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Global comparisons of organic matter in sediments across the Cretaceous/Tertiary boundary

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Abstract—The Cretaceous/Tertiary (K/T) boundary is marked by extensive changes in the sedimentary fossil record of continental and marine life. Organic matter in sediments from above and below the K/T boundary has been studied to identify consequences of the biotic extinctions and of the changes in biological productivity which occurred at this time. Data from locations encompassing a variety of marine paleoenvironments were examined to assess the global extent and local expressions of these biological changes. Characterizations of organic matter included Rock-Eval pyrolysis, stable carbon isotope ratios, and distributions of extractable biomarkers. In general, organic carbon concentrations are a few tenths of a percent in the chalks and marls above and below the K/T boundary; in some boundary clay samples concentrations up to 5% are found. The elevated amounts near the boundary result from oxidation of marine organic matter, consequent dissolution of carbonates, and concentration of the surviving organic matter. At all locations, the organic matter has been microbially reworked and evidently was deposited in oxidizing environments. Carbon isotope shifts in open marine sediments suggest biological productivity was depressed following the K/T boundary. Repetition of these changes at different locations verifies the global extent of the boundary event, yet local variations in its expression are evident.

Key words—K/T boundary, biomarkers, Rock-Eval, *anteiso*-alkanes, *n*-alkanoic acids, carbon isotopes

INTRODUCTION

The end of the Cretaceous Period, at *c.* 66 million years ago, was accompanied by massive reductions in the diversity and numbers of many organisms. The marine fossil record, for example, shows marked depletions in calcareous plankton and tropical invertebrates (e.g. Jiang and Gardner, 1986; Keller, 1988a, b). On land, dinosaurs became extinct at the end of the Maastrichtian (e.g. Sloan *et al.*, 1986), and forests were destroyed (e.g. Tschudy *et al.*, 1984; Saito *et al.*, 1986). New populations of plants and animals gradually replaced the decimated species in the early Paleocene, but an abrupt boundary separates the Cretaceous from the Tertiary virtually everywhere in the global stratigraphic record.

An explanation for this major perturbation in biotic evolution remains elusive, notwithstanding considerable discussion from a large segment of the earth science community. A number of competing hypotheses exist. The general occurrence of iridium enrichment in the boundary clay layer has been interpreted as evidence of an extraterrestrial cause—a massive meteorite impact (Alvarez *et al.*, 1984). Alternatively, this enrichment has been considered prime evidence of extensive vulcanism at the Cretaceous/Tertiary transition (Officer *et al.*, 1987). Either scenario could induce a global change in climate, yet the iridium anomaly may arise from microbial activity and authigenic precipitation of this metal from sediment pore waters (Schmitz, 1988; Schmitz *et al.*, 1988). A third possible explanation of the boundary extinctions is that of abrupt climate change brought about by the culmination of gradually accumulating, non-catastrophic factors (Crowley and North, 1988).

Regardless of the cause of this intriguing event in earth history, the effect was a major change in the nature and abundance of global life. It is this effect and its possible consequences on the organic geochemistry of the sedimentary record that led us to the results that we report here.

ORGANIC GEOCHEMICAL STUDIES OF THE K/T BOUNDARY

Published reports of the results of organic geochemical studies of the K/T boundary are few. This observation may reflect the difficulty of doing such studies on rocks lean in organic carbon, as well as the limited availability of samples suitably preserved for organic geochemical studies.

Isotopic and elemental compositions

Schimmelmann and DeNiro (1984) made measurements of carbon, nitrogen, and hydrogen isotopes in organic matter across the freshwater K/T boundary located in the York Canyon exposure of the Raton Basin, New Mexico. They found a shift of 1.8‰ to lighter organic carbon isotopic values in the early Tertiary, which parallels a similar shift of 1–2‰ found in marine carbonates from the South Atlantic (Shackleton and Hall, 1984), Israel (Magaritz, 1989), the North Pacific (Zachos *et al.*, 1989), and Tunisia (Keller and Lindinger, 1989), implying a global perturbation in the carbon cycle. The nature of this perturbation is believed to be globally depressed bioproductivity (Zachos and Arthur, 1986; Margaritz, 1989). A period during which the rate of oxidative recycling of organic matter exceeded photosynthetic carbon fixation would result in return of isotopically light carbon to the inorganic carbon reservoir and would produce the observed isotope shifts. In contrast to the systematic change in carbon isotopes, $\delta^{15}N$ values vary randomly between $+2$ and $+4‰$ in samples from the York Canyon site, and δD ratios remain between -105 and $-125‰$, suggesting no major fluctuations in the water balance or the temperature of this swampy freshwater setting during this period of other types of global change.

An exception to the general pattern of lighter carbon isotope values in sediments deposited after the K/T boundary is found in the K/T section in eastern Hokkaido, Japan. At this location, organic carbon isotopic values change from $-26‰$ in upper Maastrichtian sediments to $-23.7‰$ in basal Danian sediments (Saito *et al.*, 1986), which is opposite to the change expected from depressed marine productivity. This deviation from the typical pattern is evidenced that local conditions might have differed from the general global situation.

Like the isotopic values, elemental C/N and N/H ratios of organic matter can provide information about the paleoenvironmental and depositional conditions at the K/T boundary. The C/N ratios from the coal layers and mudstones in the Raton Basin region remain between 45 and 60 (Schimmelmann and DeNiro, 1984), typical of vascular plant material. Neither the C/N nor the N/H values change significantly across the Raton K/T boundary, even though angiosperm/fern pollen contents of strata here and at Hokkaido indicate extensive devastation of forests at the end of the Maastrichtian (Tschudy *et al.*, 1984; Saito *et al.*, 1986).

Molecular studies

Extractable biomarker compounds have been analyzed in samples from DSDP Sites 577 (northwestern Pacific Ocean) and 605 (New Jersey continental margin) and from Stevns Klint (Denmark) by Simoneit and Beller (1985, 1987). Microbial biomarkers dominate the geolipid contents of the Site 577 and Stevns Klint samples. The Atlantic Margin Site 605 material contains *n*-alkanes from continental higher plant waxes in addition to the bacterial biomarkers. Polycyclic aromatic hydrocarbons derived from abietic acid are present in the DSDP samples but not in the Stevns Klint rocks, evidently as a result of better preservation of organic matter in the marine locations, which have not been subjected to subaerial weathering. Other aromatic hydrocarbons present in the DSDP samples, including components of the phenanthrene and the pyrene series, may have originated from either combustion or from erosion of old continental deposits. A predominance of alkyl substitution in these aromatic series suggests that land-derived aromatic hydrocarbons are abundant in the sediments of the Site 605 section, consistent with the erosional origin (van Hinte *et al.*, 1987).

As noted by Wolbach *et al.* (1985), sooty graphitic carbon is a common component of the clay layer present at the K/T boundary. They postulate that the soot is evidence of widespread forest fires, which could contribute to the global extinctions at the K/T boundary by blocking sunlight and hindering photosynthesis. Organic geochemical identifications of pyrolytically formed polycyclic aromatic hydrocarbons (PAHs) provide further evidence of this "wildfire hypothesis". Venkatesan and Dahl (1989) report the existence of high proportions of non-alkylated PAHs in the boundary clays at the K/T sites at Gubbio (Italy), Stevns Klint, and Woodside Creek (New Zealand). The combined presence of these pyrosynthetic compounds and of soot at these locations support the possibility that massive forest fires contributed to the K/T boundary biotic perturbations.

Analysis of the amino acid compositions of rocks from the K/T boundary at Stevns Klint has revealed that non-protein compounds are rare in most sediments occur near the boundary. Zhao and Bada (1989) report that α-aminoisobutyric acid and racemic isovaline are present in uppermost Maastrichtian and lowermost Danian carbonate rocks, although not in the 10–15 cm thick boundary clay which has organic carbon concentrations of up to 2.3% in its black marly layer (Schmitz *et al.*, 1988; Schmitz, 1988). They conclude that the most likely origin of these non-protein amino acids is from an extraterrestrial source, possibly carbonaceous chondrites. If these amino acids actually record a bolide impact, then they have been leached completely out of the clay layer to nearby strata by migration of ground water. As noted by Cronin (1989), similar amino acid studies need to be conducted at other sites and in sediments distant from the K/T boundary to test the significance of these interesting findings.

CONTRIBUTIONS FROM THIS STUDY

We have collected samples of Maastrichtian and Danian rocks from seven locations around the world. Many of the samples are low in organic carbon; others have been small subsamples of material collected for non-geochemical studies and consequently not frozen during storage. These two factors have imposed constraints on our survey and on the analyses we could perform. Nonetheless, the results of our study provide new information about the character of organic matter derived from organisms living around the time of the K/T biotic perturbation.

Sampled locations

DSDP Site 577, Shatsky Rise. Deep Sea Drilling Project site 577 is located in 2700 m of water on the Shatsky Rise in the northwest Pacific Ocean. Our samples came from Hole 577, which was hydraulically piston cored and yielded a K/T boundary within a white calcareous nannofossil ooze sequence (Wright *et al.*, 1985). The boundary was identified from nannoplankton stratigraphy (Monechi *et al.*, 1985), and a iridium anomaly was found in Hole 577B (Michel *et al.*, 1985) at a stratigraphic level equivalent to the nannoplankton boundary in Hole 577. Samples were frozen upon collection.

DSDP Site 605, New Jersey Continental rise. Deep Sea Drilling Project Site 605 is located in 2200 m of water on the margin of North America offshore of southern New Jersey. Hole 605 was rotary drilled, penetrating a series of ocean margin deposits. The early Paleocene sediments immediately above the K/T boundary contain a large fraction of terrigenous silt, possibly as a result of lowered sealevel (van Hinte *et al.*, 1987). Our samples were collected specifically for organic geochemical study. They remained frozen until analysis.

ODP Site 761, Wombat Plateau. The Wombat Plateau is located in the Indian Ocean off the northwest coast of Australia. Ocean Drilling Program Site 761 is in 2168 m of water, and the interval containing the K/T boundary was cored using rotary drilling. The K/T boundary appears to be free of hiatuses and comprises a pelagic carbonate sequence. Samples were obtained specifically for organic geochemical study. They were freeze-dried aboard ship, where their carbonate carbon and organic carbon contents were measured using standard shipboard procedures (Emeis and Kvenvolden, 1986).

El Kef, Tunisia. This location has an expanded and nearly complete boundary record, as summarized by Keller (1988a, b; Keller and Lindinger, 1989). The paleoenvironment was on the southern Tethyan upper slope to outer shelf, resulting in virtually no interruption in sedimentation at the K/T boundary. We obtained a large number of small subsamples collected from outcrop as part of a micropaleontological study. These samples had been stored dry at room temperature for several years before they were made available to our study.

Negev Desert, Israel. This location has a sequence similar to the well-known Gubbio sequence in Italy. Its paleoenvironment was a shallow carbonate platform or shelf on the southern margin of the Tethyan Sea. A hiatus in sedimentation exists between the late Maastrichtian and the early Danian. Numerous sites have been sampled; the ones at Ein Mor and Hor HaHar have been described by Margaritz *et al.* (1985) and Margaritz (1989), who present microfossil, isotope, and paleomagnetic data for this sequence. Our samples come from two outcrop locations, one very near the Egyptian/Israeli border in the Sinai and the other at Ein Mor. Both are not far from Hor HaHar. The samples were collected in 1988 and were kept frozen until analysis began.

Stevns Klint, Denmark. The K/T boundary clays at Stevns Klint were deposited in a coastal marine environment in which the water depth was less than 100 m (Schmitz *et al.*, 1988). Our samples from this section are subsamples of unfrozen material collected from outcrop for micropaleontological study.

Brazos River, Texas. Jiang and Gartner (1986) describe the Brazos River section. It consists of an apparently continuous nannofossil record from the late Maastrichtian to the early Paleocene. This may be the most complete K/T section known. Our samples were collected from outcrop in 1989 and remained frozen until analysis. They include the postulated "tsunami layer" made up of coarse shelly sediment (Bourgeois *et al.*, 1988).

Analysis

Sample preparation. Samples were freeze-dried and coarsely ground in preparation for subsequent analyses. Inorganic carbon concentrations were measured by the carbonate bomb procedure (Müller and Gastner, 1971; Dunn, 1980) or with a Coulometrics Carbonate Carbon Analyzer (cf. Emeis and Kvenvolden, 1986). Analyses of pure calcium carbonate standards and of subsamples of the Brazos samples showed the two procedures to give equivalent results. The carbon concentrations were converted to calcium carbonate concentrations assuming the inorganic carbon was present as calcite. Organic carbon concentrations were determined by measuring the carbon remaining after the carbonate bomb determinations with a Coulometrics Total Carbon Analyzer or by using a Rock-Eval TOC module. Standards having a range of organic carbon contents were used to intercalibrate these procedures.

Rock-Eval pyrolysis. Rock-Eval analyses were done with a Delsi Rock-Eval II instrument equipped with a TOC module. Bulk samples were ground to a fine powder to facilitate uniform pyrolysis of their organic contents. Hydrogen and oxygen indices were calculated from the measured parameters (S_2, S_3, and TOC).

Carbon isotope analysis. Ratios of the stable isotopes of carbon were determined from measurements made with a VG Micromass 602 mass spectrometer. Organic carbon isotopic ratios were obtained from the carbonate-free residues of the carbonate bomb analyses; carbonate carbon isotopic values came from bulk samples. The data have been standardized to NBS standards and corrected for ${}_{17}O$, and they are presented relative to the PDB standard.

Biomarker extraction and analysis. Extractable biomarkers were isolated from smaller freeze-dried samples with dichloromethane using sonication and by Soxhlet apparatus for larger samples. Extracts were separated into subfractions (aliphatic hydrocarbons, aromatic hydrocarbons, alkanoic acids, alkanols and sterols, long-chain ketones) by silica gel column chromatography. The biomarker subfractions were analyzed by capillary gas chromatography using capillary columns (25 m × 25 micron). After initial scanning by gas chromatography, the biomarker subfractions were analyzed by capillary gas chromatography–mass spectrometry using a Finnigan quadrupole GC–MS.

Results and discussion

None of the samples we surveyed from either above or below the K/T boundary was rich in organic carbon, although carbonate carbon contents were quite variable (Table 1). The low concentrations of organic carbon could be caused by poor preservation of organic matter, or they could indicate low production of organic matter by marine and continental plants. The combination of Rock-Eval data (Fig. 1) and paleoenvironmental information (Keller, 1988a, b; Keller and Lindinger, 1989) for the El Kef samples suggests the organic matter at this site is oxidized Type II marine material. An attempt to perform Rock-Eval analyses on the extremely organic-carbon-lean Negev Desert samples was only partially successful because the carbonate matrix of the rocks contributed pyrolytic CO_2 (e.g. Katz, 1983), yet the results similarly indicate that this organic matter is heavily oxidized marine matter. Preservation of organic matter evidently was not good at either of these two shallow water locations.

Table 1. Organic carbon and calcium carbonate concentrations of K/T boundary samples in this survey. Ages of samples are shown as Maastrichtian (M) or Danian (D)

Location and sample	$\%C_{org}$	$\%CaCO_3$
DSDP Site 577, Shatsky Rise		
577-12-1, 21–21 cm (D)	ND	83
577-12-5, 72–74 cm (D)	ND	91
577-12-5, 100–102 cm (D)	ND	92
577-12-5, 111–113 cm (D)	ND	94
577-12-5, 120–122 cm (D)	ND	88
577-12-5, 132–134/147–149 cm (M)	ND	91
DSDP Site 605, New Jersey margin		
605-66-1, 20–23 cm (D)	0.19	13
605-66-1, 33–36 cm (D)	0.21	13
605-66-1, 87–90 cm (M)	0.34	28
605-66-1, 132–137 cm (M)	0.11	54
ODP Site 761, Wombat Plateau		
761C-3R-1, 14–16 cm (D)	0.02	68
761C-3R-1, 105–107 cm (D)	0.01	66
761C-3R-2, 10–12 cm (D)	0.01	67
761C-3R-3, 55–57 cm (D)	0.01	68
761C-3R-3, 85–87 cm (M)	0.15	88
761C-3R-3, 126–128 cm (M)	0.01	89
761C-3R-4, 126–128 cm (M)	0.02	91
761C-3R-5, 69–71 cm (M)	0.03	91
El Kef, Tunisia		
AFN 590 (D)	0.32	43
AFN 585 (D)	0.95	22
AFN 560 (D)	0.30	12
AFN 550 (D)	0.27	8
AFN 548 (D)	0.29	6
AFN 545 (D)	0.30	4
AFN 543 (D)	0.41	2
AFN 541 (D)	0.50	6
AFN 540D (M)	0.31	45
AFN 540L (M)	0.23	41
AFN 537 (M)	0.25	38
AFN 534 (M)	0.23	43
AFN 531 (M)	0.33	39
AFN 528 (M)	0.39	34
Negev Desert, Israel		
EM202 (D)	0.03	33
SS34.5 (D)	0.04	83
SS25 (D)	0.02	59
SS19 (D)	0.01	52
SS15 (D)	0.09	36
SS-1 (M)	0.02	73
SS-2 (M)	0.01	73
SS-3 (M)	0.02	77
SS-5 (M)	0.04	84
Brazos River, Texas		
BR6 (D)	0.67	10
BR5 (D)	0.91	7
BR4 (M)	0.47	75
BR3 (M)	0.11	13
BR2 (M)	0.83	12
BR1 (M)	0.85	12

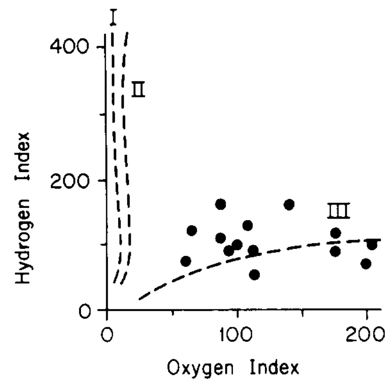

Fig. 1. Results of Rock-Eval analysis of samples from below and above the K/T boundary at El Kef, Tunisia.

Organic carbon isotopic ratios from DSDP Site 577 sediments from above and below the K/T boundary are compared to those of carbonate carbon in Fig. 2. The organic carbon isotope values are variable and do not follow the shift to lighter values across the boundary shown by the carbonate carbon isotopes. A possible explanation for the difference between the isotope ratios of organic and inorganic carbon is that the changes in planktonic species distribution at the time of the K/T boundary (cf. Wright *et al.*, 1985)

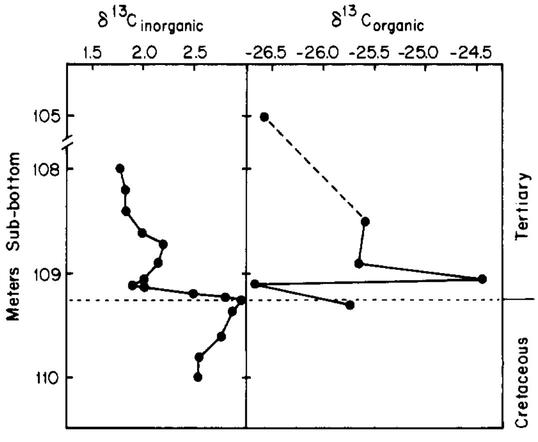

Fig. 2. Comparison of inorganic and organic carbon $\delta^{13}C$ values of sediments from DSDP Site 577 on the Shatsky Rise, North Pacific. Inorganic carbon data are from Zachos *et al.* (1985).

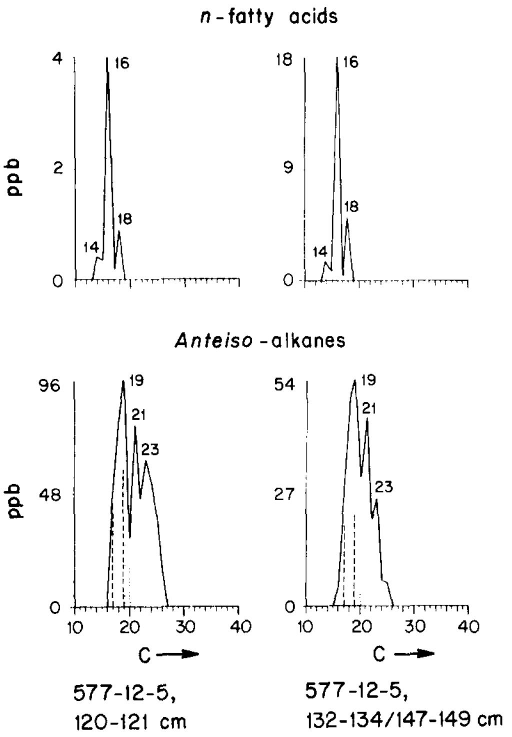

Fig. 3. Comparison of extractable *n*-alkanoic acid and alkane distributions in Danian (left) and Maastrichtian (right) sediments from DSDP Site 577 on the Shatsky Rise, North Pacific. In the alkane distributions, solid lines connect the *anteiso*-alkanes, dashed lines represent the concentrations of the C_{17} and C_{19} *iso*-alkanes, and dotted lines show the concentrations of pristane (C_{19}) and phytane (C_{20}). Data are from Simoneit and Beller (1985).

caused the isotopic ratios of organic matter at this site to deviate from the carbonate pattern. It is also possible that postdepositional reworking of organic matter by microbes has modified its molecular composition and thereby altered its isotopic content (cf. Benner *et al.*, (1988), although Jasper and Gagosian (1989) have shown that diagenesis appears not to change the $\delta^{13}C$ values of organic matter in marine sediments.

Examination of the molecular composition of extractable geolipids indicates that microbial reprocessing of organic matter has been extensive. The *n*-alkanoic acid distributions in Site 577 sediments are composed of the C_{14}, C_{16}, and C_{18} components ubiquitous to biota and lack any of the long-chain components diagnostic of continental plant waxes (Fig. 3). The extractable hydrocarbon distributions in Fig. 3 are dominated by *anteiso*-alkanes, with minor contributions of other branched alkanes. No *n*-alkanes were found in the extracts of these samples. These distributions of alkanoic acids and alkanes most likely arise from extensive microbial reworking of originally deposited organic matter. Algal and land-plant biomarker compounds have been replaced by microbial biomarkers. These hydrocarbons, in particular, are typical of bacteria, and their dominance indicates that the organic matter in these Site 577 sediments has been drastically altered by microbial reworking.

Extracts from Stevns Klint similarly contain *n*-alkanoic acid distributions indicative of bacterial origin (Fig. 4). In these distributions, the presence of dehydroabietic acid indicates that land-plants contributed lipid material to the organic matter originally deposited at this ocean margin location (cf. Simoneit, 1986). The absence of the long-chain acids typical of land-plant waxes suggests microbial alteration of the original mixture of sedimented organic matter. In addition, no unsaturated acids were found at this site, which is further evidence of postdepositional alteration of organic matter.

The admixture of organic matter from land-plants with marine material is evident in the *n*–alkane distributions in the Site 605 sediments from the New Jersey continental margin. Although dominated by algal hydrocarbons, the distributions contain significant amounts of the C_{27}, C_{29}, and C_{31} *n*-alkanes which are characteristic of the waxes of land-plants (Fig. 5). These amounts are greater in the Maastrichtian samples than in the Danian samples. Pristane/phytane ratios are greater than one in the Maastrichtian distributions, but less than one in the extracts from younger samples. The larger proportion of phytane in the Tertiary sediments may indicate greater activity by methanogenic bacteria

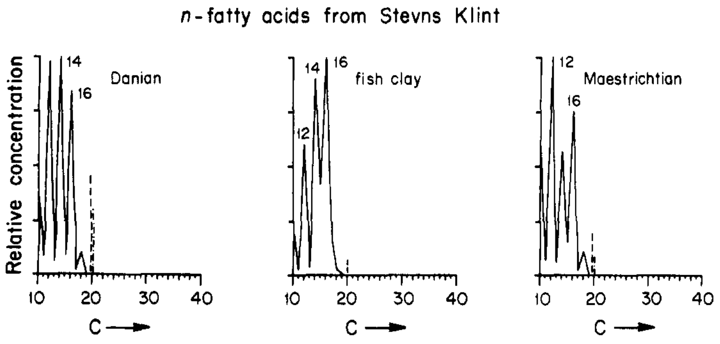

Fig. 4. Distributions of extractable *n*-alkanoic acids from sediment rocks from Stevns Klint, Denmark. Dashed lines indicate Dehydroabietic acid; dot–dashed lines are unidentified isoprenoid acids. Data are from Simoneit and Beller (1987).

(Risatti *et al.*, 1984) and possibly less reprocessing of the sedimented organic matter than in the Cretaceous sediments. Coarser sediment sizes at this site suggest that sealevel was lower in the early Tertiary than in the Maastrichtian (van Hinte *et al.*, 1987), and possibly the oxygen minimum zone intercepted the seabottom during the time that these Danian sediments were deposited. In sediments from El Kef, Tunisia, Keller (1988a) reports that epibenthic foraminiferal assemblages became dominated by species tolerant of low-oxygen conditions in the Danian. This change in composition of benthic fauna implies that an oxygen minimum zone impinged on the seabottom at this Tethyan site. A similar situation may have existed globally. If so, then the larger proportion of long-chain *n*-alkanes in the Cretaceous Site 605 sediments might arise from preferential loss of short-chain components during more vigorous microbial reworking under the more oxygenated conditions prevailing in the late Maastrichtian.

Evidence of microbial contributions to the extractable geolipids is strong in the Site 605 samples. Triterpenoids are predominantly of the 17β(H), 21β(H)hopane series (Fig. 6), which is derived mainly from bacteria (Ourisson *et al.*, 1979; Rohmer *et al.*, 1980). The presence of minor amounts of 17α(H), 21β(H)-hopanes in which the C_{22} S/R ratio ranges from 0.2 to 0.8 and of C_{29} and C_{31} triterpenes attests to the thermal immaturity of these samples. The relatively simple triterpenoid distribution in the Cretaceous sample closest to the K/T boundary may reflect a decrease in floral diversity and an enhancement of bacterial dominance in the sediments deposited at this time.

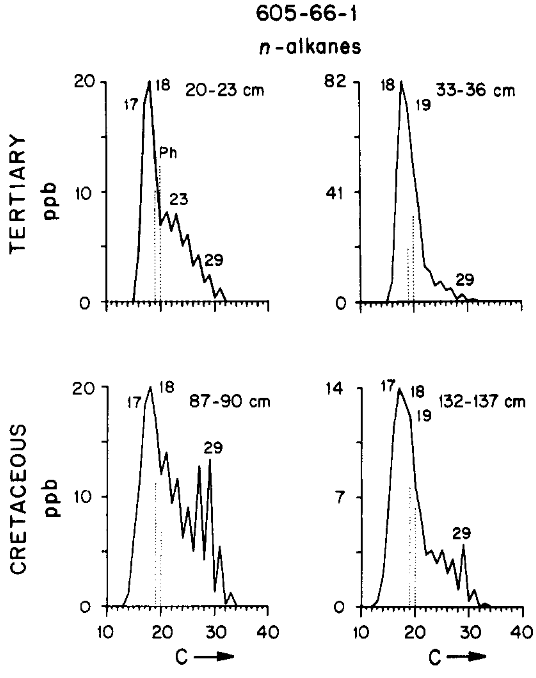

Fig. 5. Distributions of *n*-alkanes extracted from sediments from DSDP Site 605 on the New Jersey continental margin. Pristane and phytane are indicated by the dotted line at the C_{19} and C_{20} positions, respectively. Data are from Simoneit and Beller (1987).

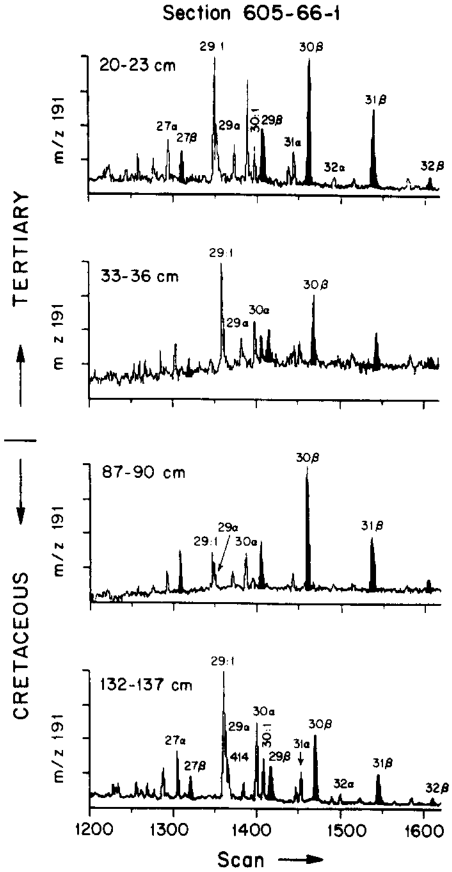

Fig. 6. Mass fragmentograms for extractable triterpenoids from sediments from DSDP Site 605 on the New Jersey continental margin. Data are from Simoneit and Beller (1987).

PALEOENVIRONMENTAL SIGNIFICANCES

Paleoproductivity

Although none of the samples listed in Table 1 has a high concentration of organic carbon, the sediments from the ocean margin paleolocations at DSDP Site 605, El Kef, and Brazos contain more organic matter than do the locations whose paleoenvironments were separated from continents (Shatsky Rise, Wombat Plateau, Negev). The margin samples contain less carbonate than do the open marine sediments, reflecting continental contributions of clastic sediment components. In the modern ocean, coastal areas commonly have enhanced rates of productivity. The continental runoff probably also included nutrients, which would encourage marine productivity. In addition, land-derived organic matter would further enhance the concentration of organic carbon in the sediments deposited in ocean margin paleoenvironments.

The low concentrations of organic matter we found in samples from the seven locations agree with the inorganic carbon isotopic shift to lighter values which indicates that marine productivity was depressed in both open-ocean and coastal locations during the dearly Danian. Microfossil data generally record major species abundance shifts at the time of the K/T boundary, but they cannot indicate whether or not productivity changes occurred unless mass accumulation rates can be determined. Geochemical isotopic and molecular data suggest productivity was depressed after the K/T boundary.

Preservation of organic matter

The general dominance of microbial biomarkers in extracts of K/T boundary sediments indicates that organic matter was poorly preserved and was mostly remineralized by benthic microbes. Little difference in the extent of remineralization is indicated in sediments deposited before or after the boundary in open marine settings. Sediments from ocean margin paleoenvironments have higher concentrations of organic carbon than do those from open ocean locations, and these sediments may contain a significant proportion of detrital terrigenous material, which would resist microbial degradation. Biomarker distributions indicate that organic matter is less microbially reworked in Danian than in Maastrichtian sediments deposited on ocean margins. Impingement of an oxygen minimum layer on the seabed during a time of lowered sealevel may have diminished bacterial activity during this time.

Concentrations of organic carbon of 2% are reported in the boundary clay in the K/T section at Stevns Klint (Schmitz *et al.*, 1988) and of 5% at El Kef (Keller and Lindinger, 1989). In both of these sections, concentrations of organic carbon in the clay layers are highest close to the boundary and diminish as carbonate concentrations recover into the Danian. The inverse relationship between the concentrations of organic carbon and calcium carbonate suggests that dissolution of carbonates may have contributed to the enhanced organic carbon concentrations. Oxidation of marine organic matter has been implicated in the formation of chalk–marl cycles in Neogene sediments (cf. Diester-Haass *et al.*, 1986). The production of CO_2 from readily oxidized organic matter makes sediment pore waters more corrosive to calcium carbonate and at the same time consumes dissolved oxygen, improving preservation of the remaining organic matter. A similar production of diagenetic CO_2 may have resulted in the elevated concentrations of the surviving organic matter in the boundary clays at these two ocean margin settings. The samples we studied did not include those having high concentrations of organic carbon, and so we cannot verify the probable residual character of the organic matter in these clays. Nonetheless, the general evidence for microbial activity and oxidation of organic matter is consistent with this hypothesis.

Evidence of biotic change in organic contents of sediments

The molecular information retained in sediments from around the K/T boundary has not yet revealed substantial evidence of the changes in marine and continental life which have been preserved in the fossil record. Microbial reworking was erased much of the organic geochemical record. Carbon isotope ratios provide tantalizing indications of changes in biota, but these data are not yet from enough locations to over-rule local effects and the possible effects of diagenetic isotopic shifts. We believe that samples collected specifically for organic geochemical analysis from submarine locations, such as DSDP and ODP sites, are best suited to provide molecular indications of biotic changes. Samples from continental outcrop sites, unless relatively rich in organic matter, are too readily contaminated by percolation of ground water and are too susceptible to subaerial weathering to yield useful organic geochemical information.

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