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Experimental evidence for the global acidification of surface ocean at the Cretaceous–Palaeogene boundary: the biogenic calcite-poor spherule layers

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Abstract: The massive amount of impact-generated atmospheric CO_2 at the Cretaceous-Palaeogene boundary (KPB) would have accumulated globally in the surface ocean, leading to acidification and $CaCO_3$ undersaturation. These chemical changes would have caused a crisis of biocalcification of calcareous plankton and enhanced dissolution of their shells; these factors together may have played a crucial role in forming the biogenic calcite-poor KPB spherule layers observed at numerous oceanic sites and marine (now on land) sites in Europe and Africa. Experimental data and observations indicate that the deposition spherule layer probably lasted only a few decades at most.

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Introduction

The Cretaceous–Palaeogene boundary (KPB) represents one of the most dramatic turnovers in the fossil record of the marine calcareous plankton (mainly coccolithophores and foraminifera) that formed the calcite deposits that gave the Cretaceous its name. In the global ocean, more than 90 % of calcareous plankton was extinguished at the KPB (Smit 1982; D'Hondt *et al.* 1996; Molina *et al.* 1998). This extinction appears to have been sudden and inevitably led to the catastrophic collapse of life in the ocean (termed 'the Strangelove ocean').

Most researchers accept that the mass extinctions at the KPB were caused by a large asteroid impact at Chicxulub (Yucatan Peninsula, Mexico, Fig. 1). On the contrary, Keller *et al.* (2003, 2007) proposed that the Chicxulub impact predates the KPB by 300,000 years and did not cause the late-Cretaceous mass extinctions or have any significant environmental effects. Their proposal is, however, inconsistent with the currently favoured interpretation that various palaeontological, mineralogical and geochemical data as well geological data all provide support for the genetic relationship between the Chicxulub impact and the deposition of spherule layers of the marine proximal and distal boundary sections worldwide, (Smit 1999; Arenillas *et al.* 2000a,b; Montanari & Koeberl 2000; Kiessling & Claeys 2001; Alegret *et al.* 2002a,b; Ortega-Huertas *et al.* 2002; Arz *et al.* 2004; Smit *et al.* 2004; D'Hondt 2005; Molina *et al.* 2006; Schulte *et al.* 2006). In addition, a number of recent experimental results and observations strongly support the single Chicxulub impact (Griscom & Beltran-Lopez 2002; Alegret *et al.* 2005; Trinquier *et al.* 2006; Arenillas *et al.* 2006; Morgan *et al.* 2006; Coccioni and Marsili 2007; MacLeod *et al.* 2007; Kaminski *et al.* 2008; Schulte *et al.* 2009).

The primary aim of this work is to discuss the possibilty of global acidification of the ocean surface (GAOS) caused by excessive atmospheric CO_2 generated by the Chicxulub impact. For this purpose, experimental results and observations of the well-preserved KPB stratigraphic sequences (sections) in the ocean at locations both proximal (2000–4500 km) and distal ($\geqslant$9000 km) to the proposed Chicxulub impact site are examined. The proximal sequences are at Blake Nose (ODP Leg 171B: Martínez-Ruiz *et al.* 2001a,b), Hatteras Rise (DSDP Leg 93: Meyers, 1987), Bass River (ODP Leg 174AX: Olsson *et al.* 1997), and Bermuda Rise (DSDP Leg 43: Norris *et al.* 2000), all in the north-western Atlantic, and Demerara Rise (ODP Leg 207: MacLeod *et al.* 2007; Schulte *et al.* 2009) in the western Atlantic. The distal sequences are at Walvis Ridge (ODP Leg 208: Alegret & Thomas 2007; DSDP Leg 73: Hsü *et al.* 1982) in the south-eastern Atlantic, Hess Rise (DSDP Leg 62: Alegret & Thomas 2005) in the northern central Pacific and Shatsky Rise (ODP Leg 198: Bralower *et al.* 2002; DSDP Leg 86: Kyte *et al.* 1995) in the north-western Pacific. (See also the ODP/DSDP Leg-related KPB publications at www-odp.tamu.edu/publications/). Fig. 1 shows the locations of these oceanic sites. For the sake of completeness (or arguments), the experimental data and observations related to the KPB sections at many distal marine sites (now on

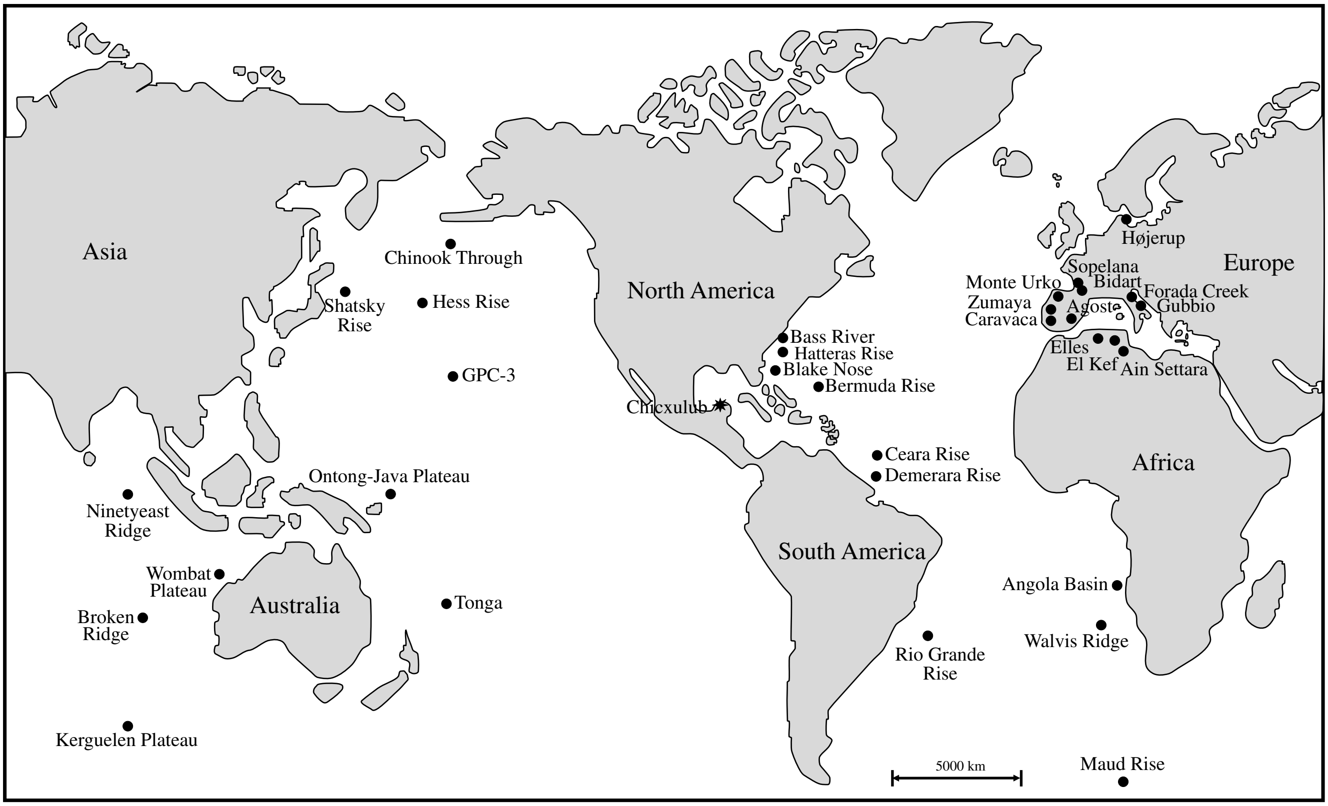

Fig. 1. Locations of all oceanic and marine sites discussed in the text.

land) in Europe and Africa (hereinafter marine sites) are also included. The potential of acidification of oceans at KPB has been discussed by many authors (O'Keefe & Ahrens 1989; D'Hondt *et al.* 1994; Pierazzo *et al.* 1998; Maruoka & Koeberl 2003; D'Hondt, 2005).

The KPB sequences at Blake Nose, Hatteras Rise, Bass River, Bermuda Rise, Demerara Rise, Walvis Ridge, Hess Rise and Shatsky Rise were deposited approximately within the bathyal depths from 1000–4000 m below the ocean surface. The general feature of these sequences (except on Shatsky Rise) is the spherule-bearing clay bed located between the top of the late Maastrichtian and the base of the early Danian sediments. There is no other spherule layer in any of these sequences. The boundary sections at Blake Nose, Bass River, Bermuda Rise, Demerara Rise, Walvis Ridge, Hess Rise and Shatsky Rise bear strong evidence for the mass extinction of calcareous plankton in the global ocean, and the initiation of this extinction coincides exactly with the spherule layers. There is no calcareous plankton data available from the boundary sequence on Hatteras Rise.

Most researchers believe that the spherule layers at proximal and distal oceanic locations are mainly derived from ejecta fallout that settled on the ocean floor over a time period lasting anywhere from a few hours to a year (see, for example, Kring 2007). The spherule distribution in the boundary sections at Blake Nose, Hatteras Rise, Bass River, Demerara Rise, Walvis Ridge and Hess Rise is pulse-like, matching the expected pattern for very sudden deposition on the ocean floor on a timescale much shorter than the ordinary deposition of the underlain uppermost Maastrichtian and overlain lowermost Danian sediments.

Experimental data and observations

Spherule layers

Spherule layers on Blake Nose

The evidence for GAOS in the spherule layers of the well-preserved KPB sequences recovered during ODP 171B at Blake Nose is first described.

ODP Program Leg 171B drilled five holes at Blake Nose. Holes were drilled at three sites (1049, 1050 and 1052), but the boundary sequences were only recovered in three adjacent holes (1049A, 1049B and 1049C). The uppermost Maastrichtian sediments in these holes comprise calcareous plankton ooze. The spherule layers are readily identified in all three holes, and their thickness varies from 7 cm (Hole 1049B) to about 17 cm (Hole 1049A, Figs. 2(a) and 3(a)) (Martínez-Ruiz *et al.* 2001a,b,c). Mineralogical and geochemical analyses indicate that these beds were derived from Chicxulub target rocks (Martínez-Ruiz *et al.* 2001a). As the spherule layer of Hole 1049B is significantly disturbed, probably from drilling, it was disregarded in this study.

Microscopic examination across the KPB sequence of Hole 1049A shows that biogenic calcite is almost completely absent in the spherule layer (Martínez-Ruiz *et al.* 2001a,b; Premović *et al.* 2004). This examination also shows that the

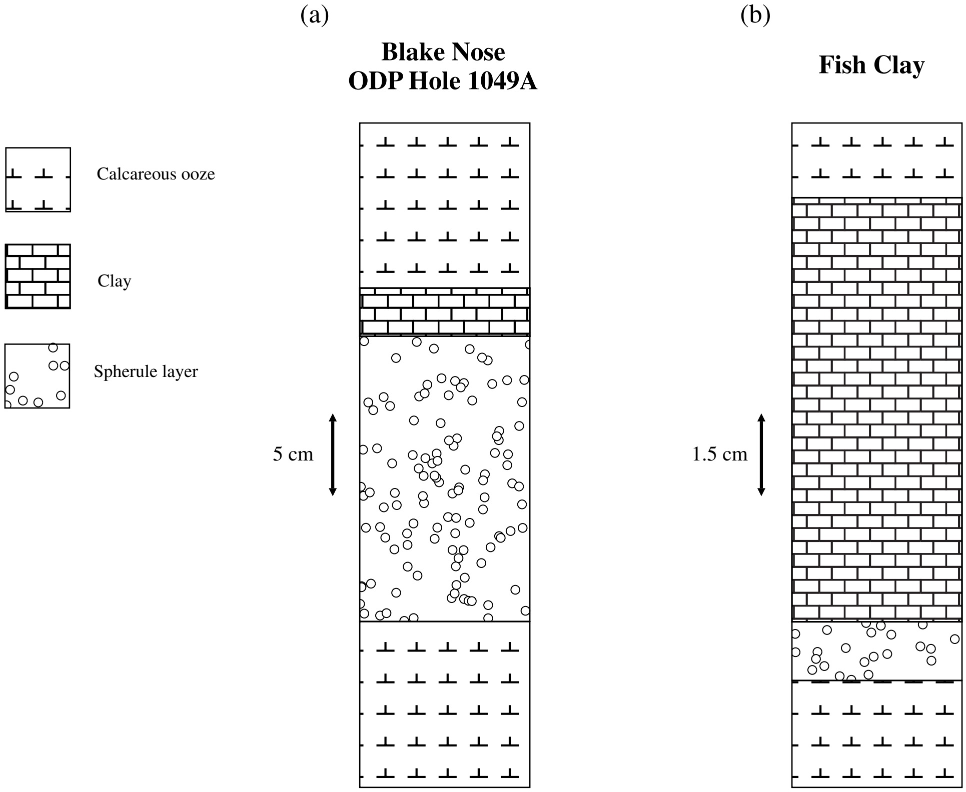

Fig. 2. Oversimplified illustration of the internal layering of: the KPB section at Blake Nose (ODP Hole 1049A) (Martínez-Ruiz *et al.* 2001a,b,c) (a) and the Fish Clay (Premović *et al.* 2008, 2009) (b).

transition from the uppermost Maastrichtian ooze to the spherule-bearing bed is extremely sharp and abrupt. Spherical impressions on the interface between these two beds indicate very rapid deposition of ejecta fallout (Martínez-Ruiz *et al.* 2001b).

The spherule layer of Hole 1049A is predominantly composed of different types of spherules. Most of them are green spherules, and sizes usually range from 0.1–1.0 mm. Spherules are composed mainly of smectite, but there is evidence for preserved unaltered glass relics (Martínez-Ruiz *et al.* 2001c). The spherule layer is overlain by a dark, clay-rich calcareous plankton ooze of early Danian age, which underlies a 5–15 cm-thick white foraminiferal ooze (Norris *et al.* 1998, 1999).

A 10 cm-thick spherule layer from Hole 1049C is also predominantly composed of 1–3 mm smectitic green spherules. The final bed is a 7 cm-thick layer of dark-gray clay from the early Danian overlain by a 15 cm-thick white calcareous plankton ooze (Huber & MacLeod 2000; Alegret & Thomas 2004).

Spherule layers at other proximal oceanic locations

The turbidite KPB sequence of DSDP Hole 603B (DSDP Leg 93) on Hatteras Rise contains a 3 cm-thick bed almost completely composed of green smectitic spherules. This bed is located between the upper Maastrichtian and the lower Danian claystones (Fig. 3(a)). Geochemical studies indicate that the spherules are composed primarily of smectite and that they were transported by a turbidite (Klaver *et al.* 1987). They are structurally and geochemically similar to the smectitic spherules at Blake Nose (Martínez-Ruiz *et al.* 2001a,b, 2002), ranging in diameter from 0.5–1.0 mm (Klaver *et al.* 1987; Bohor & Betterton 1989; Haggerty *et al.* 1986; Olsson *et al.* 1997).

At Bass River, a 6 cm-thick spherule layer of ODP Leg 174AX (Fig. 3(a)) abruptly separates the uppermost Maastrichtian glauconitic clay from the glauconitic clay of the early Danian. The smectitic spherules at Bass River are also similar to those from Blake Nose and from other locations on the northern American margin such as Hatteras Rise (Klaver *et al.* 1987; Haggerty *et al.* 1986; Olsson *et al.* 1997; Martínez-Ruiz *et al.* 2001b, 2002). According to Olsson *et al.* (1997), spherical impressions of spherules at the top of the late Maastrichtian indicate nearly immediate deposition of ejecta fallout. These authors also claim that the KPB sequence at Bass River is biostratigraphically complete and that its deposition was continuous on a scale of tens of thousands years, interrupted only briefly by the abrupt fallout of the ejecta. Microaccretionary and accretionary carbonate spherules are also present in the spherule layer (Guillemette & Yancey 2006).

The KPB sequence of DSDP Site 386 (DSDP Leg 43) at Bermuda Rise was described by Norris *et al.* (2000). A 5 cm-thick spherule layer (Fig. 3(a)), overlying the late Maastrichtian chalk, is similar to the spherule layer at Blake Nose. Spherules are sand-like and can be up to 1 mm in size.

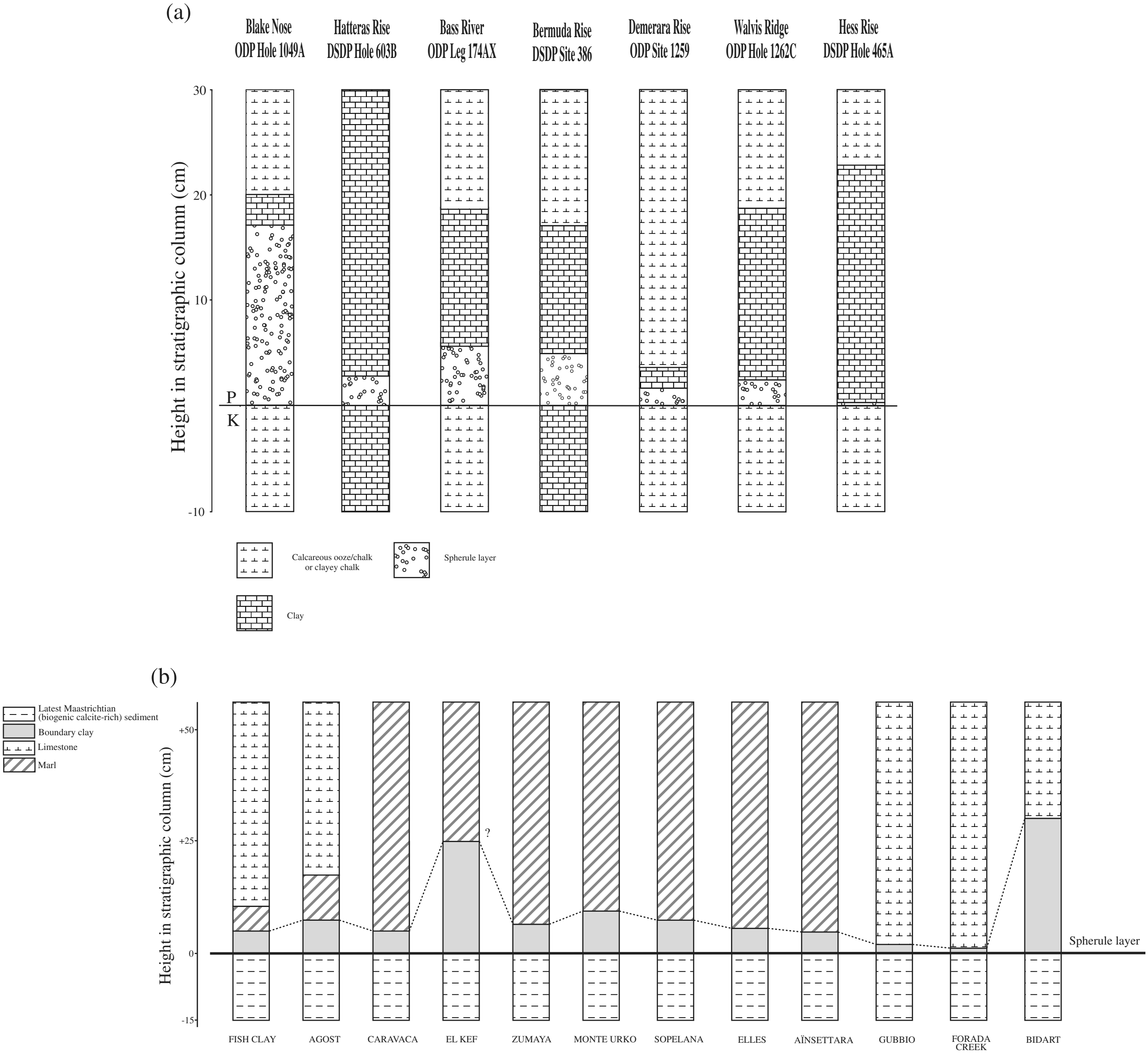

Fig. 3. Correlations of the clay-rich KPB sections discussed in the appropriate parts of the paper at: oceanic (a) and marine (b) sites.

The spherule layer is located at the base of the early Danian chalk.

The sections from Sites 1257–1261 (ODP Leg 207) on Demerara Rise preserve fine details of the sedimentological and palaeontological expression of the KPB event. The most complete boundary sequences recovered at this location reveal a well-preserved spherule layer at ODP Holes 1259B and 1259C (Erbacher *et al.* 2004; MacLeod *et al.* 2007; Schulte *et al.* 2009). The spherule layer at this location can be up to approximately 2 cm thick (Fig. 3(a)). The bed is composed predominantly of smectitic spherules with an average diameter of 0.5 mm. The top of the spherule layer typically consists of smectitic spherules less than 0.1 mm in diameter. The spherule layer occurs precisely at the KPB and rests on a thin (roughly 3 mm thick) layer composed mainly of calcareous plankton-rich chalk from the late Maastrichtian.

Spherule layers at distal oceanic locations

A remarkably well-preserved and complete KPB sequence from ODP Holes 1262B/C (ODP Leg 208), recovered on Walvis Ridge, shows a 2–3 cm-thick spherule-rich bed overlain by clay-rich calcareous plankton ooze/chalk from the early Danian (Fig. 3(a)). The spherule layer is underlain by late Maastrichtian clay-bearing calcareous plankton ooze and clay with foraminifers. The spherules are green and possibly smectitic, and were not found at higher levels in the sediments (Zachos *et al.* 2004; Alegret & Thomas 2007). The boundary section (roughly 2 cm thick) of Site 524 (DSDP Leg 73) on

Walvis Ridge is composed predominantly (90 %) of Fe-rich smectite (Hsü *et al.* 1982).

The KPB sections were cored at four sites (1209–1212 (ODP Leg 198)) on Shatsky Rise. The lithostratigraphy of the boundary succession is remarkably similar at all these sites. Although KPB sequences on Shatsky Rise were mixed by bioturbation in the interval after the boundary, the sections represent some of the best-preserved and least-disrupted oceanic records of the KPB event.

The most complete KPB sequence at Shatsky Rise is from ODP Hole 1209C, which bears biostratigraphic similarities to the record at previous oceanic sites, such as Blake Nose. This sequence consists of relatively thick calcareous plankton ooze from the late Maastrichtian overlain by a thick calcareous plankton ooze from the early Danian (Bralower *et al.* 2002). The boundary clay between these two calcareous oozes shows intensive bioturbation and/or reworking. There is no spherule layer that corresponds to those at the other oceanic sites; instead, the spherules (up to 100–150 μm in diameter) are concentrated in the first few (2–3) cm of the basal Danian and upper Maastrichtian oozes. These spherules show textures similar to the glauconite and magnetite spherules described by Smit & Romein (1985) from boundary sequences in other locations. Spherules are rarely found in the overlying 30 cm of the basal Danian.

Maastrichtian and Danian calcareous plankton oozes from the KPB sequence of DSDP Hole 465A (DSDP Leg 62) at Hess Rise are fairly well mixed and deformed due to the drilling procedure. Still, the sequence contains an identifiable 3 mm-thick spherule layer (Fig. 3(a)) with many pyrite and K-feldspar spherules (Montanari *et al.* 1983; Kyte *et al.* 1996).

The KPB sections with the spherule beds were also identified at distal oceanic sites at: Walvis Ridge (DSDP Leg 73, Site 524: Petersen *et al.* 1984); GPC-3 (Kyte & Wasson 1985) and Chinook Trough (ODP Leg 145, Site 886: Kyte *et al.* 1994, 1995; Ingram 1995), all in the central Pacific; and Tonga (DSDP Leg 91, Site 596: Zhou *et al.* 1991; Kyte *et al.* 1994) in the southern Pacific. The KPB sequences without spherule beds were identified at the following distal oceanic sites worldwide; at Maud Rise (ODP Leg 113, Sites 689 and 690: Michel *et al.* 1990); Angola Basin (Leg 175, Site 365: Smit & van Kempen 1986) and Rio Grande Rise (DSDP Leg 72, Site 516: Hamilton 1982) all in the southern Atlantic; Ceara Rise (DSDP Leg 14, Site 142: Smit & van Kempen 1986) in the western Atlantic; Ninetyeast Ridge (Site 305, Leg 116: Smit & van Kempen 1986) in the northern Indian Ocean; Wombat Plateau (ODP Leg 122, Site 761: Rocchia *et al.* 1992) and Broken Ridge (ODP Leg 121, Site 752: Michel *et al.* 1991), both in the eastern Indian Ocean; Kerguelen Plateau (ODP Leg 119, Site 738: Schmitz *et al.* 1991; Thierstein *et al.* 1991) in the southern Indian Ocean; and Ontong-Java Plateau (ODP Leg 130, Site 803: Kyte *et al.* 1995) in the central Pacific. The locations of all these sites are also given in Fig. 1. Most of these boundary sediments are pelagic clays which contain a record of important palaeogeochemical events that occurred in conjunction with the KPB (see also all ODP/DSDP Leg-related KPB publications at www-odp.tamu.edu/publications/).

Biogenic calcite profile at oceanic sites

The concentration profile of biogenic calcite across the boundary section of ODP Hole 1049A at proximal Blake Nose is presented in Figure 4(a). The concentrations of this calcite are high (approximately 85 wt %) in the late Maastrichtian layer but decrease sharply in the spherule layer, reaching a minimum of roughly 15 %. This decrease in the biogenic calcite is observed over an interval of less than 2 cm. From this layer upward, biogenic calcite accumulation returns to and remains constant at about the values seen prior to the KPB. A similar pattern in the biogenic calcite distribution is observed across the KPB sequences at Walvis Ridge (DSDP Leg 73, Site 524: Hsü *et al.* 1982; Petersen *et al.* 1984) and Kerguelen Plateau (Thierstein *et al.* 1991), Fig. 5(a). High-resolution biogenic calcite profiles – on a centimetre scale – have not been reported for the KPB sequences at other oceanic sites.

The biogenic calcite concentrations dropped dramatically in the spherule layers at Hatteras Rise (Klaver *et al.* 1987), Demerara Rise (MacLeod *et al.* 2007) and Hess Rise (Giblin 1981), Fig. 5(b).

Spherule layers at marine sites

In most marine sections the KPB is easily identified based on one or more of the following: (1) a lithology break from the uppermost Maastrichtian sediment with abundant calcareous plankton to a thin clay (here termed the boundary clay), extremely poor in calcareous plankton; (2) a 2–3 mm-thick goethite-rich (usually reddish) layer at the base of the boundary clay; and (3) anomalously high Ir values, generally concentrated in this base or immediately above it (Premović 2009). The onset of the boundary clay is coincident with the sudden mass extinction at the KPB, major negative carbon isotopic (δC^{13}) excursion, and a drop in biogenic calcite. Usually, the first appearance of Danian calcareous plankton is found near the base of the boundary clay (the P0 biostratigraphic zone) (Keller *et al.* 1995).

The Fish Clay (of earliest Danian age) near the village of Højerup (Stevns Klint) is a classic KPB lithological unit in Denmark. The basal reddish smectite-rich spherule layer is a thin layer (2–4 mm thick), overlain by the black marl (Figs 2(b) and 3(b)). These two layers are considered to constitute the main part of the Fish Clay (Schmitz 1985; Elliott 1993). The spherule layer contains goethite-rich microspherules and is underlain by the latest Maastrichtian bryozoan-rich chalk.

Like at Højerup, at Agost, Caravaca and El Kef the biogenic calcite-rich sediments of the latest Maastrichtian are sharply capped by a reddish spherule layer (Fig. 6). The KPB at Agost and Caravaca is marked by about 10–12 cm-thick dark smectite-rich bed (Ortega-Huertas *et al.* 1998; Arenillas *et al.* 2004) with the 2–3 mm-thick spherule layer (Díaz-Martínez *et al.* 2002; Arenillas *et al.* 2004). Microspherules

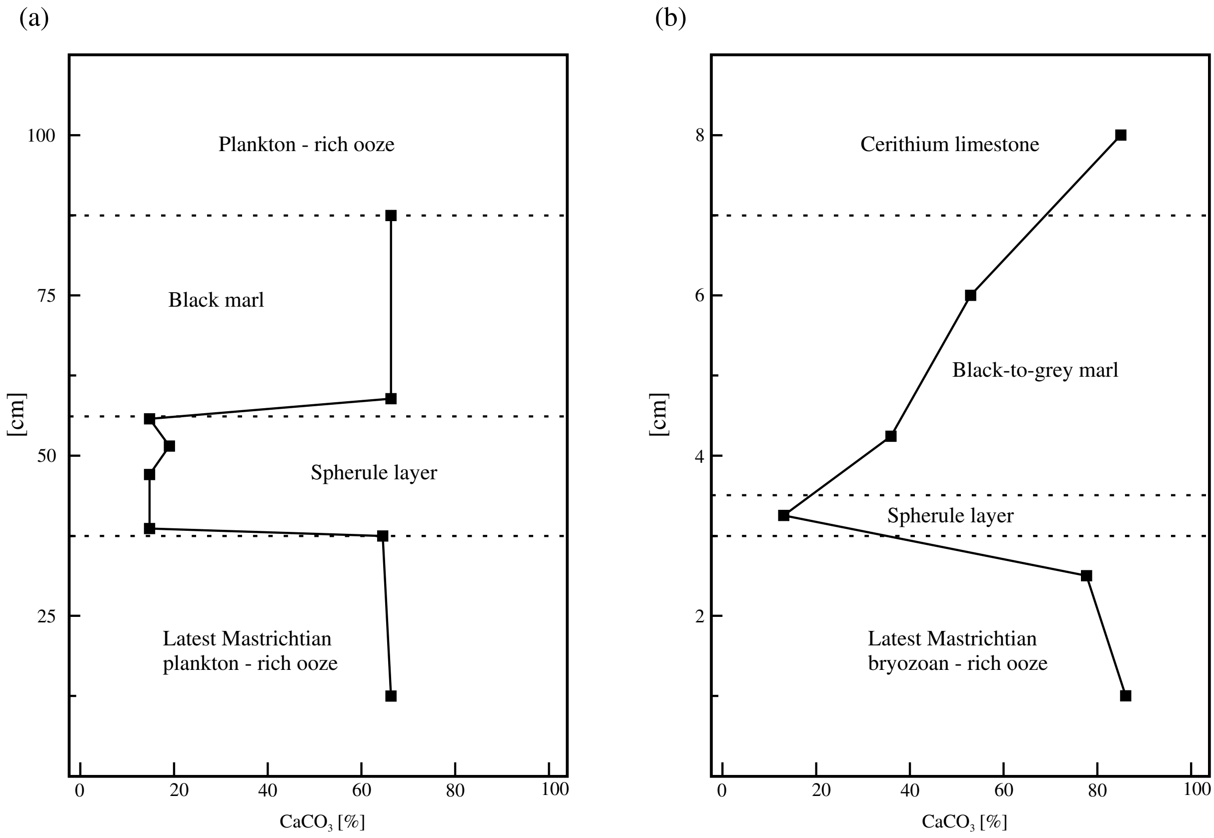

Fig. 4. Distribution of biogenic calcite (as $CaCO_3$) across the KPB section of ODP Hole 1049A (Martínez-Ruiz *et al.* 2001a; Premović *et al.* 2004) (a) and across the Fish Clay (Premović *et al.* 1993, 2008; Wendler & Willems, 2002; Premović, 2009) (b).

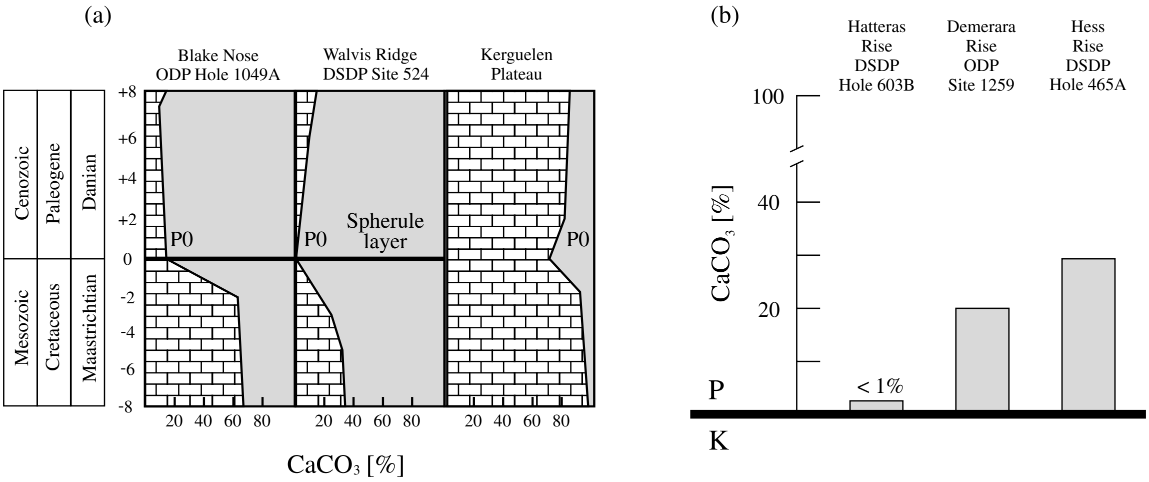

Fig. 5. The biogenic calcite profiles across the KPB at Blake Nose (ODP Hole 1049A: Martínez-Ruiz *et al.* 2001a; Premović *et al.* 2004), Walvis Ridge (DSDP Leg 73, Site 524: Hsü *et al.* 1982; Petersen *et al.* 1984) and Kerguelen Plateau (Thierstein *et al.* 1991); P_0 is a biostratigraphic zone (a). Percentages of biogenic calcite in the spherule layers at Hatteras Rise (Klaver *et al.* 1987), Demerara Rise (MacLeod *et al.* 2007) and Hess Rise (Giblin 1981) (b).

are mainly confined to this layer. Goethite microspherules at Agost are more abundant than K-feldspar microspherules; in contrast, at Caravaca K-feldspar microspherules are abundant but goethite ones are rare (Díaz-Martínez *et al.* 2002).

The sections at Agost, Caravaca and El Kef are among the most continuous and complete marine sections for the KPB transition. In addition, the base of the El Kef section has been officially designated as the boundary global stratotype section and point (GSSP) for the KPB (Cowie *et al.* 1989; Molina

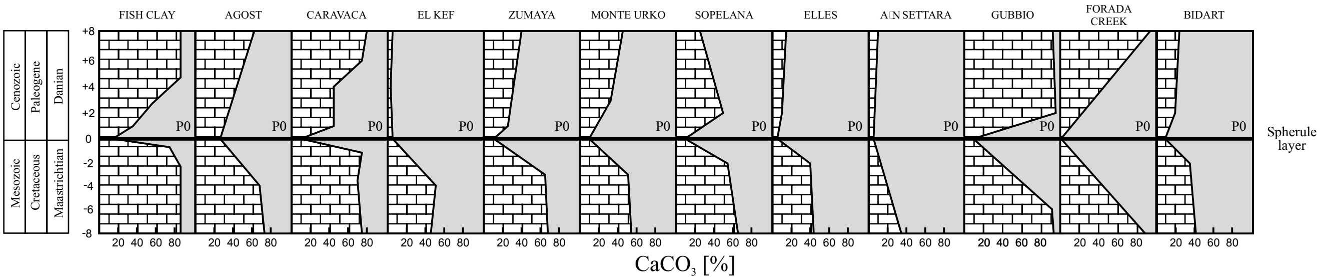

Fig. 6. The biogenic calcite profiles across the KPB at Højerup (Premović *et al.* 1993, 2008; Wendler & Willems 2002; Premović 2009), Agost, Caravaca, (Ortega-Huertas *et al.* 1995), El Kef (Keller *et al.* 1995), Zumaya, Monte Urko, Sopelana (Ortega-Huertas *et al.* 1995), Elles (Stüben *et al.* 2002), Äin Settara (Dupuis *et al.* 2001), Gubbio (Crocket *et al.* 1988); Forada Creek (Fornaciari *et al.* 2007); and Bidart (Minoletti *et al.* 2005); P_0 is a biostratigraphic zone.

et al. 2006). The International Commission on Stratigraphy estimated the age of the KPB to be 65.5 Myr but most researchers place the boundary at 65 Myr (for example, D'Hondt 2005).

At El Kef the boundary clay is 55–65 cm thick, with the 2–3 mm spherule layer (Keller *et al.* 1995); this layer contains most of the Ir (Robin *et al.* 1991). Smectite is the main component of the boundary clay at this site (Ortega-Huertas *et al.* 1998). At El Kef, the KPB is marked by an abrupt lithologic change from the marl of the late Maastrichtian to 50–60 cm boundary clay. The boundary clay passes upward into marl of the early Danian (Molina *et al.* 2006). The boundary sections at the nearby sites of Elles and Ain Settara are similar to that at El Kef (Zaghbib-Turki & Karoui-Yaakoub 2004).

In addition to the remarkable Ir anomaly, geochemical/mineralogical markers of the impact event, are identified in the spherule layers of the sections at Højerup, Agost and El Kef. Most of these markers are compatible with the idea that these layers are directly related to the KPB impact.

Other continuous and complete sections at the distal marine sites (Fig. 1) are characterized by the boundary clays with a basal spherule layer (Fig. 3(b)): in Italy (at Gubbio, Forada Creek), Tunisia (Elles and Aïn Settara), Spain (Zumaya, Sopelana, Monte Urko) and France (Bidart) (Alvarez *et al.* 1980; Smit 1982, 1999; Crocket *et al.* 1988; Keller *et al.* 1995; Ortega-Huertas *et al.* 1995; Molina *et al.* 1998; Stüben *et al.* 2002; Alegret *et al.* 2004; Arenillas *et al.* 2004; Fornaciari *et al.* 2007). The spherule layer of these sections provides an excellent record of the distal ejecta facies related to the Chicxulub impact.

The KPB has been identified in numerous marine sections (now on land) in the New Zealand region, including well-studied Woodside Creek (Hollis *et al.* 2003). Only one of these appears to have near-complete KPB records, at Flaxbourne River. The boundary clay at this location contains the geochemical record of the impact but it is without a spherule layer (Strong *et al.* 1987).

Stratigraphically, the marine boundary clays in Europe and Africa correspond to the continental boundary clays of the western interior of North America described by Pollastro & Bohor (1993). Anomalous Ir also occurs in these continental clays.

Biogenic calcite profile at marine sites

A microscopic examination across the Fish Clay shows that abiotic calcite precipitation is only a minor contributor to total calcite production (Premović *et al.* 1993, 2008; Wendler & Willems 2002; Premović 2009). This also shows that the transition from the calcareous Maastrichtian bryozoan-rich ooze to the spherule layer is extremely abrupt. Biogenic calcite is almost completely absent in this layer. The concentration profile of biogenic calcite (as $CaCO_3$) across the Fish Clay is presented in Fig. 4(b). The concentrations are high in the uppermost Maastrichtian bryozoans-rich ooze (95%) but decrease sharply in the spherule layer, reaching a minimum (32%). Up from this layer, the biogenic calcite concentrations increase gradually to much higher levels, becoming close to that of the uppermost Maastrictian ooze, in the lowermost Danian Cerithium limestone (Wendler & Willems 2002).

A similar pattern is observed in the carbonate (mainly biogenic calcite) distribution across the KPB sequences at Agost, Caravaca and El Kef, and at the other marine settings in Europe (Zumaya, Monte Urko, Sopelana, Gubbio, Forada Creek, Bidart) and Africa (Elles, Äin Settara), (Fig. 6). The carbonate contents of the boundary clays at these sites also decreased considerably at the KPB.

Dissolution of calcareous plankton tests

Calcareous plankton tests in the KPB sections at Blake Nose Plateau, Demerara Rise, Walvis Ridge, Shatsky Rise and Hess Rise show signs of enhanced dissolution, including recrystallization and fragmentation (Smit & van Kempen 1986; Bralower *et al.* 2002; Zachos *et al.* 2004; MacLeod *et al.* 2007; see also all ODP/DSDP leg-related KPB publications at www-odp.tamu.edu/publications). The boundary sections also show enhanced dissolution of calcareous plankton tests at Kerguelen Plateau (Huber 1991; Schmitz *et al.* 1991), Broken Ridge (Michel *et al.* 1991), Tonga (Zhou *et al.* 1991), Wombat Plateau (Rocchia *et al.* 1992), Chinook Through and Ontong-Java Plateau (Kyte *et al.* 1995). Smit & van Kempen (1986) identified high dissolution of calcareous plankton tests in the KPB sections of other ocean sites, including Ceara Rise, Angola Basin and Ninetyeast Ridge. The amount of dissolution at all these oceanic locations appears to be unrelated to paleodepth.

Ekdale & Bromley (1984) hypothesized that a calcite dissolution pulse of the surface seawater in Denmark at the end of Maastrichtian could be related to a sudden and significant injection of volcanic gases into the atmosphere, lowering the pH of the surface seawater. Hansen (1990, 1991) suggested that acidification of the seawater at Stevns Klint after the KPB (created by enhanced atmospheric CO_2) could generate the biogenic calcite-deprived Fish Clay. A number of other authors have also suggested that the near absence of calcareous plankton in the Fish Clay is probably a result of acid dissolution (Ekdale & Bromley 1984; Schmitz *et al.* 1992; Surlyk 1997; Wendler & Willems 2002; Culver 2003; Hart *et al.* 2004; Rasmussen *et al.* 2005). In addition, Smit & van Kempen (1986) reported that calcareous foraminiferal tests of the marine boundary sections at Højerup, El Kef, Caravaca, and Bidart show signs of enhanced acid dissolution.

Collectively, the low biogenic calcite in the spherule layers and dissolution of calcareous plankton tests adjacent to the KPB at oceanic and marine sites suggest GAOS occurred at the KPB.

Discussion and interpretations

The impact-generated CO_2

As the impact target material at Chicxulub is predominantly carbonate-rich marine sedimentary rock combined with some minor sedimentary anhydrite (calcium sulfate, $CaSO_4$), a massive amount of acid-forming CO_2 gas was instantaneously released into the atmosphere upon shock devolatilization (O'Keefe & Ahrens 1989; Ivanov *et al.* 1996; Pope *et al.* 1997) and was accompanied by lesser amounts of SO_2, another acid-forming gas (Brett 1992).

Estimates of the impact-released CO_2 levels at the KPB vary from >250 ppm V (parts per million by volume) to >2000 ppm V (Hsü & McKenzie 1985; Pope *et al.* 1997; Pierazzo *et al.* 1998; Retalack 2001; Beerling *et al.* 2002; Nordt *et al.* 2002). It seems, therefore, reasonable to propose that that the atmospheric CO_2 levels at the KPB were about ⩾1000 ppm V due to instantaneous transfer ⩾2000 Gt of C as CO_2 released from the Chicxulub impact in the atmosphere. Indeed, numerical modelling shows that ⩾1000 ppm V of atmospheric CO_2 might have been sufficient to drive and sustain GAOS (Caldeira & Wickett 2003; Blackford *et al.* 2007). It is of note that late Cretaceous–early Tertiary background CO_2 levels were about 350–500 ppm V (Beerling *et al.* 2002).

The amount of S released from the Chicxulub asteroid and target rocks is estimated to be up to about 200 Gt (Pierazzo *et al.* 2003), equivalent to 400 Gt of SO_2. At the KPB the atmosphere would have been additionally degraded by smaller quantities of additional gases such as NO_x generated by passage of the Chicxulub impactor through the atmosphere (Emiliani *et al.* 1981; Lewis *et al.* 1982; Prinn & Fegley 1987; Zahnle 1990). SO_2 and NO_x would have been converted to stratospheric sulphate (SO_4^{2-}) and nitrate (NO_3^-) aerosols, which would have been deposited to the surface as sulfuric (H_2SO_4) and nitric (HNO_3) acid rain. Nitric acid would have been equivalent to about 10% of the sulfuric acid (Maruoka & Koeberl 2003).

Acidification of the ocean surface waters

The impact-derived CO_2 would have spread rapidly through the global atmosphere, and a large amount of CO_2 would have accumulated in the ocean surface since CO_2 enters the ocean through air–ocean gas exchange. Increasing atmospheric CO_2 concentrations in the ocean surface are reducing pH and carbonate ion concentrations (CO_3^{2-}), and thus the level of $CaCO_3$ saturation. The pH of ocean surface water is, however, not predicted to fall below the neutral value of 7; surface ocean waters are naturally somewhat alkaline with an average pH of approximately 8.2.

A recent estimate of the effect of changes in atmospheric CO_2 levels on ocean pH for the last 300 million years demonstrated that when a CO_2 change occurs over a short time interval (i.e., $<10^4$ yr), the ocean pH is sensitive to added CO_2 (Caldeira & Rampino 1993; Caldeira & Rau 2000). Moreover, model simulations of the time-dependent impacts of current anthropogenic CO_2 emissions on the $CaCO_3$ saturation state of ocean indicate that if a large flux of CO_2 occurred over a brief time period (up to 300 years), the ocean surface pH would drop rapidly (Archer *et al.* 1997; Caldeira & Wickett 2003). These simulations also imply that GAOS would only have been achieved if the large influx of CO_2 occurred all at once. If the CO_2 input was gradual, i.e. over 5–10 kyr, the chemical changes would have been less severe.

The pH of ocean surface could additionally have been reduced by the impact-generated acid rain (Kring 2007), but probably not enough to acidify the global ocean surface (D'Hondt *et al.* 1994). The fluvial influx of acidic precipitation from the adjacent continental areas into the marine basins could have been high, but the rain would have been neutralized by alkaline rocks and soils, and their geochemical effects would have been only local or regional in scale (Robertson *et al.* 2004) and limited to the shallow marine sites (Bailey *et al.* 2005). It should be noted that Maruoka & Koeberl (2003) proposed an impact-derived buffer that would have lessened the impact of acid rain at the KPB.

CO_2 uptake by the deep ocean (known as the oceanic CO_2 sink) is limited by slow exchange between the surface and deeper layers, which takes place on a timescale of less than a millennium (Broecker & Peng 1982). Due to the primary buffering ability of the ocean by the dissolution of the ocean floor carbonates, GAOS at the KPB would probably not have caused immediate significant changes in the acidity of the deep ocean (Liu & Schmitt 1996; D'Hondt 2005). The impact-derived CO_2 would, therefore, have been initially confined to the ocean surface to a depth of about 1000 m. Note that ocean surface acidification is expected to increase the ocean's capacity to take up CO_2 from the atmosphere.

Many studies have pointed out the similar environmental stresses caused by volcanism and extraterrestrial impacts (Sutherland 1994). Some opponents of the KPB impact theory have suggested that large igneous provinces (e.g., the Deccan Traps in India) could produce a similar increase in atmospheric CO_2 and SO_2. Deccan volcanism began shortly after 69 Ma and lasted until 64 Ma (Hofmann *et al.* 2000). Hofmann *et al.* (2000) estimated that two-thirds of Deccan flood basalt accumulation occurred between about 65.4–65 Ma. However, it appears that the quantities of volcanic CO_2 that were likely to have been generated from large igneous provinces were very small and were released slowly in the atmosphere (Caldeira & Rampino 1990; Self *et al.* 2005).

A more recent period when GAOS could have exceedingly surpassed that of the KPB is the Palaeocene–Eocene Thermal Maximum (PETM), about 55 Ma (Zachos *et al.* 2005). The projected anthropogenic carbon inputs for the next 300 years will lead to GAOS that will be more severe than during KPB or PETM.

Plankton productivity

Most researchers think that the KPB sections at the oceanic and marine sites were deposited during a global decrease in calcareous plankton productivity after the KPB impact, especially in coccolithophores. Indeed, the most dramatic episode of coccolithophore evolutionary history is without doubt the KPB extinctions. Apparently synchronous and rapid extinctions of this phytoplankton group occurred across the KPB, and their biogenic calcite production either collapsed or was highly reduced (Arenillas *et al.* 2006). This reduction was attributed to various impact-related palaeoenvironmental stresses, particularly global cooling and darkness due to atmospheric loading of post-impact dust (Alvarez *et al.* 1980) and sulfuric aerosols (Brett 1992). However, more recent studies indicate that impact-induced darkness and global cooling are unlikely to have been severe (Twitchett 2006). Apparently, calcareous plankton productivity had not completely recovered more than 200 kyr after the KPB impact (Alegret *et al.* 2004).

High dissolution of plankton shells

Low biogenic calcite concentrations in marine sediments may also result from high dissolution of calcareous plankton tests and low biocalcification. As pointed out before, the elevated level of atmospheric CO_2 generated by the impact probably reduced ocean surface pH and $CaCO_3$ saturation level. These chemical changes would make the calcareous structures of coccolithophores and foraminifera vulnerable to dissolution.

The calcareous plankton tests are mainly produced in the euphotic zone (from the surface to depths of about 200 m). Upon the death of the microorganisms, these calcareous tests fall through the water column and either dissolve or are deposited in the marine sediments. In the modern ocean, most (60–80%) of these shells are dissolved in the upper 1000 m (see, for example Milliman *et al.* 1999). As the ocean surface becomes enriched in CO_2, the rate and extent of dissolution of calcareous plankton tests (Sanders 2003) increase as a function of the decrease in the $CaCO_3$ saturation state. Thus, the dissolution of calcareous plankton shells during the KPB was probably high or even excessive.

The dissolution levels of foraminifera tests decreased during the earliest Danian and remained unusually low for about three to four million years (D'Hondt 2005), implying that the ocean surface water during that time period was probably ordinary one with pH about 8.2.

Biocalcification crisis

Models of the impact of elevated CO_2 levels show a decrease in biocalcification of marine calcareous plankton due to acidification of the ocean surface and the associated reduction in the $CaCO_3$ saturation level (Caldeira & Wickett 2003). For coccolithophores and foraminifera, biocalcification decreases drastically with decreasing $CaCO_3$ saturation state (Gehlen *et al.* 2007). For this reason, coccolithophores form a crucial biological group that is subjected to present-day ocean acidification caused by uptake of excess (largely anthropogenic) atmospheric CO_2.

It has been suggested that the high atmospheric CO_2 levels generated by extraordinary magmatic events were responsible for the biocalcification crises at the Permian/Triassic (Fraiser & Bottjer 2007), Triassic/Jurassic (Galli *et al.* 2005), and Jurassic/Cretaceous (Weissert & Erba 2004) boundaries. Decreases in pH and $CaCO_3$ saturation during times of extreme volcanic activity and rising CO_2 may have also resulted in a biocalcification crisis in the Cretaceous (Wissler *et al.* 2003; Weissert & Erba 2004).

Thus, the excessive level of atmospheric CO_2 generated by the impact is likely to have had an exceedingly negative effect on biocalcification of marine calcareous plankton, particularly coccolithophores and foraminifera. Aside from the biocalcification decline, marine calcite-forming plankton, primarily coccolithophores and foraminifera, may have experienced other adverse impacts, including physiological effects (Seibel & Walsh 2001, 2003).

Time scale of the spherule layer

On the basis of the stratigraphic distribution of Ni-rich spinels in the spherule layer at El Kef, Robin *et al.* (1991) proposed that its deposition time did not exceed an upper limit of 100 years. This suggestion is corroborated by ^{3}He measurements, which indicate an upper limit of about 60 years (Mukhopadhyay *et al.* 2001). On the basis of calculated average sedimentation rates and estimated ages, Arenillas *et al.* (2002) estimated that the deposition time of the spherule layer at El Kef was probably less than 20 years, assuming that the sedimentation rate was about 14.9 cm kyr^{-1}. It seems reasonable to suggest that the deposition of spherule layers at oceanic and marine sites lasted for several decades. In contrast, the entire clay-rich boundary sections at these sites are generally considered to have been deposited within 40–50 kyr (Keller *et al.* 1995).

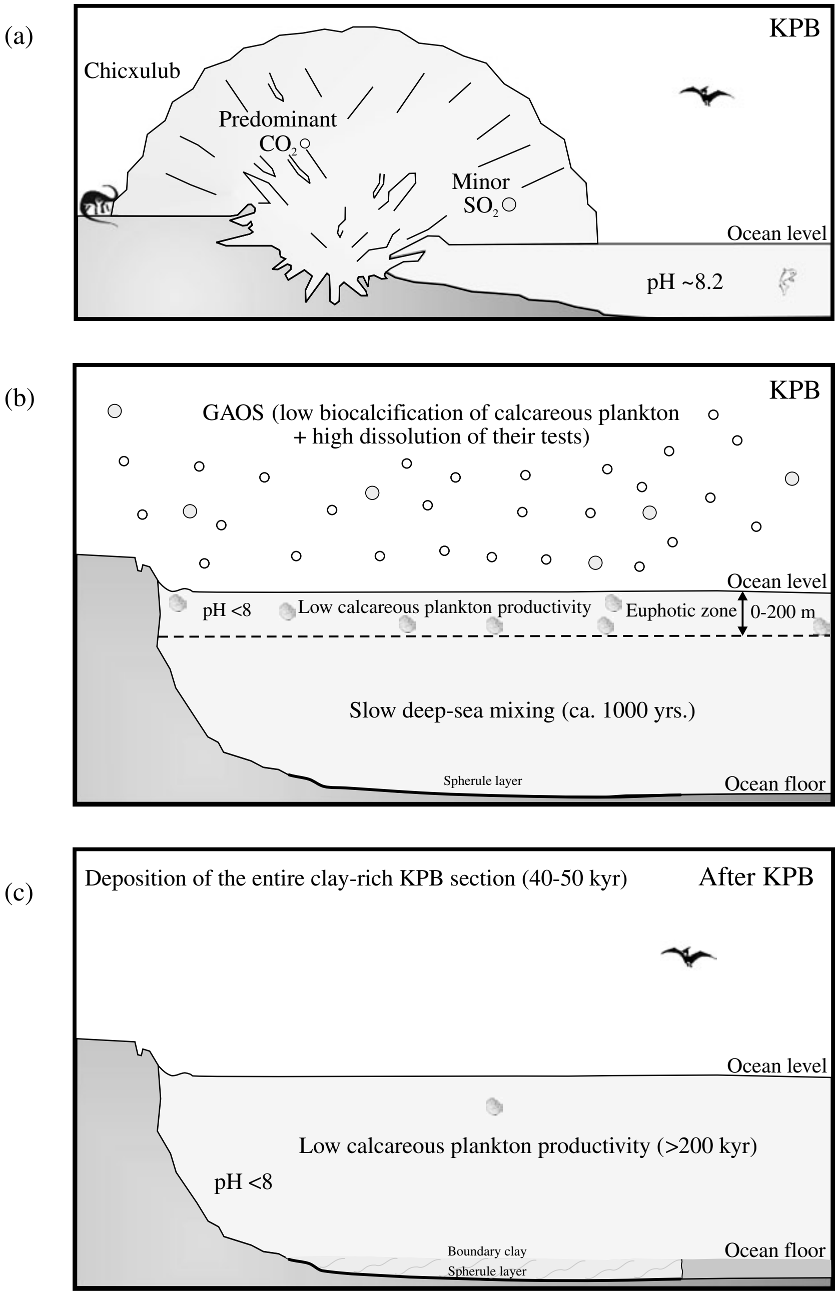

Fig. 7. Schematic drawing showing the sequence of events at the KPB: (a) generation of predominant CO_2/minor SO_2 by the Chicxulub impact; (b) GAOS by the impact-derived CO_2, subsequent biocalcification crisis of plankton and dissolution of their tests, facilitating the deposition of biogenic calcite-poor spherule layer; and, (c) deposition of clay-rich KPB section occurring for 40–50 thousands of years probably in the impact-acidified ocean water.

Taking into account the above points, the low concentrations of biogenic calcite in the spherule layers at oceanic and marine sites may be attributed to the impact-induced low biocalcification of plankton and high dissolution of their tests. It is also proposed that these two crises may have contributed considerably to the low abundance of biogenic calcite throughout the entire clay-rich boundary sections at these locations.

In summary, the following sequence of events at the KPB is indicated in Fig. 7 for the marine boundary clays and associated spherule layers: (a) generation of CO_2 and minor amounts of SO_2 by the Chicxulub impact; (b) GAOS (generated mainly by the impact-derived CO_2) induced the low biocalcification of calcareous plankton/elevated dissolution of their tests. These two crises caused the low abundance of biogenic calcite in the spherule layer; and (c) the deposition of entire clay-rich KPB section occurred for 40–50 thousands of years, probably in the impact-acidified ocean water.

Conclusions

Excessive atmospheric CO_2 generated by the impact at Chicxulub (Yucatan Peninsula, Mexico) at the KPB probably triggered the acidification and $CaCO_3$ undersaturation of the global ocean surface. These two chemical changes were likely to have induced a low biocalcification of calcareous plankton and a high dissolution of their tests. The biocalcification/dissolution crises caused the low contents of biogenic calcite in the spherule layers at oceanic sites and marine sites. The deposition of these layers probably lasted only a few decades at most.

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