areas both proximal to the impact and distal. In particular the model is based on fieldwork in Texas.
Figure 1

(A) Geological time scale showing the major changes in plankton assemblages from the Cenozoic to the Paleozoic era. The timeline includes the following phases: Neoproterozoic (N), Proterozoic (Pr), Cambrian (C), Ordovician (O), Silurian (S), Devonian (D), Carboniferous (C), Permian (P), Triassic (T), Jurassic (J), Cretaceous (K), and Cenozoic (E).

(B) Graph showing the change in mean ocean surface pH over geological time. The pH is marked as modern (pre-industrial) pH, with a sudden drop and subsequent fluctuations.

(C) Graph indicating the percentage of total pelagic deposition. The graph shows a shift from pelagic deposition dominant to neritic deposition dominant.

(D) Graph depicting the accumulation of CaCO3 over time, with a peak around 300 Ma.

(E) Diagram showing the evolution of oceanic carbonates from 45 to 560 Ma, with phases indicated by Aragonite, Calcite, and Aragonite II.
Figure 3
Figure 11