

STABLE ISOTOPE, TOC AND CaCO₃ RECORD ACROSS THE CRETACEOUS/TERTIARY BOUNDARY AT EL KEF, TUNISIA

G. KELLER¹ and M. LINDINGER²

¹*Department of Geological and Geophysical Sciences, Princeton University, Princeton, NJ 08544 (U.S.A.)*

²*Geological Institute ETH, CH 8092 Zurich, (Switzerland)*

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Abstract

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We report the results of stable oxygen and carbon isotope analysis of carbonate fine fraction and benthic and planktic foraminifers, %CaCO₃ and TOC determinations of sediments across the Cretaceous/Tertiary (K/T) boundary at El Kef, Tunisia. We used grain-size analysis of the fine fraction carbonate to determine possible compositional effects and smear-slide and scanning electron microscope examinations to evaluate possible diagenetic alteration and microfossil preservation. The data suggests the following sequence of events.

Upper Maastrichtian oxygen and carbon isotope signals indicate relatively warm temperatures, a decreasing thermal gradient possibly related to a shallowing sea and relatively high surface water productivity. A sharp cooling appears to begin just below the K/T boundary. The K/T boundary is characterized by a sudden 2‰ negative shift in fine fraction $\delta^{13}\text{C}$, a slight 0.6‰ enrichment in benthic $\delta^{13}\text{C}$ and a reduction of about 40% in CaCO₃ sedimentation. These data imply strongly reduced surface water productivity as also observed in numerous deep-sea sequences worldwide. The lower Danian (planktic foraminiferal Zones P0, P1a) is marked by generally low productivity and unstable environmental conditions as indicated by generally low but fluctuating fine fraction $\delta^{13}\text{C}$ values and low (5–15%) carbonate deposition. At the base of Subzone P1b, %CaCO₃, benthic and fine fraction $\delta^{13}\text{C}$ values increase gradually, and reach near pre-K/T boundary levels in Subzone P1c indicating initial recovery after the K/T boundary event about 300,000–400,000 years after the K/T boundary. The prolonged low productivity episode after the K/T crisis and the pre-K/T boundary cooling associated with a major reduction in planktic foraminiferal diversity are difficult to explain by a single K/T boundary bolide impact.

Introduction

Anomalies in carbon and oxygen isotopic ratios across the Cretaceous/Tertiary (K/T) boundary have been reported from many pelagic sequences with relatively condensed sedimentation records which may contain short hiatuses or periods of non-deposition (Perch-Nielsen et al., 1982; Shackleton et al., 1984; Oberhänsli et al., 1984, 1985; Oberhänsli, 1985; Zachos and Arthur, 1986; Mount et al.,

1986; D'Hondt and Lindinger, in prep.). As a result, the reported data are often difficult to interpret and correlate (Perch-Nielsen et al., 1982; Zachos and Arthur, 1986). In contrast, shallow-marine sections have received little attention although they have been shown to be more complete stratigraphically with higher rates of sedimentation (Perch-Nielsen et al., 1982; Jones et al., 1987; Keller, 1988a). The main reason for this lack of attention is probably the increased potential for diagenetic

alteration in shallow-marine sequences and hence the difficulties in interpreting the geochemical signatures. Despite these problems, shallow-marine sections warrant closer examination in order to show an extended and stratigraphically more complete K/T boundary record and to compare and contrast major paleoceanographic changes in the pelagic realm with those in shallow-marine environments. We report here the results of a geochemical investigation of a shallow-marine K/T boundary sequence that crops out in the

northwestern part of Tunisia near the town of El Kef.

The K/T boundary section, near El Kef (Fig.1) is considered to have the most complete stratigraphic record known to date with unusually high rates of sedimentation (Salaj, 1979, 1980; Perch-Nielsen, 1979, 1981; Smit, 1982; Keller, 1988, a,b). The K/T boundary clay consists of over 50 cm of black clay (Zone P0a,b) which is unusual compared with a thickness of a few mm to a few cm in deep-sea sections. The succeeding Zone P1a (*Globi-*

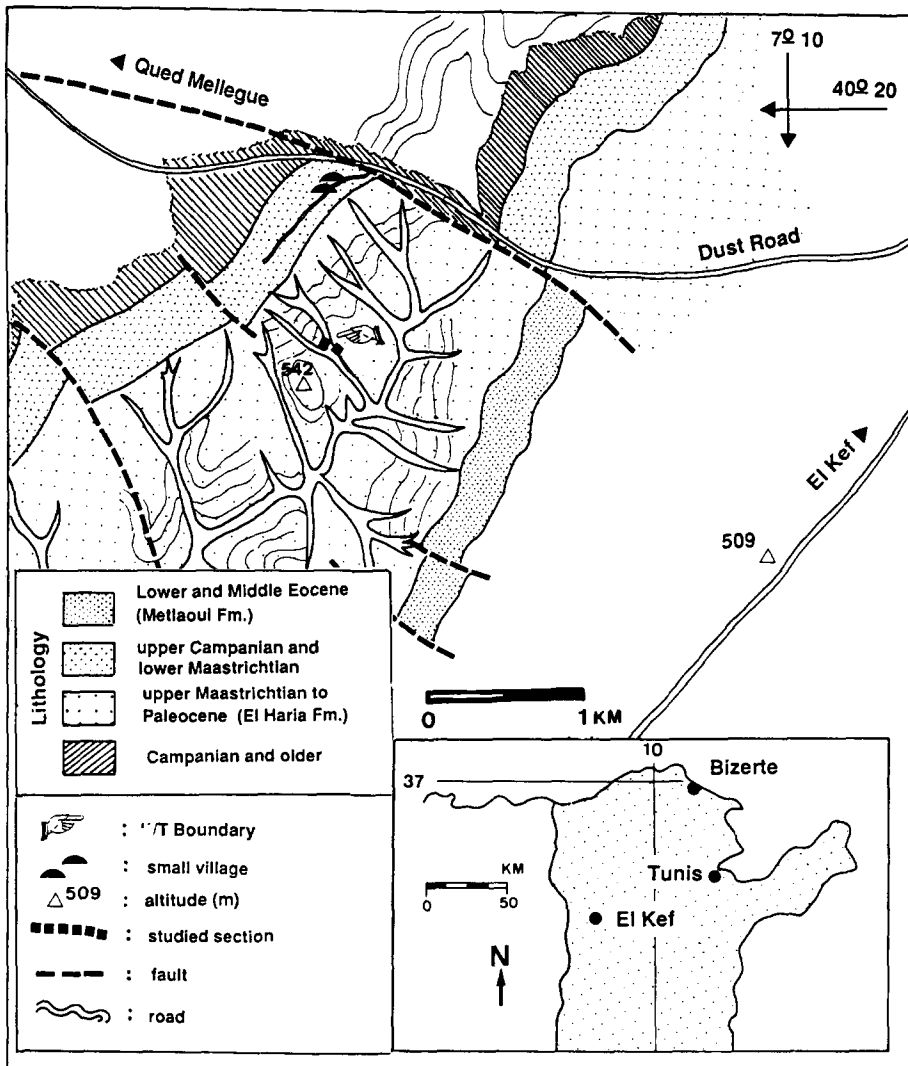


Fig.1. Location map of the El Kef section in northwestern Tunisia, 7 km west of the town of El Kef.

gerina eugubina) is represented by 250 cm of clayey shales and the overlying P1b Zone (*Globigerina taurica*) by 600 cm of increasingly carbonate-rich shale. In contrast, this extended 900 cm Danian record from El Kef is generally represented in deep-sea sections by only a few tens of centimeters (Zachos and Arthur, 1986; D'Hondt and Lindinger, in prep.). Thus, the high sedimentation record at El Kef provides the unique opportunity to study the K/T boundary event from below the boundary through the clayey transition interval to the first recovery of the ecosystem in the earliest Paleocene. This study attempts to elucidate these events based on high resolution stable isotope stratigraphy of monospecific planktic (*Pseudotextularia deformis*) and benthic (*Anomalinoidea acuta*, *Oridorsalis umbonatus* and *Cibicidoides* ssp.) foraminifera and fine fraction (< 25 μm) carbonates. In addition, we have determined the grain size distribution in the fine fraction samples and measured carbonate (CaCO_3) and total organic carbon (TOC) in bulk sediment samples. This study represents the first high resolution geochemical record across an extended K/T boundary section.

Sediment deposition at El Kef during K/T boundary time occurred in an upper slope to outer shelf environment (Esler, 1968; Peyrouquet et al., 1986; Keller, 1988b). Our data therefore represent conditions of the outer shelf or continental platform of the Tethyan Sea and may not be directly comparable to pelagic or hemipelagic environments.

Materials and methods

Sample collection was sponsored by the Cretaceous/Paleocene working group of the International Committee on Stratigraphy. Additional sample collection and field investigations were subsequently made by the authors. All sample numbers used in this report represent original designations given by the Cretaceous/Paleocene working group collecting team. The section was sampled at 20 cm intervals below the K/T boundary and continuous sampling at 5 cm for the first 1.60 m above

the boundary, then at 20 cm intervals between 1.60 and 3.00 m, and at 50 cm intervals between 3 and 10 m above the boundary. A total of 74 samples were analyzed for this study.

For percent CaCO_3 analysis bulk sediment samples were powdered, dried and measured with a Coulometric 5030 Carbonate-Carbon-Apparatus. Total organic carbon (TOC) was determined with a CNS analyzer. The precision (based on double measurements) is $\pm 0.35\%$ for CaCO_3 . Data are provided in Table I.

Stable isotope analyses were based on the benthic foraminifera *Anomalinoidea acuta* (size fraction 150–250 μm) and fine fraction (< 25 μm) sediment, consisting primarily of calcareous nannoplankton carbonate and juvenile planktic foraminifera. For the Latest Maastrichtian the planktic species *Pseudotextularia deformis* (size fraction > 250 μm) and the benthic foraminifer *Oridorsalis umbonatus* (size fraction 150–250 μm) were also measured. Unfortunately, no Paleocene planktic foraminifera could be measured because of their low abundance and extremely small size.

For fine fraction stable isotopic analysis bulk sediment samples were dried, weighed, disaggregated with 10% H_2O_2 and wet sieved through a 25 μm screen. The fraction < 25 μm was then thoroughly washed with deionized water through 0.45 μm filters in a vacuum apparatus and dried at 50°C. Before isotopic processing both foraminiferal and fine fraction samples were cleaned ultrasonically, crushed and afterwards heated in a vacuum at 400°C for 30 min. The carbon dioxide was released by reaction with 100% orthophosphoric acid at 25°C and 50°C. The isotopic composition of the gas was measured with a Mass-Spectrometer Micromass 903 at ETH-Zurich. The isotopic ratios are reported in the δ -notation as per mil deviation from the PDB standard. Data are provided in Table II.

For the grain size analysis a representative split of the < 25 μm sediment fine fraction was diluted in deionized water that had been passed through a < 2 μm filter. The solution was shortly treated ultrasonically (5 s.) and afterwards measured with a HIAC Particle-Size

TABLE I

El Kef section, Tunisia: CaCO₃ and TOC data from Upper Maastrichtian to Danian sediments.

| Sample no. | Distance (cm) | CaCO ₃ (%) | TOC (%) | Sample no. | Distance (cm) | CaCO ₃ (%) | TOC (%) |
|------------|---------------|-----------------------|---------|------------|---------------|-----------------------|---------|
| 528 | -450 | 32.44 | 0.31 | 564 | +117 | 07.02 | 0.35 |
| 529 | -400 | 28.42 | 0.73* | 565 | +122 | 09.23 | 0.71 |
| 530 | -350 | 40.42 | 0.76* | 566 | +127 | 07.65 | 0.61 |
| 531 | -300 | 38.38 | 0.30 | 567 | +132 | 07.95 | 0.21 |
| 532 | -250 | 41.75 | 0.29 | 568 | +137 | 07.42 | 0.51 |
| 533 | -200 | 42.70 | 0.52* | 569 | +142 | 07.69 | 0.41 |
| 534 | -150 | 41.77 | 0.95 | 570 | +147 | 07.47 | 0.83 |
| 535 | -100 | 42.52 | 0.23 | 571 | +152 | 07.62 | 0.87 |
| 536 | -090 | 36.12 | 0.29 | 572 | +157 | 09.87 | 0.41 |
| 537 | -065 | 37.02 | 0.31 | 573 | +162 | 16.20 | - |
| 538 | -045 | 36.24 | 0.35 | 574 | +167 | 13.95 | 0.14 |
| 539 | -025 | 41.49 | 0.56 | 575 | +172 | 16.02 | - |
| 540 | -005 | 48.82 | 0.43 | 576 | +177 | 11.00 | - |
| 541 | -002 | 06.04 | 2.80 | 577 | +182 | 13.77 | - |
| FL | 0 | 00.89 | 4.87 | 578 | +187 | 12.84 | 0.57 |
| 542 | +007 | 04.47 | 1.06 | 579 | +192 | 12.96 | - |
| 543 | +012 | 02.55 | 0.70 | 580 | +197 | 07.21 | 0.94* |
| 544 | +017 | 02.10 | 0.56 | 581 | +202 | 13.50 | 0.41 |
| 545 | +022 | 03.30 | 0.52 | 582 | +222 | 11.20 | - |
| 546 | +027 | 05.07 | 0.51 | 584 | +262 | 22.53 | - |
| 547 | +032 | 05.62 | 0.54* | 585 | +282 | 23.68 | 0.84 |
| 548 | +037 | 05.76 | 0.47 | 586 | +302 | 39.17 | 0.64 |
| 549 | +042 | 05.61 | 0.52 | 587 | +350 | 37.41 | 0.80 |
| 550 | +047 | 08.58 | 0.57 | 588 | +400 | 35.36 | 0.69 |
| 551 | +052 | 07.18 | 0.42 | 589 | +450 | 55.98 | 0.40 |
| 552 | +057 | 07.67 | 0.44 | 590 | +500 | 41.35 | 0.72 |
| 553 | +062 | 10.50 | 0.54 | 591 | +550 | 42.15 | 0.52 |
| 554 | +067 | 04.80 | 0.55* | 592 | +600 | - | - |
| 555 | +072 | 06.67 | 0.38 | 593 | +650 | - | - |
| 556 | +077 | 07.36 | 0.58* | 594 | +700 | - | - |
| 557 | +082 | 08.70 | 0.44 | 595 | +750 | - | - |
| 558 | +087 | 08.03 | 0.48 | 596 | +800 | 41.23 | 0.69 |
| 559 | +092 | 09.75 | 0.38 | 597 | +850 | - | - |
| 560 | +097 | 09.75 | 0.67* | 598 | +900 | - | - |
| 561 | +102 | 08.74 | 0.71 | 599 | +950 | 53.76 | 0.49 |
| 562 | +107 | 07.60 | 0.60 | 600 | +10m | - | - |
| 563 | +112 | 09.92 | 0.57 | | | | |

*indicates average of two samples.

Analyzer PA 520 at ETH-Zurich. All samples were measured against deionized water (<2 µm) as standard. Each measurement is based on 100,000 particle counts. Samples 535 and 540 were prepared twice and measured independently several times to estimate the analytical precision of the method. Additionally, we have used as a standard sample from DSDP 502B, core 1 section 1 at 62–64 cm which contains more than 70% Thoracosphaerids. The grain-

size distribution of this sample has been determined with a Coulter-Counter and is published in Paull and Thierstein (1987). Measurements are provided in Table III. To test for diagenetic alteration of calcareous nannoplankton and foraminiferal tests, fine fraction samples and specimens of foraminifera (not treated ultrasonically) were examined with a JEOL SM 840 and the fine fraction (<25 µm) sediments with a Hitachi S-2300

TABLE II

Grain-size analysis of fine fraction (<25 µm) sediment used for carbon and oxygen isotope analysis.

| Sample | Fraction in µm | | | | | |
|---------|----------------|------|------|-------|-------|-------|
| | <2 | 2-5 | 5-10 | 10-15 | 15-20 | 20-25 |
| 531 | 3.0 | 15.0 | 45.0 | 30.0 | 5.5 | 1.5 |
| 533 | 14.0 | 58.0 | 21.0 | 5.0 | 1.0 | 1.0 |
| 535 | 10.5 | 55.5 | 29.0 | 3.0 | 1.0 | 1.0 |
| 535 | 12.0 | 54.5 | 29.5 | 2.5 | 1.0 | 1.0 |
| 537 | 10.5 | 34.5 | 43.0 | 10.0 | 2.0 | 0.0 |
| 540 | 18.0 | 62.0 | 14.0 | 3.0 | 2.0 | 1.0 |
| 540 | 15.0 | 58.5 | 14.5 | 6.0 | 4.0 | 2.0 |
| 541 K/T | 34.0 | 60.0 | 4.0 | 1.0 | 0.5 | 0.5 |
| 542 | 23.0 | 37.5 | 15.0 | 12.0 | 8.5 | 4.0 |
| 543 | 23.0 | 45.0 | 16.0 | 11.0 | 4.0 | 1.0 |
| 544 | 28.0 | 37.5 | 18.0 | 10.5 | 4.5 | 1.0 |
| 545 | 22.0 | 50.0 | 16.5 | 9.0 | 2.5 | 0.0 |
| 545 | 20.0 | 55.5 | 7.5 | 12 | 4.0 | 1.0 |
| 546 | 22.0 | 45.5 | 17.0 | 11.0 | 4.0 | 1.0 |
| 547 | 21.0 | 40.5 | 15.0 | 12.5 | 8.0 | 3.0 |
| 548 | 22.0 | 46.0 | 17.5 | 10.5 | 3.0 | 1.0 |
| 552 | 26 | 47.0 | 13.0 | 8.0 | 4.5 | 1.5 |
| 562 | 8.0 | 50.0 | 34.5 | 6.5 | 0.5 | 0.5 |
| 570 | 17.0 | 49.5 | 20.0 | 9.5 | 2.5 | 1.0 |
| 581 | 17.5 | 43.5 | 14.5 | 12.0 | 9.0 | 3.5 |
| 591 | 9.5 | 56.5 | 30.0 | 3.0 | 0.5 | 0.5 |
| 599 | 9.0 | 50.0 | 36.0 | 4.0 | 0.5 | 0.5 |
| INMD | 689.0 | 50.0 | 36.0 | 4.0 | 0.5 | 0.5 |

scanning electron microscope (SEM) (Plates I and II).

Lithology and biostratigraphy

The K/T boundary section, located near the town of El Kef in northwestern Tunisia, is contained within the El Haria Formation (Fig.1). This formation spans Maastrichtian to Eocene sediments which are characterized by marly and clayey layers with limestone intercalations (Burollet, 1966). The lithology of the K/T boundary interval is characterized by five units labelled A-E. A white-grey clayey marl (Unit A) with about 40% CaCO₃ and an average of 0.46% TOC marks the upper 4.5 m of the Maastrichtian (Table I). A few burrows up to 3 cm long were observed in this unit. Stratigraphically this unit is assigned to the nannofossil Zone *Micula prinsii* (Perch-Niel-

sen, 1979) and to the planktic foraminiferal Zone *Pseudotextularia deformis* (Keller, 1988a), because it does not contain the index species *Abathomphalus mayaroensis*. Biostratigraphically, the K/T boundary lies between the top of the marl and the overlying 50 cm thick black boundary clay (Unit B).

A 1-3 mm thick rust colored ferruginous layer at the base of the black clay (sample FL, Tables I and III) marks the K/T boundary event. We did not observe any burrows through this layer or in the overlying black clay either in outcrops or thin sections. This thin ferruginous layer contains less than 1% CaCO₃, a maximum in TOC of 4.8% and anomalously high Ir and Os values (Kuslys and Krähenbühl, 1983). The reddish color of this layer originates from an enhanced hematite and goethite content. This layer and the base of the black clay (sample 541) contain many compressed spherules, 300-500 µm in diameter, which consist mainly of hematite with fragments of pyrite. The pyritic component of these spherules may have originated authigenically in an anoxic environment at the sediment/water interface, directly after the K/T catastrophe and later oxydized into hematite (Lindinger and Preisinger, unpublished data). Smit (1982) originally described similar spherules from the K/T boundary of El Kef and Caravaca, Spain as altered microtektites. However, the spherules at Caravaca are also believed to be authigenic in origin (Izett, 1987).

The 50 cm thick black clay layer (Unit B) overlying the thin ferruginous layer has an average of 5% CaCO₃ and 0.55% TOC (Table I). The black clay contains benthic and planktic foraminifera and calcareous nannofossil survivors from the upper Maastrichtian and the evolution of the earliest Tertiary species (Perch-Nielsen et al., 1982; Keller, 1988a). Biostratigraphically this unit belongs to the nannofossil Zone *Biscutum romeinii* (CP1a) and to the planktic foraminiferal Zone P0 which has been subdivided into Subzones P0a and b based on the first appearance of *Globocornusa conusa* (Keller, 1988a). The black clay of this unit was deposited under low oxygen

TABLE III

El Kef section, Tunisia: oxygen and carbon isotope data from benthic and planktic foraminifers and fine fraction sediments (<25 μm) across the K/T boundary expressed as per mil deviation from PDB. Samples are listed as cm below (-) and above (+) the K/T boundary.

| Sample no. | Distance (cm) | <i>A. acuta</i> | | <i>Cibicidoides</i> sp. <i>O. umbonatus</i> * | | <i>P. deformis</i> | | Bulk sed. (< 25 μm) | |
|------------|---------------|-----------------------|-----------------------|--|-----------------------|-----------------------|-----------------------|---------------------------------|-----------------------|
| | | $\delta^{13}\text{C}$ | $\delta^{18}\text{O}$ | $\delta^{13}\text{C}$ | $\delta^{18}\text{O}$ | $\delta^{13}\text{C}$ | $\delta^{18}\text{O}$ | $\delta^{13}\text{C}$ | $\delta^{18}\text{O}$ |
| 528 | -450 | +0.256 | -3.105 | +0.235* | -2.569* | +0.963 | -4.765 | +0.960 | -2.923 |
| 529 | -400 | +0.414 | -2.868 | +0.164* | -2.751* | +1.296* | -4.247* | +1.032* | -2.880* |
| 530 | -350 | +0.640 | -2.528 | +0.432* | -1.701* | +1.426 | -4.315 | +0.979 | -2.662 |
| 531 | -300 | +0.813 | -2.077 | +0.274* | -2.377* | +1.370* | -4.158 | +0.942 | -2.538 |
| 532 | -250 | +0.354 | -2.643 | +0.252* | -2.098* | +1.140* | -4.315* | +0.960 | -2.381 |
| 533 | -200 | +0.468* | -2.541* | +0.229* | -2.130* | +1.103 | -4.779 | +0.787 | -2.811 |
| 534 | -150 | +0.185 | -3.355 | +0.194* | -2.500* | +0.772 | -5.271 | +0.893 | -2.664 |
| 535 | -100 | +0.428 | -2.627 | +0.154* | -2.498* | +1.272 | -4.483 | +0.770 | -2.790 |
| 536 | -090 | +0.357 | -2.922 | - | - | +1.047 | -4.680 | +0.995 | -2.571 |
| 537 | -065 | +0.113 | -3.956 | - | - | +1.169* | -4.436* | +0.974 | -2.673 |
| 538 | -045 | +0.257 | -3.295 | - | - | +1.276 | -4.352 | +0.779 | -3.219 |
| 539 | -025 | +0.300 | -3.259 | - | - | +1.314 | -4.243 | +0.843 | -1.785 |
| 540 | -005 | +0.061 | -3.814 | - | - | +1.063 | -4.545 | +1.112* | -2.829* |
| 541 | -002 | +0.388 | -2.583 | - | - | +0.222 | -4.212 | -1.113 | -2.738 |
| 542 | +007 | +0.783 | -2.477 | - | - | - | - | -0.726* | -3.469* |
| 543 | +012 | - | - | - | - | - | - | -0.502 | -4.073 |
| 544 | +017 | +0.558 | -2.762 | - | - | - | - | -0.705* | -3.139* |
| 545 | +022 | +0.920 | -1.859 | - | - | - | - | -0.955 | -2.156 |
| 546 | +027 | +0.556 | -2.773 | - | - | - | - | -1.250 | -3.540 |
| 547 | +032 | +0.839 | -1.976 | - | - | - | - | -1.696* | -2.931* |
| 548 | +037 | +0.710 | -2.347 | - | - | - | - | -1.219 | -2.789 |
| 549 | +042 | +0.737 | -2.369 | - | - | - | - | -0.319 | -2.318 |
| 550 | +047 | +0.496 | -2.778 | - | - | - | - | -0.504 | -3.105 |
| 551 | +052 | +0.627 | -2.276 | - | - | - | - | -1.878 | -3.792 |
| 552 | +057 | +0.523 | -2.322* | - | - | - | - | -1.838* | -3.199* |
| 553 | +062 | +0.375* | -2.532* | +1.219? | -1.350? | - | - | -1.926 | -3.085 |
| 554 | +067 | +0.637 | -2.891 | - | - | - | - | -1.065* | -3.215* |
| 555 | +072 | +0.423 | -3.156 | - | - | - | - | -0.293 | -2.467 |
| 556 | +077 | +0.523* | -2.841 | - | - | - | - | -0.836 | -2.831 |
| 557 | +082 | +0.281 | -2.961 | - | - | - | - | -0.801 | -2.813 |
| 558 | +087 | +0.438 | -2.746 | +0.636 | -2.810 | - | - | -0.921 | -0.388 |
| 559 | +092 | +0.290 | -2.945 | +1.950? | -2.631 | - | - | -1.118 | -2.510 |
| 560 | +097 | +0.045 | -3.452 | - | - | - | - | -1.347* | -2.089* |
| 561 | +102 | +0.328* | -2.781* | - | - | - | - | -1.459 | -3.046 |
| 562 | +107 | - | - | - | - | - | - | -1.400 | -3.640 |
| 563 | +112 | +0.433 | -2.541 | - | - | - | - | -1.517 | -3.010 |
| 564 | +117 | +0.400 | -2.528 | - | - | - | - | -1.219 | -3.075 |
| 565 | +122 | +0.034 | -3.354 | - | - | - | - | -1.068 | -2.603 |
| 566 | +127 | +0.423 | -2.706 | - | - | - | - | -1.250 | -3.800 |
| 567 | +132 | -0.090 | -3.156 | +0.371 | -3.219 | - | - | -1.314 | -3.307 |
| 568 | +137 | +0.231 | -3.178 | - | - | - | - | -1.037 | -3.327 |
| 569 | +142 | +0.623 | -2.157? | - | - | - | - | -1.090 | -2.678 |
| 570 | +147 | +0.182 | -3.178 | +0.389 | -3.042 | - | - | -1.701 | -4.016 |
| 571 | +152 | +0.315 | -3.463 | - | - | - | - | -1.035 | -4.795 |
| 572 | +157 | - | - | - | - | - | - | -1.282 | -2.704 |
| 573 | +162 | - | - | +0.575 | -3.071 | - | - | -1.381 | -2.565 |
| 574 | +167 | +0.327 | -3.115 | - | - | - | - | -1.670 | -3.257 |
| 575 | +172 | +0.301 | -3.472 | - | - | - | - | -1.443 | -3.851 |
| 576 | +177 | +0.121 | -3.565 | - | - | - | - | -1.078 | -3.780 |

TABLE III (continued)

| Sample no. | Distance (cm) | <i>A. acuta</i> | | <i>Cibicidoides</i> sp. <i>O. umbonatus</i> * | | <i>P. deformis</i> | | Bulk sed. (<25 µm) | |
|------------|---------------|-----------------------|-----------------------|--|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | | $\delta^{13}\text{C}$ | $\delta^{18}\text{O}$ | $\delta^{13}\text{C}$ | $\delta^{18}\text{O}$ | $\delta^{13}\text{C}$ | $\delta^{18}\text{O}$ | $\delta^{13}\text{C}$ | $\delta^{18}\text{O}$ |
| 577 | +182 | - | - | - | - | - | - | -0.968 | -3.372 |
| 578 | +187 | +0.236 | -3.159 | - | - | - | - | -1.296 | -2.546 |
| 579 | +192 | +0.138 | -3.384 | - | - | - | - | -1.527 | -2.173 |
| 580 | +197 | +0.241 | -3.081 | +0.464 | -3.217 | - | - | -1.563 | -2.970 |
| 581 | +202 | +0.192 | -4.108 | - | - | - | - | -1.856 | -1.645 |
| 582 | +222 | - | - | - | - | - | - | -1.990 | -1.573 |
| 583 | +242 | +0.315 | -2.548 | - | - | - | - | - | - |
| 584 | +262 | +0.159 | -2.986 | - | - | - | - | -1.250 | -2.187 |
| 585 | +282 | +0.289 | -3.550 | - | - | - | - | -0.711 | -1.925 |
| 586 | +302 | +0.696 | -2.990 | - | - | - | - | -1.061 | -2.321 |
| 587 | +350 | +1.246 | -3.387 | - | - | - | - | +0.413 | -3.123 |
| 588 | +400 | +1.059 | -3.168 | - | - | - | - | +0.350 | -3.056 |
| 589 | +450 | +1.409 | -3.198 | - | - | - | - | +0.072 | -2.869 |
| 590 | +500 | +0.991 | -3.713 | - | - | - | - | -0.285 | -2.479 |
| 591 | +550 | +1.021 | -3.158 | - | - | - | - | +0.357 | -2.130 |
| 592 | +600 | +0.872 | -3.239 | - | - | - | - | +0.554 | -2.367 |
| 593 | +650 | +1.047 | -3.348 | - | - | - | - | +0.843 | -2.103 |
| 594 | +700 | +1.254 | -3.212 | - | - | - | - | -0.315 | -2.924 |
| 595 | +750 | +1.131 | -3.543 | - | - | - | - | -0.064 | -2.687 |
| 596 | +800 | +1.426 | -3.128 | - | - | - | - | - | - |
| 597 | +850 | - | - | - | - | - | - | +0.219* | -2.190* |
| 598 | +900 | - | - | - | - | - | - | -0.293 | -2.265 |
| 599 | +950 | +0.705 | -2.950 | - | - | - | - | - | - |
| 600 | +10m | +1.156 | -2.951 | - | - | - | - | -0.409 | -2.379 |

*Indicates average of two samples; question marks indicate questionable data.

conditions as indicated by benthic foraminifera and ostracods (Peypouquet et al., 1986; Keller, 1988b).

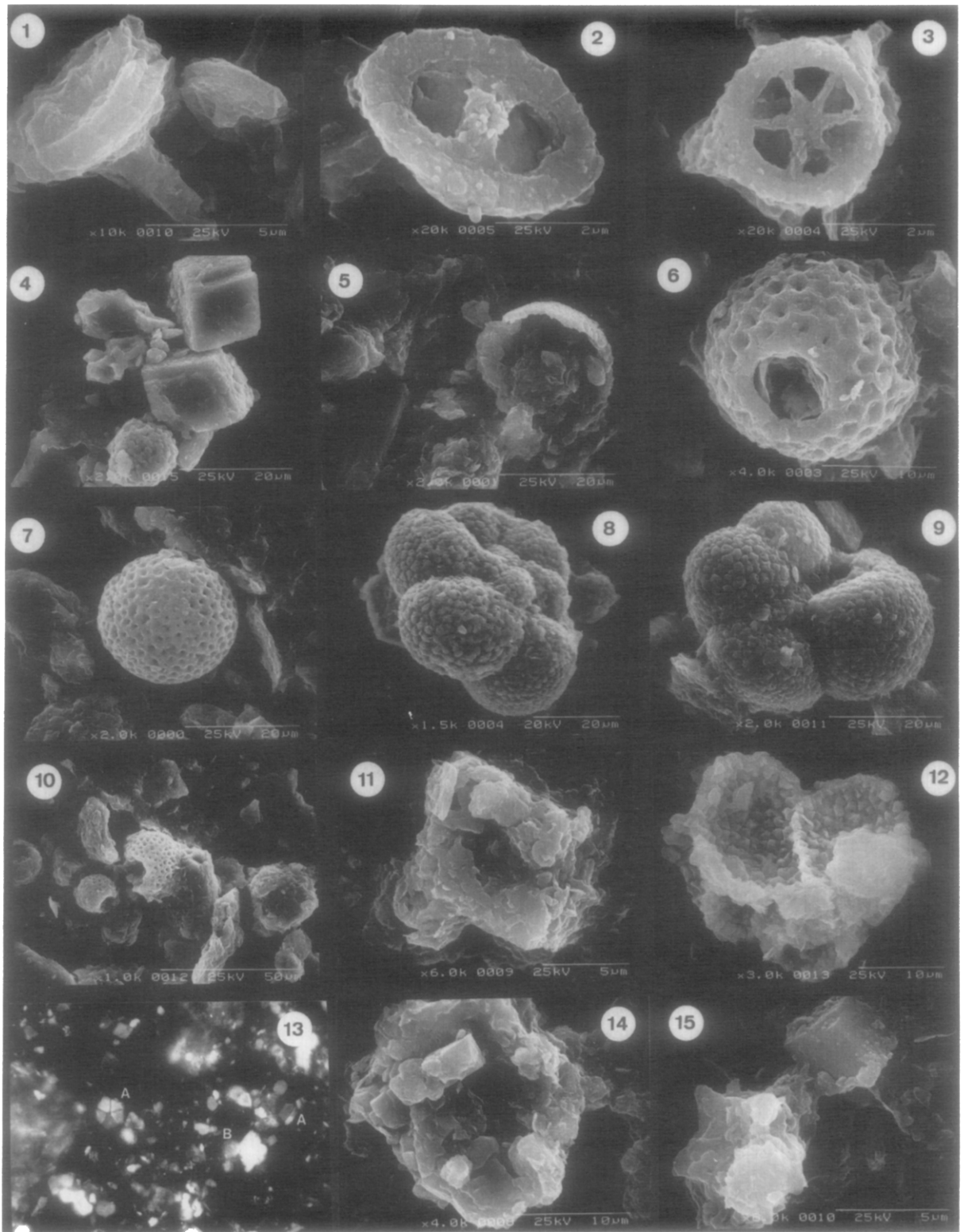
Nearly 50 cm dark grey clays with about 5% CaCO_3 and average TOC values of 0.48% over the black clay layer (Unit C). Deposition of these sediments continued in a low oxygen environment with a low diversity fauna and flora (Perch-Nielsen et al., 1982; Peypouquet et al., 1986; Keller, 1988a,b). The base of this layer is marked by the first appearance of the index species *Globigerina eugubina* which defines the boundary between Zones P0 and P1a. The dark clay of this unit grades upwards into a grey clay-rich shale (Unit D). The first significant post-K/T boundary increase in CaCO_3 (from 6% to 16%) occurs in this shale at 1.6 m above the boundary. Ostracod faunas indicate low but increasingly oxygenated bottom water (Peypouquet et al., 1986). Planktic

foraminifera consist of a relatively stable but low diversity fauna (Keller, 1988a).

The grey clay-rich shales grade upwards into a white-grey clayey marl (Unit E) characterized by a rapid increase in CaCO_3 from 20 to 40% between 2.5 and 3.0 m above the K/T boundary (Table I). At 3 m above the K/T boundary a group of *Eoglobigerina* species appears defining the base of Subzone P1b (*Globigerina taurica*). The first major diversification in planktic foraminiferal faunas after the K/T boundary mass extinction occurs during the rapid rise in carbonate sedimentation (Keller, 1988a). The carbonate increase also corresponds to the nannofossil Zone boundary between *B. romeinii* and *B. parvulum* (Perch-Nielsen, 1979).

The most significant biostratigraphic changes across the K/T boundary at El Kef occur at the base of the boundary clay where much of the

PLATE I



Cretaceous fauna disappears and carbonate drops temporarily to below 1%. Mass mortality of the phytoplankton is expressed by the extinction of 78% of planktic foraminifera over an interval beginning 25 cm below the boundary, but only 26% of the species extinctions directly coincide with the K/T boundary (Keller, 1988a). The second significant biostratigraphic change occurs at the top of Subzone P1a between 2.5 and 3.0 m above the K/T boundary when carbonate deposition increases significantly and planktic foraminifers experience the first major evolutionary diversification followed by faunal stabilization in Subzone P1c.

Preservation and grain-size analysis

Coccolithophores are the dominant component of Quaternary carbonate ooze with foraminiferal juveniles and test fragments a secondary component along with variable amounts of unrecognizable fine carbonate debris. Paull and Thierstein (1987) have shown that because of the polyspecific nature of the carbonate ooze $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ ratios of fine fraction (< 38 μm) deep-sea carbonate particles vary systematically with size over a range of 1.25–4.0‰. In addition to the effects of polyspecific taxa the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope values of fine fraction carbonate of ancient sediments are also influenced by burial-diagenesis and

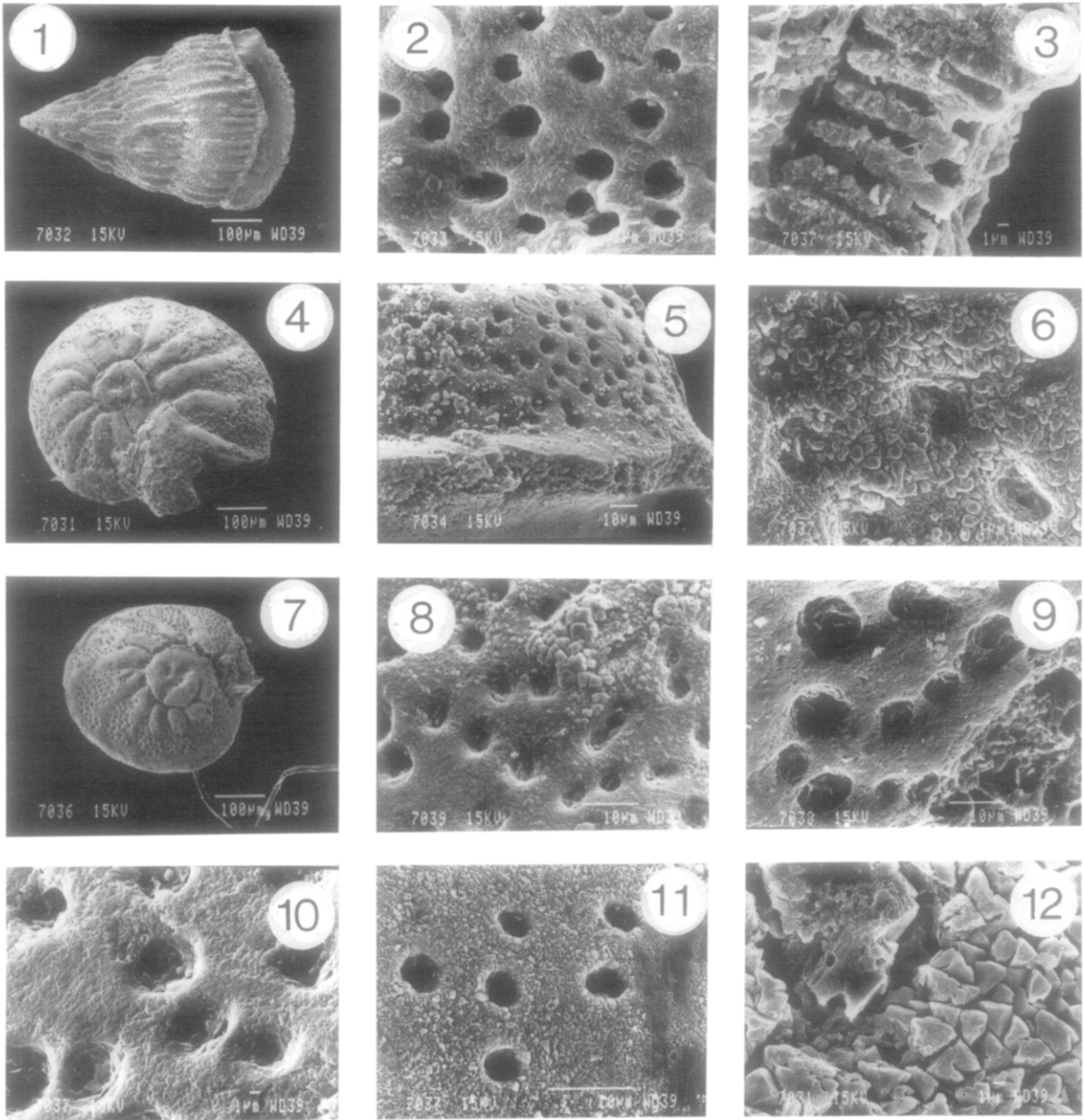
lithification. However, similar isotopic cycles have been observed in both fine fraction carbonate and monospecific foraminifera which suggests that major paleoceanographic trends are preserved (Douglas and Savin, 1971; Scholle and Arthur, 1980; Margolis et al., 1975, 1987). In a recent analysis of bulk sediment isotope measurements of Maastrichtian to lower Tertiary sediments at Zumaya, Spain, Margolis et al. (1987) observed that although the diagenetic overprint resulted in depletion of $\delta^{18}\text{O}$ values by 2‰ or more, $\delta^{13}\text{C}$ values appear less affected by diagenesis. Margolis and co-workers conclude that although burial-diagenesis and lithification has variably affected these rocks, the major isotopic excursions reflect paleoceanographic changes. Similar conclusions were reached by other workers based on bulk or fine fraction carbonate isotope analysis (Hsu et al., 1984; Williams et al., 1985; Zachos and Arthur, 1986). Similarly, in a study of the recrystallization of benthic foraminiferal calcite Barerra and Savin (1986) concluded that recrystallization does not erase the primary paleochemical signals of the water in which the foraminifera lived. Based on these studies diagenesis in organic carbon-poor marine sediments generally does not alter the $\delta^{13}\text{C}$ of the whole rock CaCO_3 ; therefore the measured $\delta^{13}\text{C}$ values should reflect paleoceanographic changes. Oxygen isotope values, however, are more strongly influenced

PLATE I

Fine sediment (< 25 μm) fraction

1. Sample 535 (– 100 cm); *Rhagodiscus splendens*.
- 2,3. Sample 540 (– 5 cm); coccoliths with calcite overgrowth.
4. Sample 541 (K/T boundary); Calcite rhombohedron.
5. Sample 541 (K/T boundary); *Thoracosphaera operculata*, broken and filled with clay minerals.
6. Sample 542 (+ 7 cm); *Thoracosphaera operculata*.
7. Sample 545 (+ 22 cm); *Thoracosphaera operculata*.
- 8,9. Sample 548 (+ 37 cm); juvenile foraminifera.
10. Sample 550 (+ 47 cm); *Thoracosphaera* and clay particles.
11. Sample 550 (+ 47 cm); *Micula prinsii* (?) strongly recrystallized.
12. Sample 589 (+ 450 cm); inner part of chamber of a juvenile foraminifera with calcite encrustations.
13. Sample 591 (+ 500 cm); *Braarudosphaera bigelowii*, enlargement $\times 180$.
14. Sample 599 (+ 950 cm); strongly recrystallized coccoliths.
15. Sample 599 (+ 950 cm); part of *Rhagodiscus splendens*.

PLATE II



by carbonate cementation and recrystallization and may therefore not represent original paleotemperatures.

The clays and marls of the Upper Maastrichtian to lower Tertiary sediments at El Kef are variably affected by burial diagenesis and

lithification. An additional complicating factor is the low CaCO_3 (5–15%) and high clay content in the first 2 m of the Tertiary which may introduce lithologic effects. We have tested for vital effects and diagenetic potential of these sediments by studying the grain size

distribution in the fine fraction carbonate (<25 μm) (Table III) that was used for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope measurements and by smear-slide examination and SEM analysis of the fine fraction and monospecific foraminifera.

Preservation

Preservation of coccoliths and foraminifera was examined in smear-slides of fine fraction carbonate in the range from 25 μm to 1.8 μm and with the scanning electron microscope (SEM). The coccoliths of the Upper Maastrichtian are moderately well preserved and show evidence of dissolution and encrustations of calcite crystals (Plate I). The first meter of Paleocene clay (Units B,C) contain relatively few but well preserved coccoliths with *Thoracosphaera operculata* dominant and few juvenile foraminifera. Over the same interval there is a marked increase in calcite crystals, clay minerals and other unidentified detritus. Plate I shows SEM illustrations of selected components of the fine fraction sediment. The average carbonate content is 5% through this interval. Coccolith and foraminiferal fragments increase upsection. About 2.5 m above the K/T boundary clay-rich shales change into clayey marls (Unit E) with rapidly increasing CaCO_3 content to 45–55%. *Thoracosphaera* spherules are still common at this time and Paleocene coccoliths become increasingly

abundant. Preservation of coccoliths is moderate with evidence of dissolution and calcite encrustation. Our study thus indicates that coccoliths and juvenile foraminifera in the carbonate-poor clays of the lowermost Tertiary are generally better preserved than in the carbonate-rich sediments above and below the boundary clay. Similar observations were made by Thierstein and Okada (1979) and Zachos et al. (1985).

Planktic and benthic foraminifera are generally well preserved at El Kef, Tunisia. The Upper Maastrichtian planktic foraminifera *Pseudotextularia deformis* which was used as surface water isotopic signal carrier is well preserved and shows little evidence of recrystallization or calcite overgrowth (Plate II, 1–3). Benthic foraminiferal isotope measurements are based on the species *Anomalinoides acuta*. Preservation of this species is variable. Generally, Upper Maastrichtian benthic foraminifera show calcite overgrowth (Plate II, 4–6), but specimens from the carbonate-poor lowermost Paleocene (Unit B–D) generally do not (Plate II, 7–11) with the exception of *Cibicidoides* sp. (Plate II, 12). *Anomalinoides acuta* is only moderately well preserved in the carbonate-rich sediments of the Lower Paleocene (Unit E) with calcite overgrowths common. Improved carbonate preservation in low CaCO_3 basal Paleocene sediments was also observed by Zachos et al., (1985) at DSDP Site 577.

PLATE II

Foraminiferal preservation

1. *Pseudotextularia deformis*, sample 539, (–5 cm) \times 180, U. Maastrichtian.
2. *Pseudotextularia deformis*, detail of pores, sample 539, (–5 cm) \times 4000, U. Maastrichtian.
3. *Pseudotextularia deformis*, detail of pore structure, sample 538, (–45 cm) \times 1000, U. Maastrichtian.
4. *Anomalinoides acuta*, sample 530, (–350 cm) \times 180, U. Maastrichtian.
5. *Anomalinoides acuta*, surface pore detail, sample 530 (–350 cm), \times 1000 x, U. Maastrichtian.
6. *Anomalinoides acuta*, pore openings with secondary calcite overgrowths, sample 532 (–250 cm) \times 4000, U. Maastrichtian.
7. *Anomalinoides acuta*, sample 541 \times 180, K/T boundary.
8. *Anomalinoides acuta*, surface pore detail, sample 541 \times 1000, K/T boundary.
9. *Anomalinoides acuta*, pore detail, sample 541 \times 4000, K/T boundary.
10. *Anomalinoides acuta*, pore openings, sample 580 (+197 cm) \times 4000, Lower Paleocene.
11. *Anomalinoides acuta*, pore openings, sample 548 (+37 cm) \times 3000, Lower Paleocene.
12. *Cibicidoides* sp. calcite overgrowth, sample 551 (+52 cm) \times 700, Lower Paleocene.

Grain-size analysis

The grain-size distribution in the fine fraction $< 25 \mu\text{m}$ was determined from sample splits ranging from $1.8 \mu\text{m}$ to $25 \mu\text{m}$ (Table II). As standard for our analysis we have used a glacial split from DSDP Site 502B, a sample which contains more than 70% *Thoracosphaerids* as described by Paull and Thierstein (1987). The results of our grain-size analysis allows a separation of Upper Maastrichtian marls (samples 581, 591, 599) from the clays and shales of the Lowermost Paleocene (Fig. 2). Upper Maastrichtian samples show a trend towards an increase in the grain size abundance maximum from $4 \mu\text{m}$ to $7 \mu\text{m}$ upsection. This trend is reversed in the uppermost Maastrichtian sample 540 (5 cm below K/T boundary) which has an abundance peak at a grain size near $3 \mu\text{m}$. A further decrease in the grain size abundance maximum to below $2 \mu\text{m}$ is found in the lowermost Paleocene due to the dominance of clay particles. A minor secondary peak in the ranges from 13 to $17 \mu\text{m}$ (samples 542–552) may be indicative of the relatively large *Thoracosphaera* spherules in these samples (Plate I). These forms are not present above sample 591 where early Paleocene coccoliths dominate, a fact that is also indicated by the grain size distributions (Fig. 2). Nearly all samples show a peak near $3 \mu\text{m}$ which we believe to represent the detrital component. This would imply that no major changes in the detrital sedimentary input occurred across the K/T boundary except for the boundary sample 541. The major changes associated with the K/T boundary therefore appear to be due to changes in biological productivity primarily of surface-water plankton.

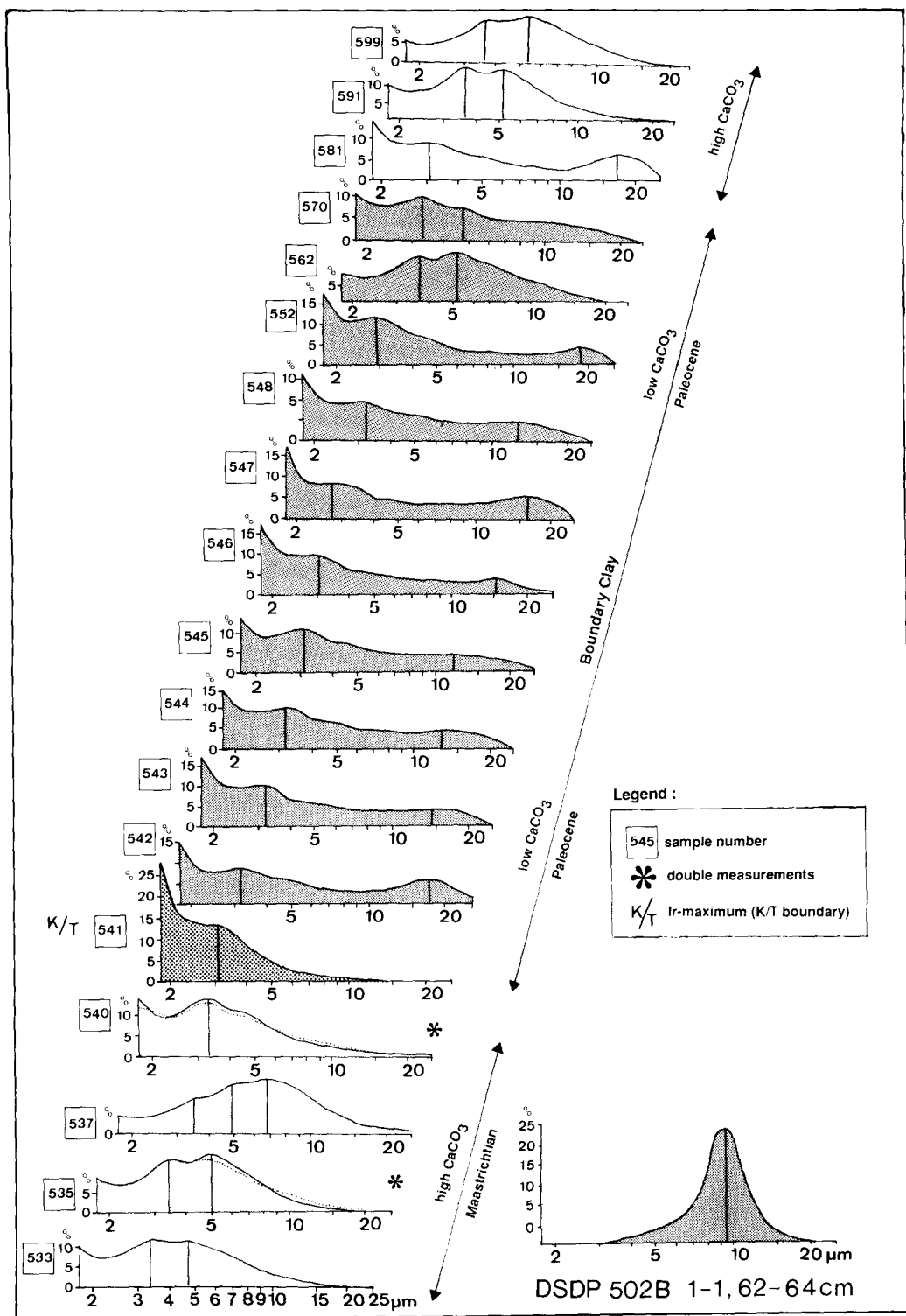
Diagenesis as well as compositional effects

are likely to have influenced oxygen and carbon isotope values. Diagenetic and preservational effects are variable with preservation generally improved in the low CaCO_3 sediments of the Lower Danian. Oxygen isotope values are therefore unlikely to represent original paleotemperatures but indicate general trends. Because carbon isotope values are less affected and our major $\delta^{13}\text{C}$ signals at El Kef correspond to similar signals in numerous deep-sea sections globally in both timing and magnitude (Hsu et al., 1984; Zachos and Arthur, 1986), we believe they represent global oceanographic changes.

Oxygen isotopes

Under equilibrium conditions isotopic ratios of foraminiferal or calcareous nannoplankton calcite tests reflect the temperature and the oxygen isotopic composition of the ambient water mass (Epstein et al., 1953; Craig, 1965). In recent sediments most planktic foraminifera have $^{18}\text{O}/^{16}\text{O}$ ratios consistent with growth conditions in isotopic equilibrium with sea water at or near the surface (Savin and Douglas, 1973; Fairbanks et al., 1980). Benthic foraminifera also show departures from isotopic equilibrium with dissolved HCO_3^- of the ambient sea water (Graham et al., 1981). Woodruff et al. (1981) and Vincent et al., (1981) found that the benthic species *Oridorsalis umbonatus* and *Cibicidoides* calcify their tests close to the oxygen isotopic equilibrium. In this study we have measured *Anomalinoidea acuta* an epifaunal species that scavenges for food in a relatively low oxygen environment (B Corliss, pers. comm. 1985). Repeated measurements of *A. acuta*, *Cibicidoides* and *Oridorsalis umbonatus* in paired samples show similar isotopic values (Table III). We therefore as-

Fig. 2. Grain-size analysis of the fine fraction ($< 25 \mu\text{m}$) sediment across the K/T boundary. DSDP 502B sample 1-1 (62–64 cm) represents the grain-size distribution from a split from DSDP Site 502B used as standard and discussed in Paull and Thierstein, 1987. Shaded areas mark the low CaCO_3 "boundary clay" characterized by dominance of clay sized particles ($\sim 2 \mu\text{m}$). Minor peak around $17 \mu\text{m}$ represent *Thoracosphaera* spherules. Non-shaded areas mark high CaCO_3 sediments. Note the larger average grain-size which largely represents calcareous nannofossils. Also note the shift towards smaller average grain-size just below the K/T boundary (sample 540).



sume that *A. acuta* also calcifies close to isotopic equilibrium.

The stable isotopic ratios measured in coccolith calcite also show species dependent departures from equilibrium known as vital effects (Berger et al., 1978; Dudley et al., 1980; Goodney et al., 1980). Moreover, Paull and Thierstein (1987) found that $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ ratios from coccoliths in individual grain size splits of fine fraction sediment ($<38\ \mu\text{m}$) vary systematically with size over a range of 1.25–4.0‰. In addition, diagenetic alteration such as secondary calcite overgrowth and dissolution significantly alter the $\delta^{18}\text{O}$ isotopic signal (Garrison, 1981). Nevertheless, it was found that major paleoceanographic changes dominate possible vital-, compositional- and diagenetic effects in oxygen and carbon isotope signals (Douglas and Savin, 1971; Berger et al., 1978; Sholle and Arthur, 1980; Anderson and Steinmetz, 1981; Paull and Thierstein, 1987). A more complete discussion on this subject is provided in the previous section.

Results

Oxygen and carbon isotope curves are illustrated in Fig.3 along with CaCO_3 and TOC data. The interval from 1 m below to 2 m above the K/T boundary is detailed in Fig.4. All data are presented in Tables I and III. The $\delta^{18}\text{O}$ ratios of planktic (*Pseudotextularia deformis*) and benthic (*Anomalinoidea acuta*, *Oridorsalis umbonatus*) foraminifera generally show parallel trends during the lower part of the uppermost Maastrichtian at El Kef (Fig.3). A negative excursion of about 0.6‰ occurs in both planktic and benthic foraminifera in sample 534 and a similar excursion may be present at the base of our section. During the topmost 65 cm below the K/T boundary benthic $\delta^{18}\text{O}$ ratios shift to more negative values whereas planktic values remain stable. Fine fraction ($<25\ \mu\text{m}$) $\delta^{18}\text{O}$ ratios of the uppermost Maastrichtian are about 2‰ heavier than corresponding *P. deformis* values and heavier than benthic *A. acuta* values. These anomalously heavy values apparently reflect the

diagenetic alteration of calcareous nannofossils evident in smear slide and SEM studies as discussed earlier.

At the K/T boundary divergent trends can be seen in the oxygen isotopic record of the benthic foraminifer *A. acuta* and fine fraction carbonates as detailed in Figs.3 and 4. About 25 cm below the K/T boundary there is a 1.5‰ positive excursion in the fine fraction $\delta^{18}\text{O}$ values followed by a 1‰ negative excursion 5 cm below the boundary. This negative trend continues across the K/T boundary reaching a maximum of -4.0‰ 12 cm above the boundary. Thus, the negative excursion of nearly 2‰ begins 25 cm below and ends 12 cm above the K/T boundary. Benthic $\delta^{18}\text{O}$ ratios also show 0.6‰ positive excursion between 40 and 25 cm below the K/T boundary followed by a 0.6‰ negative excursion 5 cm below the boundary. But in contrast to planktic $\delta^{18}\text{O}$ ratios benthic foraminifera (*A. acuta*) show a positive shift of 1.3‰ at the K/T boundary and values generally remain heavier throughout the Danian with the exception of a significant negative excursion in the upper part of Zone P1a (Sample 581, Fig.3).

During the Lower Danian (Units B,C,D) both fine fraction sediment and benthic *A. acuta* show high frequency $\delta^{18}\text{O}$ fluctuations of 1.5‰ and 0.7‰ respectively. The most significant negative $\delta^{18}\text{O}$ peaks of *A. acuta* occur at 12 cm, 27 cm, 52 cm, 107 cm, 127 cm, 152 cm and 172 cm above the K/T boundary with major positive excursions at 22 cm, 42 cm and 50 cm. Both planktic and benthic $\delta^{18}\text{O}$ ratios center around -3.0‰ (Units B,C,D; Figure 3). Benthic $\delta^{18}\text{O}$ ratios remain relatively stable through Zone P1b (*G. taurica*). Fine fractions $\delta^{18}\text{O}$ ratios are consistently heavier than benthic values in Zone P1b and probably reflect diagenetic alteration of calcareous nannoplankton in the carbonate-rich sediments of Unit E.

Interpretation

The fine fraction planktic to benthic foraminiferal $\delta^{18}\text{O}$ gradient in the Upper Maastrichtian varies between 1.6 and 2.2‰ and

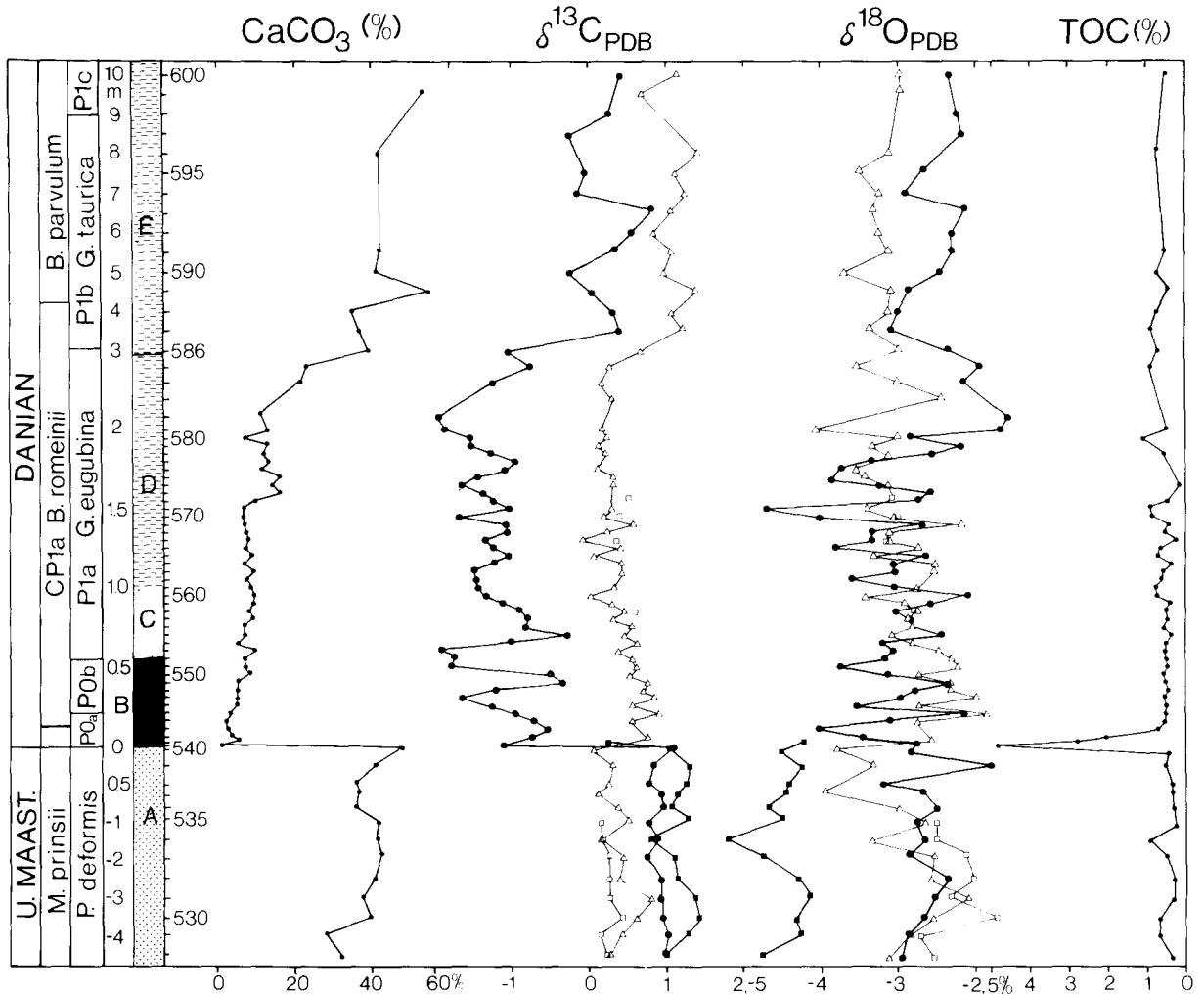


Fig.3 El Kef section, Tunisia: CaCO_3 , TOC, $\delta^{13}\text{C}$ isotope data from planktic and benthic foraminifera and fine fraction sediment ($< 25 \mu\text{m}$). ■ = Planktic foraminifera *Pseudotextularia deformis*. □ = Benthic foraminifera *Oridorsalis umbonatus* and *Cibicidoides* sp. △ = Benthic foraminifer *Anomalinoides acuta*, ● = Fine fraction sediment ($< 25 \mu\text{m}$). Note samples are plotted at expanded scale for 2 m above the K/T boundary. Planktic foraminiferal zonation from Keller, 1988a; nanofossil zonation from Perch-Nielsen, 1981a. Lithology discussed in text.

decreases to between 0.5 and 1.0‰ in the 65 cm below the K/T boundary. The decreased gradient, due to a negative shift in benthic $\delta^{18}\text{O}$ ratios, implies a gradual warming of deeper waters. The temperature gradient change follows a distinct negative excursion in both benthic and planktic $\delta^{18}\text{O}$ ratios implying a warm event. Warming of deeper waters at El Kef may have resulted from shallowing of the epicontinental sea as a result of a sea-level regression at the end of the Cretaceous (Haq et al., 1987). Faunal data from El Kef indicate

shallowing from an upper slope to outer shelf environment at this time (Peypouquet et al., 1986; Keller, 1988b).

The positive $\delta^{18}\text{O}$ excursion in benthic and fine fraction values about 25 cm below the K/T boundary may reflect a cool event although diagenetic alteration of the signal cannot be ruled out. A short pre-boundary positive excursion in benthic and/or fine fraction $\delta^{18}\text{O}$ values has been observed in DSDP Site 527 (Shackleton et al., 1984), Site 524 (Hsu et al., 1982), Site 516 (Williams et al., 1985) and Site 577 (Zachos

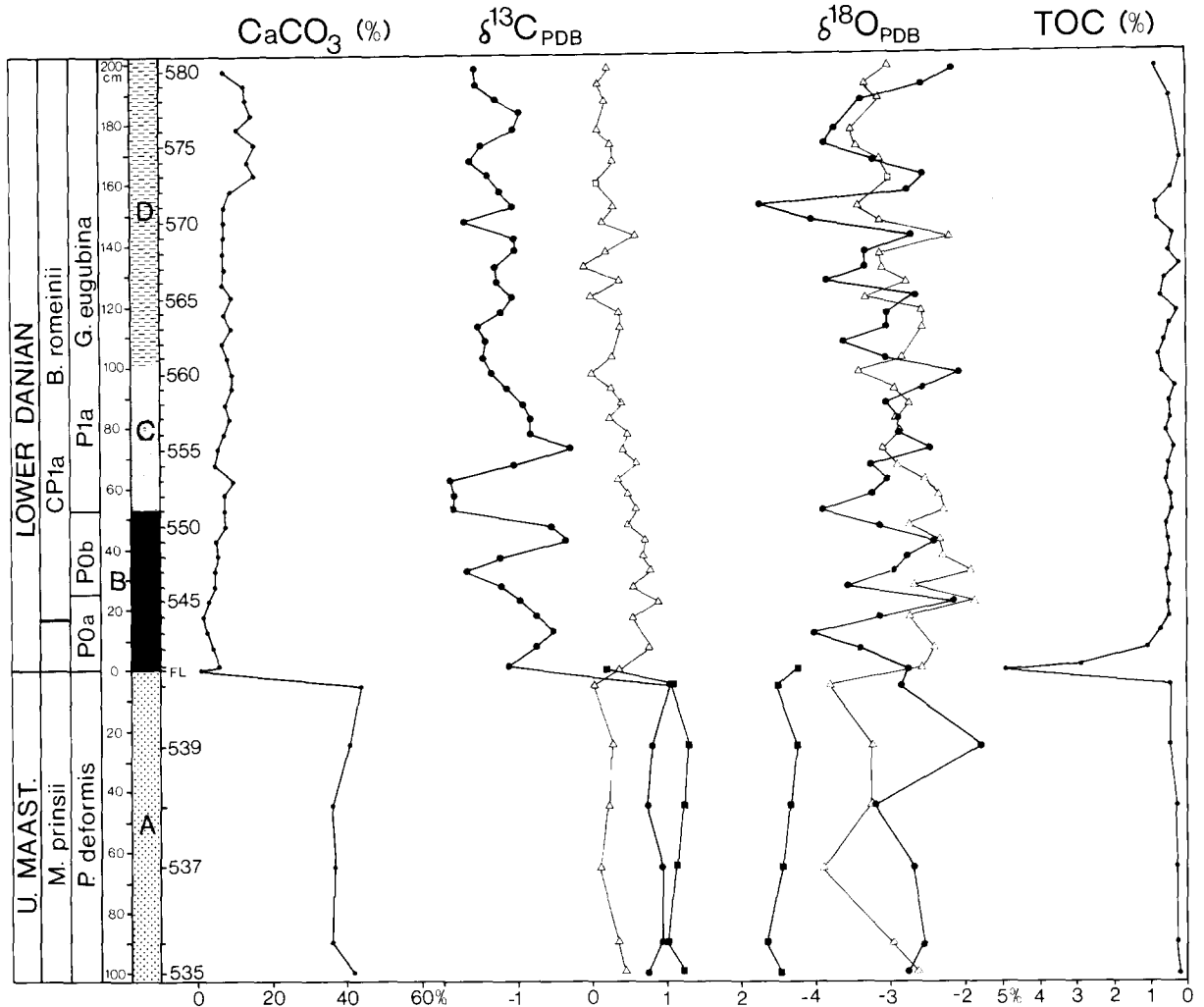


Fig.4 El Kef section, Tunisia expanded interval across the K/T boundary detailing CaCO_3 , TOC, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope data from planktic and benthic foraminifers and fine fraction sediment. ■ = *Pseudotextularia deformis* (planktic). □ = *Oridorsalis umbonatus* and *Cibicidoides* (benthic). △ = *Anomalinoidea acuta* (benthic). ● = fine fraction sediment (< 25 μm). Planktic foraminiferal zonation after Keller, 1988a; nanofossil zonation from Perch-Nielsen, 1981a. Lithology discussed in text.

et al., 1985). Because calcareous nanoplankton assemblages do not change significantly during the latest Maastrichtian (Thierstein, 1982; Jiang and Gartner, 1986) compositional effects are not likely a major source of this positive excursion. We believe that the available data implies a significant pre-boundary global cooling. Planktic foraminiferal assemblages at El Kef show a major decrease in diversity correlative with the positive $\delta^{18}\text{O}$ excursion 25 cm below the K/T boundary; about 30% of the species disappear below the

boundary (Keller, 1988a). The species disappearing are large complex tropical forms. Their demise may have been related to cooling as well as a shallowing sea during the latest Maastrichtian.

The benthic $\delta^{18}\text{O}$ ratios of the basal Paleocene at El Kef show a 0.5‰ positive excursion implying cooler water temperatures. Positive benthic $\delta^{18}\text{O}$ excursions were also observed at DSDP Site 398 (Arthur et al., 1979), Site 356 (Boersma, 1984) and Site 577 (Zachos et al., 1985). In contrast, the fine fraction $\delta^{18}\text{O}$ ratios

show a significant (2‰) negative excursion (Figs. 3, 4) which has also been observed in many other sections such as the Negev, Israel (Magaritz et al., 1985), Caravaca, Spain and Biarritz, France (Romein and Smit, 1981a,b), Lattengebirge, Austria (Perch-Nielsen et al., 1982), South Atlantic Site 524, (Hsu et al., 1982), Sites 384 and 356 (Boersma and Shackleton, 1979) and Braggs, Alabama (Jones et al., 1987). Zachos and Arthur (1986) interpret the $\delta^{18}\text{O}$ change across the K/T boundary as a preservational signal reflecting better preservation in clay-rich boundary clays. A change in coccolith assemblages across the K/T boundary may also have influenced the $\delta^{18}\text{O}$ fine fraction signal. Considering the conflicting benthic and fine fraction $\delta^{18}\text{O}$ ratios at El Kef and in many deep-sea sections, we also interpret these ratios as reflecting diagenetic and compositional effects. Alternatively, Boersma and Shackleton (1979) interpret the negative excursion in Sites 384 and 356 as a rise in near-surface water temperature. A post-K/T boundary warming could be explained by the greenhouse effect postulated to have occurred after the hypothesized impact event or large scale volcanicity (Hsu et al., 1982; McLean, 1985).

SEM and smear-slide examinations of foraminifera and coccoliths indicate better preservation in the low CaCO_3 clay and shale of the Lower Danian than in the high CaCO_3 marls of the Upper Maastrichtian and Upper Danian. Although diagenetic and compositional effects cannot be ruled out, we believe that the highly fluctuating benthic and fine fraction $\delta^{18}\text{O}$ records of the Lower Danian reflect unstable environmental conditions. Average temperatures appear to have been appreciably cooler during the early Danian as observed in both the benthic and fine fraction $\delta^{18}\text{O}$ ratios which are on average 1‰ and 1.8‰ respectively heavier than in the upper Maastrichtian. In the black boundary clay (Zone P0) there are nearly synchronous fluctuations in benthic and fine fraction $\delta^{18}\text{O}$ ratios with the latter consistently more negative (Fig. 4). This implies mixing of the water-mass and the pres-

ence of a minor temperature gradient. This temperature gradient may have largely disappeared during the succeeding P1a Zone where both fine fraction and benthic $\delta^{18}\text{O}$ ratios vary around a mean of -3‰. The fluctuations observed in Zones P0 and P1a may continue through Zone P1b although the reduced number of data points is inconclusive and there is increased diagenetic alteration of calcareous microfossils. High frequency fine fraction $\delta^{18}\text{O}$ fluctuations in the early Danian have also been observed by Magaritz et al. (1985) in the Negev although direct comparison is not possible because their sections are more condensed. No such high resolution record is available from the deep sea.

Assuming that diagenetic alteration of microfossils is not a serious problem in Zones P0 and P1a (discussed earlier), the near absence of a temperature gradient may be explained by a thoroughly mixed water column and by the shallow water depth of El Kef. A water depth of about 75–150 m was estimated by Peypouquet et al. (1986) based on ostracods. Shallowing of the sea during the latest Maastrichtian and into the Danian was also observed by Jones et al. (1987) from the Braggs section in Alabama. These observations contradict Haq et al. (1987) who show a rising sea-level during the early Danian.

Carbon isotopes

the $\delta^{13}\text{C}$ ratios of planktic and benthic calcareous tests reflect the isotopic composition of dissolved CO_2 in ambient sea water, if formed under equilibrium conditions. Photosynthesis in the photic zone preferentially incorporates the isotopically lighter ^{12}C in organic matter and returns this carbon to the ocean TCO_2 by oxidation at depth (Deuser and Hunt, 1969; Kroopnick, 1974). The surface water is thus enriched in the heavier ^{13}C and the bottom water is enriched in the lighter ^{12}C resulting in a vertical carbon isotope gradient. Heavier $\delta^{13}\text{C}$ values are therefore generally found in planktic tests and lighter values in benthic tests.

As discussed earlier, tests of calcareous micro-organisms are also influenced by dissolution, diagenetic recrystallization and little understood metabolic processes. However, diagenesis in organic carbon-poor marine sediments generally does not alter the $\delta^{13}\text{C}$ of the whole rock CaCO_3 (Barrera and Savin, in prep.). Therefore, the measured $\delta^{13}\text{C}$ values of calcareous tests should closely reflect the water conditions in which the organisms grew and hence are indicators of paleoceanographic changes.

Results

Carbon isotopic trends across the K/T boundary are illustrated in Figure 3 and details of the boundary event are shown in Fig.4. Benthic (*A. acuta* and *O. umbonatus*) and fine fraction planktic $\delta^{13}\text{C}$ ratios of the upper Maastrichtian average about 0.4‰ and 1‰ respectively without significant variations. Planktic foraminifer *P. deformis* averages about 0.4‰ heavier than fine fraction values and a significant negative excursion occurs in sample 534 as also observed in $\delta^{18}\text{O}$ ratios.

A major sudden negative shift of 2‰ is observed in the fine fraction $\delta^{13}\text{C}$ ratios at the K/T boundary correlative with a drop in CaCO_3 to less than 1% and a rise in TOC to 4.8% (Fig.4). Planktic foraminifer *P. deformis* which disappears above sample 541 displays a negative shift of 0.8‰ in the last sample of its occurrence. In contrast, benthic *A. acuta* shows a positive shift of 0.7‰ over two samples 3 and 7 cm above the K/T boundary (Table III).

During the Lower Danian (Zones P0–P1a) benthic $\delta^{13}\text{C}$ ratios remain slightly heavier than in the Upper Maastrichtian with low amplitude fluctuations (Fig.3). Fine fraction $\delta^{13}\text{C}$ values show significant variability with pronounced peaks in the black boundary clay and dark grey shale (Units B,C) and lower amplitude fluctuations continue through Zone P1a (*G. eugubina*). Major positive excursions in the fine fraction $\delta^{13}\text{C}$ ratios are observed at 12 cm, 42 cm, 72 cm and 182 cm above the K/T boundary. Major negative excursions are ob-

served at 32 cm, 52 cm, 62 cm, 102 cm, 147 cm, 167 cm and 202 cm above the K/T boundary. Positive excursions generally correlate with heavier $\delta^{18}\text{O}$ ratios (cooling) and negative excursions correlate with lighter $\delta^{18}\text{O}$ ratios (warming or low salinity water).

At the base of Zone P1b a major positive shift is observed in both fine fraction and benthic $\delta^{13}\text{C}$ ratios. The shift begins about 262 cm and reaches a maximum at 350 cm above the K/T boundary. The positive shift in $\delta^{13}\text{C}$ corresponds to an increase in carbonate sedimentation to near pre-K/T boundary values (Fig.3). Both benthic and fine fraction values remain heavier through Zone P1b with fine fraction values consistently lighter than benthic values.

Interpretation

Carbon isotopic data indicate relatively stable bioproductivity during the late Maastrichtian at El Kef. This interpretation is consistent with results from other K/T boundary sections (Romein and Smit, 1981a,b; Margaritz et al., 1985; Zachos and Arthur, 1986). The consistently heavier planktic (*P. deformis*) $\delta^{13}\text{C}$ ratios as compared with benthic (*A. acuta*) ratios indicate a vertical carbon isotope gradient with high surface water bioproductivity. Carbon-13 values of *P. deformis* are consistently heavier than the fine fraction $\delta^{13}\text{C}$ ratios. This may reflect the compositional effects of the polyspecific fine fraction carbonate as compared to the monospecific *P. deformis* values. The negative $\delta^{13}\text{C}$ excursion (sample 534) 150 cm below the K/T boundary implies a temporary decrease in bioproductivity coincident with warmer water temperatures and a slight increase in organic carbon (Fig.3). A similar fluctuation is indicated at the bottom of our section, but cannot be confirmed without further samples. The K/T boundary transition is not anticipated in the uppermost Maastrichtian $\delta^{13}\text{C}$ record. This lends support to a sudden catastrophic event.

The sudden negative fine fraction $\delta^{13}\text{C}$ shift at the K/T boundary is parallel to a decrease in

CaCO₃ accumulation and a major change in planktic foraminifera from a complex high diversity Upper Maastrichtian assemblage to a primitive low diversity Danian assemblage (Gerstel et al., 1987; Keller, 1988a). A negative $\delta^{13}\text{C}$ shift in fine fraction carbonate, reduced CaCO₃ accumulation and faunal changes have been observed in every K/T boundary sequence examined globally (Thierstein and Berger, 1978; Scholle and Arthur, 1980; Perch-Nielsen et al., 1982; Zachos and Arthur, 1986; Arthur et al., 1987). Paleocene calcareous microfossils are generally better preserved than in the Upper Maastrichtian indicating no major long-term changes in dissolution rates are responsible for the decreased carbonate accumulation (Thierstein, 1981; Arthur et al., 1987). Moreover, at El Kef drastically reduced carbonate accumulation rates continued through Zone P1a (*G. eugubina*, Fig.3) or to the top of Chron 29N about 230,000 years after the K/T boundary event (Berggren et al., 1985) indicating a lengthy period of reduced surface water carbonate production. Thereafter carbonate accumulation increases to near pre-K/T boundary levels. Zachos and Arthur (1986) and Arthur et al. (1987) estimate that carbonate accumulation rates in the deep-sea remained depressed for at least 1–2 m.y. Our data suggests that initial recovery occurred much earlier.

The negative fine fraction $\delta^{13}\text{C}$ shift observed at El Kef and in marine sequences globally is not recorded in the benthic $\delta^{13}\text{C}$ records (Figs.3, 4) (see Zachos and Arthur, 1986 for a global survey) suggesting that the decrease was confined to surface waters. The global decrease in $\delta^{13}\text{C}$ of surface water is generally interpreted as resulting from a sudden reduction of oceanic primary productivity (Thierstein and Berger, 1978; Hsu et al., 1982; Perch-Nielsen et al., 1982; Arthur et al., 1987). This interpretation is based on the observation that the $\delta^{13}\text{C}$ distribution in the oceans is largely controlled by primary productivity in surface waters and organic carbon oxidation and CO₂ regeneration in deep waters (Williams et al., 1977; Kroopnick, 1980). At El Kef

primary productivity remained low but fluctuating throughout the Danian Zones P0 and P1a (Figs.3 and 4). Such prolonged low primary productivity has not been observed in deep-sea sequences probably because of lower sediment accumulation rates resulting in absence of planktic foraminiferal Zone P0 and a highly condensed Zone P1a (Perch-Nielsen et al., 1982; D'Hondt and Lindinger, in prep.).

Although a major change in surface water productivity is expected to affect the entire water column, this appears not to have been the case. Benthic foraminifera at El Kef indicate relatively minor faunal changes across the K/T boundary and these appear largely associated with a shallowing sea from an upper slope to shelf conditions and a low oxygen environment (Keller, 1988b). Low oxygen conditions at the sediment/water interface are indicated by a low diversity generally low oxygen tolerant fauna and the dominance of *Anomalinoidea acuta* a low O₂ tolerant epifaunal species scavenging for food on the ocean floor (Corliss, 1985). Low oxygen conditions and a shallowing sea at El Kef are also indicated by ostracod faunas (Peypouquet et al., 1986). Benthic foraminiferal communities have also remained relatively unchanged in the deep-sea (Douglas and Woodruff, 1981; Dailey, 1983; Thomas, 1988).

In contrast to the negative shift in fine fraction values, benthic $\delta^{13}\text{C}$ values show enrichment of about 0.6‰ across the K/T boundary and return to pre-boundary conditions by early Zone P1a time (Figs.3 and 4). Examination of benthic $\delta^{13}\text{C}$ values in deep-sea sections shows a similar slight enrichment (e.g. Zachos and Arthur, 1986). Zachos and Arthur (1986) interpret this enrichment as a decrease in organic carbon oxidation at the sediment/water interface as a result of decreased surface water production and hence decreased flux of organic matter to the ocean floor. The increase in organic carbon (TOC) at the K/T boundary at El Kef may be due to several processes such as a change in marine and/or terrestrial productivity, a change in sedimentation rates or low oxygen conditions at the sediment/

water interface. We favor the latter interpretation because there is good faunal evidence of low oxygen conditions whereas productivity and sedimentation rates decreased across the K/T boundary. Kerogen analysis now under way (P. Meyers, pers. comm., 1988) should indicate which particular processes most likely account for the TOC anomaly.

Surface water primary productivity in the early Danian (Zones P0, P1a) at El Kef appears to have been variable and unstable as indicated by the fluctuating $\delta^{13}\text{C}$ values (Fig.4). Similar $\delta^{13}\text{C}$ variability has been observed from other continental platform sections (Margaritz et al., 1985; Jones et al., 1987) as well as pelagic and hemipelagic sections (Perch-Nielsen et al., 1982; Oberhansli and Hsu, 1985; Oberhansli, 1986; Zachos and Arthur, 1986; D'Hondt and Lindinger, in prep.). Both nannofossil and planktic foraminiferal assemblages during this interval are dominated by opportunistic species such as *Braarudosphaera* and *Thoracosphaera* (Perch-Nielsen, 1979) and *Guembelitra* and *Woodringa* respectively (Keller, 1988a).

The first recovery after the K/T boundary catastrophe is apparent in the lower part of Subzone P1b and 2.6 m and 3.5 m above the K/T boundary (Fig.3). Both benthic and fine fraction $\delta^{13}\text{C}$ values increase significantly at this time along with increasing carbonate sedimentation to near pre-K/T boundary levels. The first major species diversification in planktic foraminifers after the K/T boundary occurs at this time (Keller, 1988a).

Conclusions

The extended K/T boundary record from El Kef, Tunisia sheds light on the environmental conditions before, during and after the K/T boundary catastrophe on a continental shelf in proximity to North Africa. Despite its location the planktic foraminifera and isotopic records are very similar to coeval open ocean records indicating relatively unrestricted communication through the Tethyan Sea. Moreover, $\delta^{13}\text{C}$ isotopic changes mirror similar changes in

deep-sea sections globally both in timing and magnitude. For these reasons we believe that El Kef is representative of the major global K/T boundary disturbance and subsequent recovery period and does not represent isolated local conditions. Our data permit the following conclusions.

(1) The uppermost Maatrichtian is characterized by relatively stable high productivity and a decrease in the temperature gradient possibly due to a shallowing sea at El Kef.

(2) Oxygen isotope data indicate decreasing temperatures beginning just below (-25 cm) the K/T boundary.

(3) The K/T boundary at El Kef as well as globally is marked by a negative shift in fine fraction $\delta^{13}\text{C}$ and sharply reduced CaCO_3 accumulation rates interpreted as a sudden reduction of primary productivity.

(4) Benthic $\delta^{13}\text{C}$ values of *A. acuta* show a slight enrichment ($\sim 0.6\text{‰}$) interpreted as decreased organic carbon oxidation at the sediment/water interface due to a reduced flux of organic matter to the ocean floor.

(5) Unstable environmental conditions prevailed after the K/T boundary event through planktic foraminiferal Zones P0 and P1a or to the top of Chron 29N about 230,000 years later.

(6) $\delta^{13}\text{C}$ values of fine fraction and benthic foraminifera as well as carbonate content increase significantly between 2.6 m and 3.5 m above (base Subzone P1b) the K/T boundary and nearly reach pre-K/T levels for the first time. This implies a prolonged recovery period spanning Zones P0 and P1a at El Kef. This long recovery period may not have been observed in the deep-sea record because of its highly condensed and frequently absent lower Danian record (Zones P0, P1a).

What caused the K/T boundary catastrophe? Although our data provides much detailed information of the environmental effects of the catastrophe, it does not provide the answers to the cause. All indications are that the boundary event was sudden, even catastrophic, and its effects were apparently global and prolonged. Current theories of the K/T boundary catastrophe include a large extraterrestrial

bolide impact (Alvarez et al., 1980), large scale volcanicity (McLean, 1985), Arctic spillover or injection of low salinity water (Gartner and Keany, 1978; Thierstein and Berger, 1978). Each theory can plausibly explain some aspects of the K/T boundary catastrophe but fails in others. Perhaps the one aspect of the K/T boundary catastrophe most difficult to explain is the long recovery period. What single instantaneous event could drastically reduce primary productivity for at least 230,000 years? Is it more plausible that a series of repeated events account for these prolonged adverse conditions?

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