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Impact Theory of Mass Extinctions and the Invertebrate Fossil Record

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Summary. There is much evidence that the Cretaceous-Tertiary boundary was marked by a massive meteorite impact. Theoretical consideration of the consequences of such an impact predicts sharp extinctions in many groups of animals precisely at the boundary. Paleontological data clearly show gradual declines in diversity over the last 1 to 10 million years in various invertebrate groups. Reexamination of data from careful studies of the best sections shows that, in addition to undergoing the decline, four groups (ammonites, cheilostomate bryozoans, brachiopods, and bivalves) were affected by sudden truncations precisely at the iridium anomaly that marks the boundary. The paleontological record thus bears witness to terminal-Cretaceous extinctions on two time scales: a slow decline unrelated to the impact and a sharp truncation synchronous with and probably caused by the impact.

In his 1969 presidential address to the Paleontological Society concerning the abrupt Late Devonian faunal turnover, McLaren (*1*) proposed that the impact of a large extraterrestrial body on the earth could trigger a mass extinction. This idea was almost completely ignored. A different extraterrestrial mechanism, explosion of a nearby supernova, was invoked by a few researchers to explain mass extinctions, particularly the one that is used to mark the boundary between the Cretaceous and the Tertiary (*2*). This idea also failed to receive much support. Throughout the 1970's, the weight of informed paleontological opinion held that the terminal-Cretaceous extinction was gradual on a time scale of (1 to 10) × 10^6 years, could best be accounted for by such environmental factors as climatic deterioration and a lowering of sea level, and clearly contradicted the predictions of a sudden, extraterrestrial triggering mechanism (*3*).

In 1978, anomalous concentrations of iridium were found in precise correspondence with the Cretaceous-Tertiary (K/T) boundary, as defined by a very abrupt change in calcareous microplankton in pelagic limestone sequences (*4*). After negative tests of the supernova hypothesis, the iridium anomaly was interpreted as indicating the impact of an asteroid or comet nucleus, roughly 10 km in diameter (*5*). Iridium anomalies have now been found worldwide in all but two of the approximately 50 essentially complete boundary sections that have been studied by researchers at seven different laboratories (*6*). The interpretation that the iridium anomaly is due to an impact is supported by probability arguments (*5, 7*), ratios among platinum-group elements (*6, 8*), the mineralogical and isotopic composition of the K/T boundary clay where it occurs (*9*), the presence of sanidine spherules (*10*) that are thought to have originated as droplets of impact melt (*11*), and calculations which show that such an impact would produce severe environmental stresses, including darkness (*5, 12*), abrupt temperature increase (*13*) or decrease, or both (*12*), and massive production of nitric acid in the atmosphere (*14*).

Subsequently a second iridium anomaly has been located, close to the Eocene-Oligocene boundary (*15*). This anomaly has now been found in seven deep-sea cores, coinciding precisely or nearly so with the North American microtektite horizon (*16*), which provides direct evidence for a major impact. [Keller *et al.* have recently reported evidence for more than one microtektite horizon in this part of the section (*17*), in which case the situation may be more complex than previously recognized.] Substantial extinctions of mammals (*18*) and various other faunal and floral groups (*19*) occurred at or near the Eocene-Oligocene boundary; these extinctions were not comparable in magnitude or stratigraphic precision to those at the K/T boundary, and it is not yet clear if there is any relation between impacts and worldwide extinctions in the middle Tertiary (*20*).

Despite the growing evidence that large impacts produce iridium anomalies and that at least the dramatic K/T calcareous plankton extinction occurred at exactly the same horizon as the iridium and the spherule concentration, the classical paleontological view has been repeatedly restated—that the terminal-Cretaceous extinctions were largely gradational and most were not related to any impact event (*21*). If this were true, it would strongly contradict the impact explanation for extinctions in its present form.

This article gives a different view of the terminal-Cretaceous fossil record of various marine invertebrate groups, which has been recognized by a few workers for some time but has not yet been widely published or accepted. It has generally been held that most invertebrate groups did not undergo serious extinction at the K/T boundary, and that groups that did become extinct at the boundary, notably the ammonites, had

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been in decline for some millions of years, a decline that was much more important in their disappearance than the effects of the suggested terminal-Cretaceous asteroidal impact. We will show that published data on the fossil record strongly contradict this view.

Recent developments in research on the terminal-Cretaceous extinctions have been widely viewed in terms of a conflict between gradualistic and catastrophic interpretations. This notion is counterproductive and should be discarded. It seems evident to us that major biotic turnovers occur on two completely different time scales. The classical paleontological view recognizes the importance of gradual turnovers on a time scale of 10^5 to 10^7 years. The evidence for changes of this kind is so strong that their existence cannot be denied by any reasonable person. The novelty resulting from the recent work on the K/T boundary is the recognition that very rapid turnovers can also occur, with characteristic times of 1 to 10^3 years. In accepting the evidence for very rapid turnovers, one need not reject the reality of gradual turnovers.

We present evidence that very rapid turnovers occurred in a number of invertebrate groups whose terminal-Cretaceous records were previously thought to show only gradual changes or none at all. We intend to establish beyond question the reality and importance of rapid faunal turnovers in these groups. By focusing on the rapid changes, we do not mean to imply that gradual changes are unimportant. However, there is clearly a need for reevaluation of the evidence relevant to gradual versus sudden extinctions in many different fossil groups.

It seems probable that the biologic effects of a large impact may depend on the conditions of diversity and robustness in which various groups find themselves at the moment of impact. Detailed paleontological and stratigraphic studies suggest that the initiation of terminal-Cretaceous extinctions for many groups may have been associated with widespread deterioration of global marine environments during large-scale eustatic fall and epicontinental regression, rapid shifts in ocean chemistry and circulation patterns, and rapid climate and temperature fluctuations during the middle and late Maastrichtian, within the last 1×10^6 years of the Cretaceous. Depleted lineages of typical groups such as ammonites, inoceramid bivalves, reef organisms (including rudists), and marine reptiles, in many cases represented mainly by generalized, long-lived stocks and endangered species of specialists in low population numbers, would have been highly susceptible to abrupt extinction in response to the same event that so dramatically eliminated the calcareous microplankton at a peak in their Cretaceous evolution.

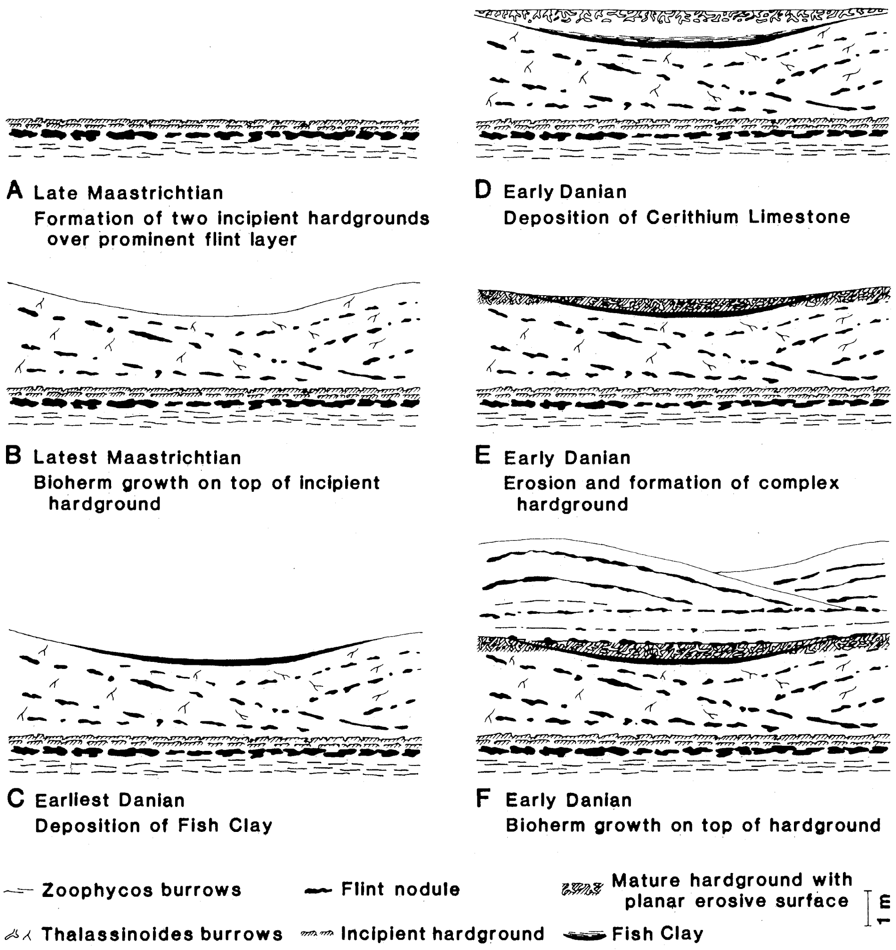

Fig. 1. Interpreted depositional history of the informal Cretaceous-Tertiary boundary section at Stevns Klint, Denmark, prepared by F. Surlyk. The critical point is that the prominent hardground developed well after the boundary event and does not provide evidence for a break in sedimentation at the boundary. Gravesen (*49*) has reviewed the gradual recognition that the boundary itself is undulating, so that in some places the hardground affects Cretaceous sediments and in other places Tertiary sediments.

Methodology

In attempting to decide whether the asteroidal impact inferred from geochemical information had a significant effect on particular fossil groups, one encounters three notable difficulties. The first problem is that taxonomic diversity is generally presented in the literature as number of taxa per stage or, at best, per substage [that is, a resolution of (1 to 5) $\times 10^6$ years]. Thus, even if a notable difference in the number or composition of taxa can be shown to exist between the Maastrichtian and the Danian, one cannot say, in the great majority of boundary sequences, whether the change took place over a span of 1 to 10 years, as predicted by the impact hypothesis, or over as much as (0.1 to 5) $\times 10^6$ years, in agreement with the gradualistic extinction hypothesis.

The second problem concerns the taxonomic level chosen for the analysis. At a high taxonomic level (family, order, class), a few major Cretaceous groups, such as the inoceramids, belemnites, and ammonites, show substantial or complete extinction right at the K/T boundary. Yet the real fabric of extinction reflected by species- and genus-level patterns of diversity is hidden at this level of analysis. At these lower taxonomic levels it is difficult to find broadly representative samples of the total diversity and composition, and there is the possibility of artifacts in the reported data resulting from differing criteria for naming genera and species, or from the different intensity with which various sections have been collected and studied.

Finally, it has long been recognized that many K/T sections are incomplete across the boundary, with gaps ranging from one or a few fossil zones to several stages. For our purposes, sections with gaps of as much as, say, one substage are simply irrelevant, and any detectable gap reduces the resolution with which an extinction can be said to be instantaneous. There is room within a gap of 1 × 10^6 years or more for either a graded or a sudden extinction. On the other hand, there is usually no way to detect gaps of 10^3 to 10^4 years or less, which places an ultimate limit on our resolution.

To reduce the effects of these three problems as much as possible, we have based our conclusions on a small number of outstanding sections that have little or no recognizable stratigraphic discontinuity across the boundary, are richly fossiliferous in both microbiota and macrofauna, and have been carefully studied with the use of high-resolution stratigraphy and modern recovery techniques. For the most part, such sections are located in Denmark (*22*) and Spain (*23*). Although this approach excludes an enormous amount of potentially significant data, it also reduces the possibility, on the one hand, of smearing out and thus missing the record of an abrupt extinction, and, on the other hand, of seeing an abrupt event where one does not exist, as a result of stratigraphic gaps or artifacts in the diversity data.

Our conclusions are based not on new data but on an alternate view of existing, published data. To emphasize this, our illustrations are largely taken from the published literature.

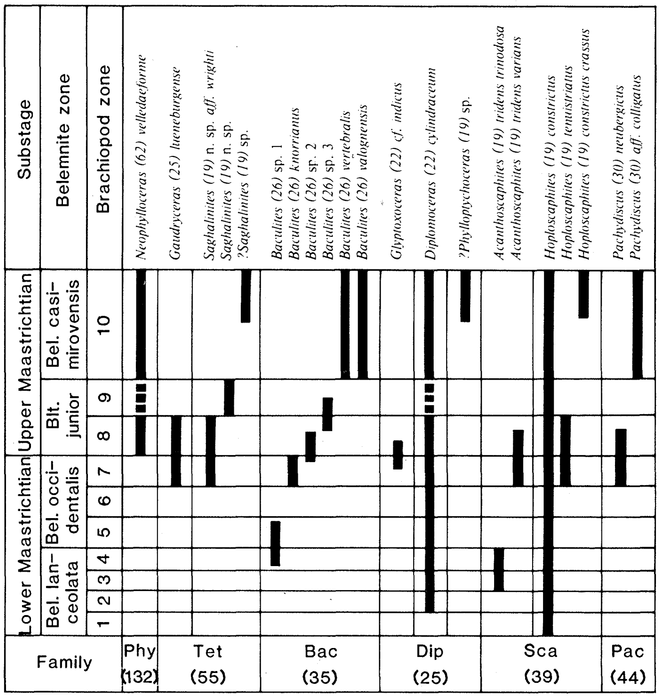

Fig. 2. Ranges of Maastrichtian ammonites in Denmark [after Birkelund (*31*); ranges (in millions of years within parentheses) are from (*30*)]. Families are as follows: *Phy*, Phylloceratidae; *Tet*, Tetragonitidae; *Bac*, Baculitidae; *Dip*, Diplomoceratidae; *Sca*, Scaphitidae; and *Pac*, Pachydiscidae. The families and genera found here are long lived; *Bel.*, *Belemnella*; *Blt.*, *Belemnitella*. The distributions for all ammonites are strongly skewed toward the long-lived end; the mode of generic longevities for all ammonites is 5 × 10^6 years; the mode of familial longevities is 10 × 10^6 years (*30*).

Continuity in the Danish Sections

The famous cliff section at Stevns Klint, south of Copenhagen, presently serves as an informal type section for the K/T boundary. It is sometimes suggested that this section is not suitable for detailed K/T boundary studies because of the presence of a hardground, indicative of a hiatus, precisely at the K/T boundary. However, on the basis of existing literature (*22*) and the common knowledge of Danish geologists (including F. Surlyk), it is clear that the hardground is actually younger than the boundary (Fig. 1).

The K/T boundary sections of Denmark are characterized by uniform carbonate lithologies. The actual boundary is marked by a thin marl bed, and locally a hardground is developed about 0.5 m above the marl. The boundary sequence at Stevns Klint is somewhat more complex than the majority of the sections. This is due to the wavy biohermal nature of the top of the Maastrichtian (Fig. 1). The crests of the bioherms are truncated and cemented by the early Danian hardground, and the cemented layer thus consists of alternating Maastrichtian and Danian chalk. The critical point is that the hardground formed well after the K/T boundary event, and its presence does not imply a stratigraphic gap at the boundary.

Probably the best of the Danish sections is at Nye Kløv in Jutland (*24*). This site has similar lithologies in the top Cretaceous and the basal Tertiary, a well-defined, 3-cm boundary clay layer, and absolutely no sign of a hardground.

Ammonites

The widespread, rapidly evolving ammonites are the best biochronological indices for the Mesozoic, and their final extinction occurs in association with the iridium peak at the end of the Cretaceous. It has been widely accepted for some time that a reduction in the diversity of the ammonites had been in progress for several million years prior to the extinction (*25*) and possibly as long as (15 to 20) × 10^6 years (*26*). The apparent decline may be due to the fact that there are very few upper Maastrichtian sections to sample, and most of those are in chalk in which the aragonitic ammonites are poorly preserved; careful statistical testing of this question is needed. Nevertheless, there is a widespread view that the ammonite extinction was a gradual process and that, if a boundary impact event did occur, it merely removed the last remnants of the ammonites, a group so far gone in decline that it was probably doomed anyway. However, in the light of detailed information on the diversity, ecology, and evolutionary longevity of ammonites at the generic level and on the occurrence of ammonites up to the K/T boundary in the essentially complete Danish sections, this gradualistic view of ammonitic extinction requires significant revision.

Cretaceous ammonite diversity through time was marked by alternating maxima and minima, a pattern recognized by numerous investigators (*25*, *27*–*30*). Since the ammonites had recovered from drastic diversity minima, for example, in the vicinity of the Triassic-Jurassic boundary and in the Albian-Cenomanian and Coniacian-Santonian boundary zones, the decline prior to the final extinction loses some of its significance. The ammonites might well have recovered from that decline as well, had it not been for the blow of the impact event, because ecologically generalized, cosmopolitan forms dominated the final ammonite assemblages.

But the case is even more striking in the light of Ward and Signor's recognition (*29*, *30*) that ammonite genera and families fall into two groups: (i) long-lived taxa which neither increase nor decrease dramatically in diversity through time, and (ii) short-lived taxa which account for most of the variation in abundance and diversity of ammonites through time, and which therefore have attracted the most attention because of their biostratigraphic usefulness. In view of this pattern, extinction of a few long-lived taxa at a time of low diversity could be fatal to the entire ammonite group, whereas a gradual decline of the short-lived taxa, although superficially more impressive, would not necessarily lead to extinction. Ammonites had survived the extinction of short-ranging taxa several times during the Mesozoic.

With this background, Birkelund's data on ammonite occurrence in the Danish Maastrichtian (*31*) are of particular importance (Fig. 2). Whereas only nine species, representing seven genera (*Neophylloceras*, *Saghalinites*, *Baculites*, *Diplomoceras*, ?*Phylloptychoceras*, *Hoploscaphites*, and *Pachydiscus*) and six families, are found in the uppermost Maastrichtian of Denmark (brachiopod zone 10), Birkelund specifically noted that representatives of all seven genera occur in the uppermost bed of the Cretaceous, that is, immediately below the iridium-rich Fish Clay which coincides with the terminal Cretaceous plankton extinction. Preservation is good in this bed because it was lithified in some places by the episode of hardground formation during the early Danian. Ward and Signor (*30*) have given durations for the six nonqueried genera, ranging from (19 to 62) × 10^6 years (mean, 30 × 10^6 years), which places all six far out on the long-lived tail of the strongly skewed longevity distribution (mode = 5 × 10^6 years). Birkelund noted the abundance of ammonites in the very uppermost Maastrichtian (*31*):

> The topmost Maastrichtian chalk of Stevns Klint, where locally lithified by a [Danian] hardground, contains many mature *Hoploscaphites* and *Baculites* of normal size and rare mature specimens of other genera. Together with these there are abundant juvenile specimens of scaphites and baculites, and juvenile *Saghalinites* sp., ?*Phylloptychoceras* sp. and *Pachydiscus* sp. have also been collected. . . . In conclusion it is important to stress that there is no evidence to suggest that the ammonites were affected by poor living conditions to cause dwarfing or stunting (as supposed by Wiedmann, 1969, for a late Maastrichtian fauna of Zumaya, Spain); on the contrary, they seem to have lived perfectly well to the end.

Ward and Wiedmann (*32*) have recently restudied the section at Zumaya in northern Spain, the only other locality with a K/T boundary ammonite record comparable to the one at Stevns Klint. Ammonites are common up to about 15 m below the iridium-rich boundary layer and are entirely gone by 12 m below the boundary. At Zumaya, as at Stevns Klint, dwarfing does not occur among the latest Cretaceous ammonites.

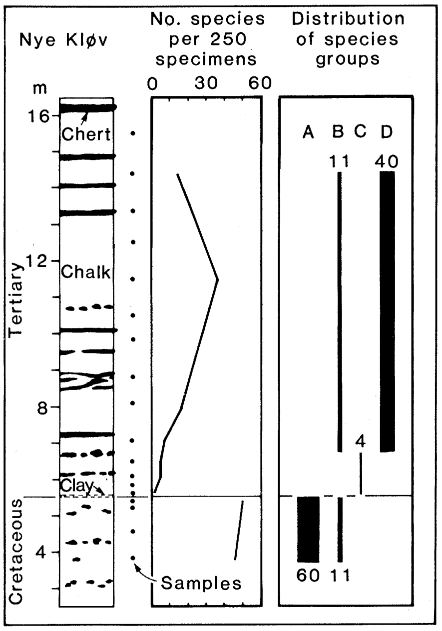

Fig. 3. Data on cheilostomate bryozoans at Nye Kløv, Denmark [simplified from Håkansson and Thomsen (*34*), figure 2]. The critical point here is that 60 out of 71 latest Cretaceous species (85 percent) disappear precisely at the Cretaceous-Tertiary boundary clay. For more detail, see Birkelund and Håkansson (*35*), figure 8.

It is not easy to understand why even the long-ranging ammonites disappeared at Zumaya, although they were thriving until the end at Stevns Klint. Nevertheless, in our view the pattern at Stevns Klint strongly supports the idea that the terminal-Cretaceous impact caused the final extinction of the ammonites. The prior decline in short-ranging taxa certainly weakened the ammonites as a group, but the common long-ranging taxa in Denmark were evidently in no difficulty whatsoever until the impact occurred. This suggests a subtle but significant change in the conclusion that should be drawn from the paleontological data. Formerly the extinction of all short-ranging ammonites was taken to mean that a gradual extinction was nearing completion, with the final dying out of remaining long-ranging taxa a predictable denouement. In the view presented here, the extinction of those long-ranging taxa was the critical and unpredictable event—without it the ammonites probably would not have disappeared.

Bryozoans

The Danish sections are very useful for studies of bryozoan evolution across the K/T boundary. Bryozoans are of such importance in the Danish uppermost Cretaceous and basal Tertiary that lithologies are distinguished by the quantity of bryozoan skeletal material they contain, ranging from chalk through bryozoan chalk to bryozoan limestone (*33*).

The cheilostomate bryozoans were evolving rapidly at this time. Håkansson and Thomsen studied (*34*) this group across the boundary, upgrading the work of Voigt (*33a*); their work is based on the section at Nye Kløv (*24*), which has little or no lithologic difference between the top Cretaceous and the basal Tertiary. Unfortunately, they do not present species identifications but only diversity data. Figure 3 shows the cheilostome bryozoan record at Nye Kløv (*34, 35*). The number of species in a 250-specimen sample, based on rarefaction analysis, drops significantly at the boundary, from about 50 species in the uppermost Maastrichtian to one species in the lowest sample of the Danian, then recovers substantially in the first few meters of the Danian (Fig. 3). Although not necessarily indicative of a mass extinction, this diversity crash certainly indicates that the North Sea shelf area was hit by a very sudden ecological crisis, from which it gradually recovered.

Figure 3 shows that there is also a major difference in the species composition across the boundary. Of 71 species found in the top Maastrichtian, only 11 are found in the Danian; that is, 60 species (85 percent) disappear immediately below the iridium anomaly (*36*). This event can best be explained as a sudden, major extinction, directly or indirectly caused by the impact.

The abruptness of this extinction distinguishes it from an inferred prior decline in the cheilostomate bryozoans. This apparent decline was stressed by Håkansson and Thomsen (*34*), and by Håkansson (*37*) who estimated that the cheilostome fauna earlier in the late Maastrichtian approached "200 species in the Danish chalk alone (a good portion of which are undescribed)," compared to the 71 species seen in the highest Maastrichtian of Nye Kløv. We note, however, that Nye Kløv is a benthos-poor locality and that the inferred decline is probably an artifact that arises from comparing a single locality with the entire Danish chalk.

Brachiopods

For a number of years, Surlyk (*38, 39*) has carried out detailed studies of the brachiopods of the Upper Cretaceous chalk of Denmark. He has noted (*39*, p. 48): "The brachiopods have proved to be of great biostratigraphical value in the chalk of NW Europe because many of the species have a limited vertical distribution, occur in great numbers, and are easy to determine." Recently, Surlyk and Johansen (*40*) and Johansen (*41*) have extended these studies upward into the Danian, based on samples from the section at Nye Kløv. Most of the brachiopod species encountered are very small (a few millimeters), and hundreds or thousands of individuals can be obtained from each sample (*40*), so statistical problems do not affect the determination of biostratigraphic ranges. Surlyk and Johansen summarized their findings as follows (*40*, p. 112).

> Our results show an extinction pattern compatible with that reported for coccoliths and pelagic foraminifera. About 20 species occur in the Upper Maastrichtian. Extinction is abrupt and there is no warning in the form of decreasing diversity or early extinction of specialized groups. The basal few meters of the Danian are almost devoid of brachiopods, and a Danian brachiopod fauna starts almost as abruptly as the Maastrichtian disappeared. The new fauna is similar to the Maastrichtian as regards density and diversity, and at maximum five species are common to both faunas.

Surlyk and Johansen (*40*, *42*) have made three points about this mass extinction of brachiopods. First, it was very sudden and coincided exactly with the abrupt, nearly complete extinction of coccoliths and planktonic foraminifera. Second, there was absolutely no decline in diversity of brachiopods prior to the sudden extinction. Third, the synchroneity of this event with the extinction of plankton (coccoliths and foraminifera) and bryozoans suggests a common cause, that is, that both are direct effects of the impact. They noted, however, that the brachiopod fauna was highly specialized and adapted to life on a chalky bottom composed primarily of coccoliths and foraminifera and suggested that the brachiopod extinction may have been a result of the plankton extinction, which destroyed the habitat the brachiopods required. A similar cause might be proposed for the large bryozoan extinction; the substrate requirements of bryozoans are similar to those of brachiopods. This point is very important. We would stress that our purpose in this article is to show that mass extinction did occur in a number of fossil groups, at essentially the same time as the inferred impact. The exact sequence of extinctions, and their causal relations to the impact itself and to each other, will be a difficult problem for future work.

Bivalves

Among bivalves, the cosmopolitan and rapidly evolving inoceramids and the reef-building rudists disappeared at or near the end of the Cretaceous. The maximum development of rudists occurred during the late Campanian and early to middle Maastrichtian, and this group declined rapidly during the last few million years of the Cretaceous (*27*, *43*).

These diversity declines raise the question whether the bivalve record is comparable with that of the ammonites. The best information comes from the fossiliferous Danish sections, but the record is complicated by a mineralogical problem concerning the relative stability of calcite and aragonite shells, as discussed in the legend to Fig. 4. The majority of bivalve shells are wholly or predominantly aragonite (*44*), a mineral that is unstable; shell dissolution occurs early in chalk diagenesis. Aragonitic fossils are commonly absent or poorly preserved in chalks such as those of the Danish boundary sequence. Calcite dominates the shells of a smaller number of bivalve taxa (for example, oysters and scallops) and is an important component of shells with mixed mineralogy, where it normally forms the outer layer. Calcite is stable and selectively preserved in chalks and limestones. Thus, the fossil record of most chalks is highly distorted by the artificial dominance of calcite-shelled taxa unless the carbonates were tightly cemented early in diagenesis, forming hardgrounds.

Heinberg (*45*) has studied the bivalve fauna at Stevns Klint, in the uppermost Maastrichtian sediments lithified by the Danian-age hardground and in the adjacent strata, and his range chart is reproduced in Fig. 4. The 45 genera in the hardground represent a broad ecological and taxonomic spectrum of bivalves, representing four of the five subclasses and eight of the 11 orders existing in the Cretaceous. Both of the major groups of bivalves that disappeared at the end of the Cretaceous, the inoceramids and the rudists, are represented in the highest Maastrichtian collection, by *Tenuipteria* [= "*Inoceramus*" sensu lato of Heinberg (*45*)] and *Gyropleura*, respectively. No rudists or rudist-dominated reefs are known from the latest Maastrichtian of Cretaceous tropical environments, but one species of *Gyropleura*, one of the

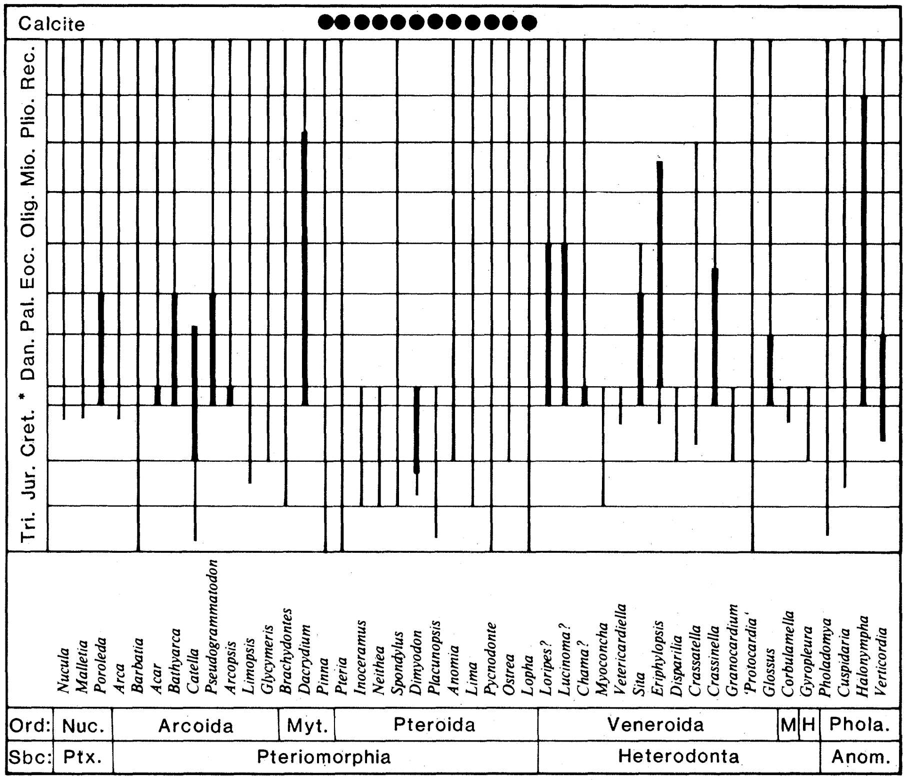

Fig. 4. Ranges of bivalve genera found in the strata near the Cretaceous-Tertiary boundary at Stevns Klint, Denmark [based on Heinberg (*45*), figure 1]. The asterisk marks the uppermost Cretaceous layer lithified by the Danian hardground and the black dots at the top mark calcite-dominated genera. Genera are grouped by order (*Nuc.*, Nuculoida; *Myt.*, Mytiloida; *M*, Myoida; *H*, Hippuritoida; *Phola.*, Pholadomyoida) and subclass (*Ptx.*, Palaeotaxodonta; *Anom.*, Anomalodesmata). Most bivalve shells are either dominantly calcitic or dominantly aragonitic. Dominantly aragonitic shells are easily dissolved and are thus absent in most chalks; they are likely to be preserved only as molds in hardgrounds, so their reported ranges in carbonate facies are not reliable. This is emphasized by the heavy lines, which show new range extensions based on the hardground fauna. Of the 12 genera that are dominantly calcitic and therefore have reliable ranges in the Danish chalk, four go extinct at the iridium-bearing boundary clay; the other eight are still living.

most generalized and widespread of small epibiont rudists, does occur in the uppermost Cretaceous chalks of Denmark, immediately beneath the iridium-bearing Fish Clay. Similarly, the Inoceramidae show a long, gradual diversity decline since the Turonian, with a final rapid decline in the Maastrichtian, but are still represented at the Danish top Maastrichtian by one species of *Tenuipteria*.

Heinberg noted that 13 typically Tertiary genera first appear in the lithified top beds of the Maastrichtian. He therefore concluded that the terminal Cretaceous faunal turnover in bivalves was under way before the boundary as marked by the Fish Clay (subsequently found to be iridium-rich), indicating a graded faunal transition. This conclusion and the known history of rudist and inoceramid decline have reinforced the common impression of a gradual faunal transition at the end of the Cretaceous (*46*).

However, an examination of Heinberg's data shows that, of the 13 genera that first appear in the lithified top Maastrichtian, 12 are dominantly aragonitic and the other is an uncertain identification ("*Chama*?") of a genus with more than 30 species that are aragonitic and only two that are calcitic (*47*). Of the 13 genera, ten had their ranges substantially extended back in time (thick lines in Fig. 4) when they were recognized by Heinberg in the hardground. Because these taxa are rarely preserved in chalk, which dominates the Upper Cretaceous of western Europe, we take this to mean that their earlier recognition was most probably limited by preservation, and that the oldest specimen found in Denmark probably does not represent the origination of the group. These aragonitic taxa almost certainly represent older Cretaceous groups that survived the extinction event, rather than the sudden advanced appearance of Tertiary forms before the mass extinction.

The question thus arises whether the last occurrences of bivalves in the lithified top Maastrichtian are also meaningless. Of the ten genera last appearing in this hardground (that is, apparent terminal-Cretaceous extinctions), five are aragonitic and their ranges should be questioned for the reasons given above. However, four definitely had partially calcitic shells, and their apparent extinctions at this level are therefore probably real, and one, *Gyropleura*, probably had calcite layers (*48*). The importance of these four extinctions is underlined by Fig. 4, which shows that these genera, and the families to which they belong, had lived for very long time spans prior to their extinction. As a further indication of the importance of this extinction, we note that, of the 12 bivalve genera in the hardground sample that are definitely calcite-bearing and should therefore have reliable longevity records, four went extinct at the level of the iridium anomaly, and the other eight have all survived to the Recent. Moreover, Heinberg's data (*45*) are at the generic level, which may well mask a more dramatic extinction at the species level, such as that seen in the brachiopods and the bryozoans.

This reinterpretation of the bivalve record leads to the conclusion that, although some groups, such as the rudists and inoceramids, underwent a prominent Maastrichtian evolutionary decline, the terminal-Cretaceous extinction itself was probably very sudden, unpredictable, and of major importance in the disappearance of these groups.

Conclusion

The four groups of marine invertebrates reviewed here show unmistakable evidence for sudden and unanticipated extinction of small to large numbers of taxa in precise correspondence with the iridium anomaly at the K/T boundary. There can be little doubt that these extinctions resulted in some way from the inferred impact, although it is not presently possible to trace the chains of direct and indirect causality. It will be important to make this kind of detailed evaluation for other invertebrate groups, such as gastropods, corals, and echinoderms, which are currently regarded as having been little affected by the terminal-Cretaceous extinction event. Detailed paleontological study of as many groups as possible, in the very best available sections, is thus an important challenge in the next few years.

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Hydrogen-Evolving Solar Cells

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Summary. Sunlight is directly converted to chemical energy in hydrogen-evolving photoelectrochemical cells with semiconductor electrodes. Their Gibbs free energy efficiency of solar-to-hydrogen conversion, 13.3 percent, exceeds the solar-to-fuel conversion efficiency of green plants and approaches the solar-to-electrical conversion efficiency of the best *p–n* junction cells. In hydrogen-evolving photoelectrodes, electron-hole pairs photogenerated in the semiconductor are separated at electrical microcontacts between the semiconductor and group VIII metal catalyst islands. Conversion is efficient when the island diameters are small relative to the wavelengths of sunlight exciting the semiconductor; when the island spacings are smaller than the diffusion length of electrons at the semiconductor surface; when the height of the potential energy barriers that separate the photogenerated electrons from holes at the semiconductor surface is raised by hydrogen alloying of the islands; when radiationless recombination of electron-hole pairs at the semiconductor-solution interface between the islands is suppressed by controlling the semiconductor surface chemistry; and when the semiconductor has an appropriate band gap (1.0 to 1.8 electron volts) for efficient solar conversion.

Optimal conversion of sunlight by a single-threshold converter, whether semiconductor-based or molecular, requires an energy gap near 1.4 electron volts (*1–3*). Tandem systems, based on two semiconductors or on two light-harvesting molecules, require materials with gaps near 1.8 and 1.0 eV (*4*). At normal solar irradiance and at 27°C, the thermodynamic limit to the solar conversion efficiency is 27 percent for a single converter and 36 percent for tandem cells (*4*). For nonconcentrated sunlight the actual efficiency that has been attained is 21.9 percent (*5*). Although the thermodynamic efficiency limits for semiconductor and molecular systems are the same, all efficient systems today are semiconductor-based.

The foundations of the science of semiconductor-based photoelectrodes were laid between 1955 and 1970 (*6–16*). In 1972 it was shown that when an oxygen-evolving metal anode is replaced by the stable semiconducting anode n-TiO_2 (*17*), a substantial part of the electrical energy required for the electrolysis of water is conserved (*18*). Unfortunately, the band gap (E_{BG}) of n-TiO_2 is 3.0 eV, so the excitation spectrum of this material is confined to the ultraviolet. Consequently, sunlight could not be efficiently converted in early cells based on n-TiO_2 or n-$SrTiO_3$ (E_{BG} = 3.2 eV) photoanodes (*19–24*).

Photoanodes with band gaps appropriate for efficient solar conversion were first reported in 1960 (*9*), before the introduction of the concept of power-producing ("regenerative") cells (*25*). However, these were quite unstable. Ideas for their stabilization emerged in 1966 (*26*), but the introduction of relatively stable photoanodes took nearly a decade (*27–50*).

Simultaneously, the second key problem of photoelectrodes, the reduction of quantum yield from radiationless recombination of electron-hole pairs at the semiconductor-solution interface, was addressed. It was shown that recombination can be reduced by properly controlling the interfacial chemistry (*37, 51–66*). These advances led to the first power-producing photoelectrochemical cells of greater than 10 percent solar conversion efficiency (*51, 52, 63, 64, 67*). Stabilization and reduction of surface recombination also opened the way to efficient and direct photoelectrochemical cells for producing hydrogen. These cells are the subject of this article.

Photoelectrodes

Hydrogen can be evolved in either photocathode- or photoanode-based cells. Photocathodes and photoanodes are based on electrical contacts between semiconductors and electrolytes, between semiconductors and metallic electrocatalysts, or between semiconductors and both electrolytes and catalysts. Associated with these contacts is a barrier, ψ_B, which separates the photogenerated electrons (e^-) and holes (h^+) (Fig. 1). Hydrogen evolution at photocathodes requires the presence of a catalyst on or near the surface. When the catalyst is on the surface of the semiconductor, photogenerated electrons diffuse or drift to the interface of the semiconductor and the catalyst (Fig. 1a), where they reduce adsorbed protons to form hydrogen, according to $2e^- + 2H^+ \rightarrow H_2$. Electrical neutrality is maintained by transport of holes through both the bulk of the semiconductor and its back electrical contact to the anode, where they oxidize either dissolved anions such as chloride, through the reaction $2h^+ + 2Cl^- \rightarrow Cl_2$, or water itself, through the reaction

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