

Oceanic primary productivity and dissolved oxygen levels at the Cretaceous/Tertiary boundary: Their decrease, subsequent warming, and recovery

Kunio Kaiho,¹ Yoshimichi Kajiwara,² Kazue Tazaki,³ Masato Ueshima,³
Nobuyori Takeda,⁴ Hodaka Kawahata,⁵ Tetsuya Arinobu,⁶
Ryoshi Ishiwatari,⁷ Akio Hirai,⁸ and Marcos A. Lamolda⁹

Abstract. Thirty-six different geochemical and foraminiferal analyses were conducted on samples collected at closely spaced intervals across the Cretaceous/Tertiary (K/T) boundary exposed at Caravaca, Spain. A rapid reduction in the gradient between $\delta^{13}\text{C}$ values in fine fraction carbonate and benthic foraminiferal calcite and a decrease in the abundance of phosphorus (a proxy for organic carbon) and calcium were recorded in sediments 0-0.5 cm above the K/T boundary. These trends imply that an abrupt mass mortality occurred among pelagic organisms, leading to a significant reduction in the flux of organic carbon to the seafloor. In addition, variations in sulfur isotope ratios, the hydrocarbon-generating potential of kerogen (measured as the hydrogen index), and foraminiferal indices of dissolved oxygen level all imply that a rapid decrease in dissolved oxygen was coincident with the $\delta^{13}\text{C}$ event. Evidence of the low oxygen event has also been recognized in Japan and New Zealand, suggesting that intermediate water oxygen minima were widely developed during earliest Danian time. A threefold increase in the kaolinite/illite ratio and a 1.2‰ decrease in $\delta^{18}\text{O}$ (carbonate fine fraction) were recorded in the basal 0.1-2 cm of Danian age sediments. These trends suggest that atmospheric warming and an increase in surface water temperature occurred 0-3 kyr after the $\delta^{13}\text{C}$ event. Recovery in the difference between $\delta^{13}\text{C}$ values in the carbonate fine fraction and in benthic foraminiferal calcite as well as increases in phosphorus and calcium contents occur at the base of planktonic foraminiferal Zone P1a, implying that an increase in primary productivity commenced some 13 kyr after the K/T boundary.

1. Introduction

The largest mass extinction during the past 200 m.y. occurred at the Cretaceous/Tertiary (K/T) boundary. Detailed studies of environmental changes across the K/T boundary are needed to understand the mass extinction event and its aftermath. Although many paleoenvironmental studies have been carried out on the K/T boundary [Alvarez *et al.*, 1980; Smit, 1982, 1990; Smit and Romein, 1985; Wolbach *et al.*, 1985; Brinkhuis and Zachariasse, 1988; Keller, 1988; Zachos *et al.*, 1989a, b; Venkatesan and Dahl, 1989; Hsü and McKenzie,

1990; Barrera and Keller, 1990; Kaiho, 1992, 1994b; Schmitz *et al.*, 1992; MacLeod and Keller, 1994; D'Hondt *et al.*, 1998], the timing and sequence of key environmental changes across the boundary remain controversial or unknown. This study was focused on evidence of change in oceanic productivity, dissolved oxygen, and surface water temperature across the K/T boundary.

A negative excursion of $\delta^{13}\text{C}$ at the K/T boundary is observed globally [Smit, 1982; Perch-Nielsen *et al.*, 1982; Margolis *et al.*, 1987; Keller and Lindinger, 1989; Zachos *et al.*, 1989a, 1992]. A normal biologically productive ocean is characterized by a $\delta^{13}\text{C}$ gradient from surface to deep waters. However, evidence of negative to absent surface to deep water $\delta^{13}\text{C}$ gradients were recorded at the K/T boundary of Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) sites in the North and South Atlantic, Pacific, and Antarctic Oceans [Zachos and Arthur, 1986; Zachos *et al.*, 1989a, 1992; Ivany and Salawitch, 1993], a pattern implying a rapid and complete breakdown in this biologically mediated gradient [Zachos *et al.*, 1989a, 1992]. Fluxes of barium and CaCO_3 also decreased significantly at the time of the major marine plankton extinction, and the implied reduction in primary productivity persisted for ~0.5 m.y. before the carbon isotope gradient was gradually reestablished [Zachos *et al.*, 1989a]. Recently D'Hondt *et al.* [1998] demonstrated that it had taken 3 m.y. for recovery of biomass on the basis of $\delta^{13}\text{C}$ data from the deep sea.

Kajiwara and Kaiho [1992] indicated that low oxygen conditions developed in earliest Tertiary intermediate water in the northwestern Pacific Ocean on the basis of sulfur isotope

¹Institute of Geology and Paleontology, Tohoku University, Sendai, Japan.

²Institute of Geoscience, University of Tsukuba, Ibaraki, Japan.

³Department of Earth Sciences, Kanazawa University, Kanazawa, Japan.

⁴Japex Research Center, Chiba, Japan.

⁵Marine Geology Department, Geological Survey of Japan, Ibaraki, Japan.

⁶Mineral and Fuel Resource Department, Geological Survey of Japan, Ibaraki, Japan.

⁷Department of Chemistry, Tokyo Metropolitan University, Tokyo, Japan.

⁸Technical Research Center, Teikoku Oil Company Limited, Tokyo, Japan.

⁹Paleontología Facultad de Ciencias, Universidad del País Vasco, Lejona, Spain.

Copyright 1999 by the American Geophysical Union.

Paper number 1999PA900022.
0883-8305/99/1999PA900022\$12.00

analyses. *Coccioni and Galeotti* [1994] also reported low oxygen benthic foraminiferal assemblages from the basal Danian sediments at Caravaca, Spain.

Evidence of variations in $\delta^{18}\text{O}$ from the Caravaca K/T sequence [Romein and Smit, 1981], Agost [Smit, 1990], Zumaya, Spain [Mount et al., 1986; Margolis et al., 1987], and at El Kef, Tunisia [Perch-Nielsen et al., 1982] indicate that warming occurred during earliest Danian time.

Elemental analyses [Alvarez et al., 1980; Kyte et al., 1980; Smit, 1982; Strong et al., 1987; Zachos et al., 1989a; Tredoux et al., 1989; Bhandari et al., 1993; Elliot et al., 1994; Dolenc and Pavsic, 1995], clay mineral associations [Robert and Chamley, 1990], and carbon and oxygen stable isotopes [Boersma and Shackleton, 1981; Romein and Smit, 1981; Perch-Nielsen et al., 1982; Hsü et al., 1982; Mount et al., 1986; Kaminski and Malmgren, 1989; Zachos et al., 1989a, b; Stott and Kennett, 1990; Sarkar et al., 1992; Dolenc and Pavsic, 1995; Huber, 1996] have been carried out across the K/T boundary at many localities. However, high-resolution analyses are limited. Moreover, no one has undertaken multiple analyses of the same samples across the K/T boundary. This study involves high-resolution sampling and a full spectrum of analyses including $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of fine fraction carbonate and benthic foraminiferal calcite, $\delta^{13}\text{C}$ of kerogen, total organic carbon (TOC), visual kerogen, sulfate sulfur and sulfide sulfur isotope ratios, concentration of 15 elements, clay minerals, hydrogen index (HI), oxygen index (OI), benthic foraminiferal oxygen index (BFOI), and carbonate content.¹

The most continuous K/T boundary sequences are exposed at Caravaca and Agost in southeastern Spain [Smit, 1982; 1990; Canudo et al., 1991] and at El Kef in Tunisia [Keller, 1988, 1989; Smit and Nederbragt, 1997; Olsson, 1997; Canudo, 1997]. The boundary clays in these sections range from 6 to 50 cm in thickness representing ~13 kyr (T. Arinobu et al., Spike of pyrosynthetic polycyclic aromatic hydrocarbons coincident with a sudden decrease in $\delta^{13}\text{C}$ of terrestrial biomarker at the Cretaceous/Tertiary boundary at Caravaca, Spain, submitted to *Geology*, 1999) of deposition; the basal portions of the clay units contain evidence of a bolide impact (Ir and Os concentrations) [Smit, 1982, 1990]. The effect of sea level changes [Brinkhuis and Zachariasse, 1988] on geochemical and foraminiferal assemblages at Caravaca is thought to be smaller than that observed at El Kef because paleowater depths through the K/T boundary at Caravaca were deeper than those at El Kef [MacLeod and Keller, 1994]. Therefore we selected samples from the well-known section exposed on the east bank of Barranco del Gredero, ~4 km southwest of the town of Caravaca (Figure 1) in order to address paleoenvironmental changes across the K/T boundary.

The Caravaca K/T section is composed of marl (~70% carbonate) except for the so-called fallout lamina (1 mm thickness; the base of which is the K/T boundary; 5% Ca) and the subsequent blackish gray clay (7-10 cm thickness; 9-14% Ca; 32-43% carbonate). High Ir and Os concentrations occurred

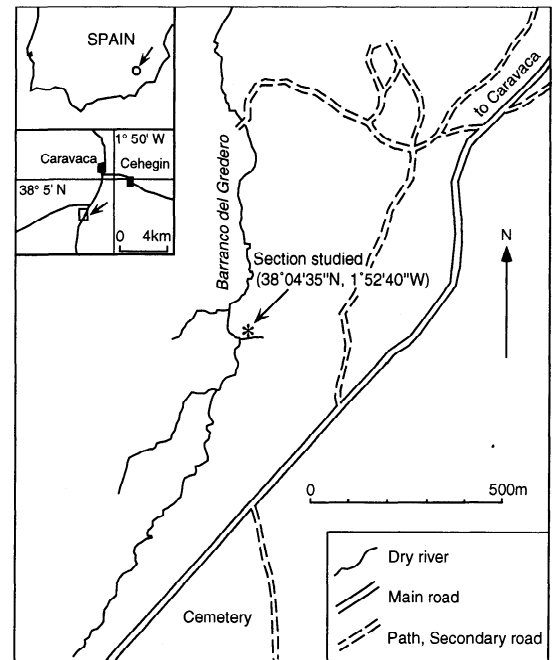


Figure 1. Location map showing the Caravaca section in southeastern Spain.

in the fallout lamina [Smit and Hertogen, 1980] (Figure 2). The Caravaca section represents paleowater depths of ~200-1000 m [Coccioni and Galeotti, 1994; MacLeod and Keller, 1994]. The paleolatitude of this sequence is estimated as 27°N on the basis of the paleocontinental world map of Smith et al. [1981].

2. Methods

2.1. Purpose

We measured clay-mineral assemblages, carbonate content, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of fine fraction carbonate (<10 μm) and benthic foraminiferal calcite, and $\delta^{13}\text{C}$ of kerogen to clarify changes of climate and oceanic primary productivity. In addition, we measured sulfur isotope ratios of sulfide and sulfate, TOC, organic carbon/insoluble residue (OC/IR) for HCl, HI (hydrocarbon-generating potential of kerogen), OI (measured by pyrolysis), BFOI, the ratio of thick-walled oxic foraminifera such as *Linaresia* spp. relative to all oxic foraminifera including *Cibicides* spp. (thick-walled/oxic ratio, annotated as T/O in the following), and microscopic examination of organic particles in order to assess variations in dissolved oxygen conditions.

2.2. Sample Material

We focused our efforts on the 80 cm thick interval spanning the K/T boundary at Caravaca (-40 to +40 cm in which the base of the fallout lamina is defined as 0 cm; positive and negative numbers in our plots correspond to thickness above and below the latter horizon). We trenched the exposures across the K/T boundary and obtained fresh unweathered samples. Two different scales of sampling were used. Thirteen samples of

¹ Tables A1-A3 are available on diskette or via Anonymous FTP from kosmos.agu.org directory APENO (Username = anonymous, Password = guest). Diskette may be ordered from American Geophysical Union, 2000 Florida Avenue, N.W., Washington, DC 20009 or by phone at 800-966-2481; \$15.00. Payment must accompany order.

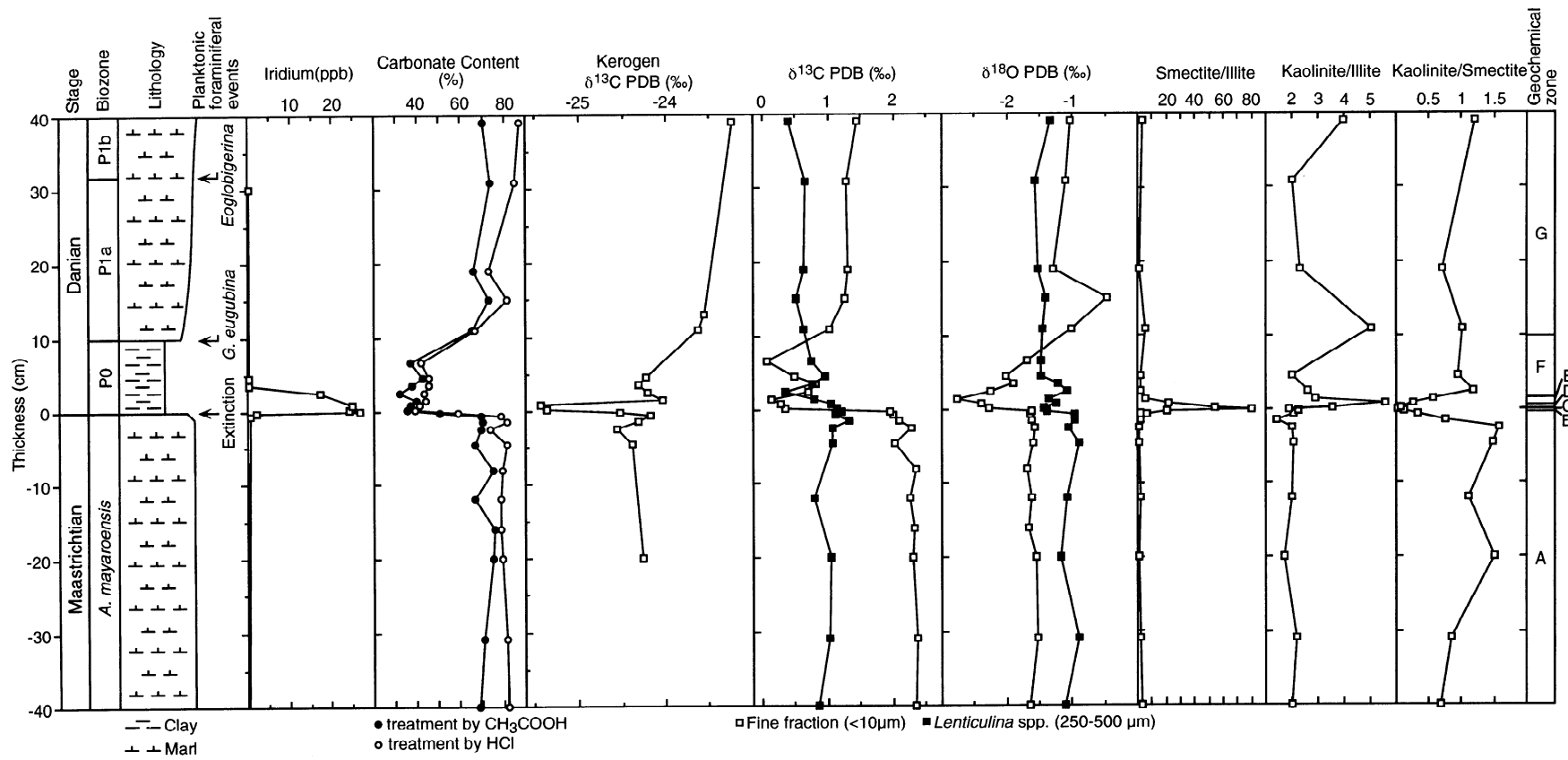


Figure 2. Lithology and geochemical fluctuations between -40 and +40 cm (relative to the Cretaceous/Tertiary (K/T) boundary designated as 0 cm) in the upper Maastrichtian and lower Danian in the Caravaca section. Ir data are after Smit and Hertogen [1980].

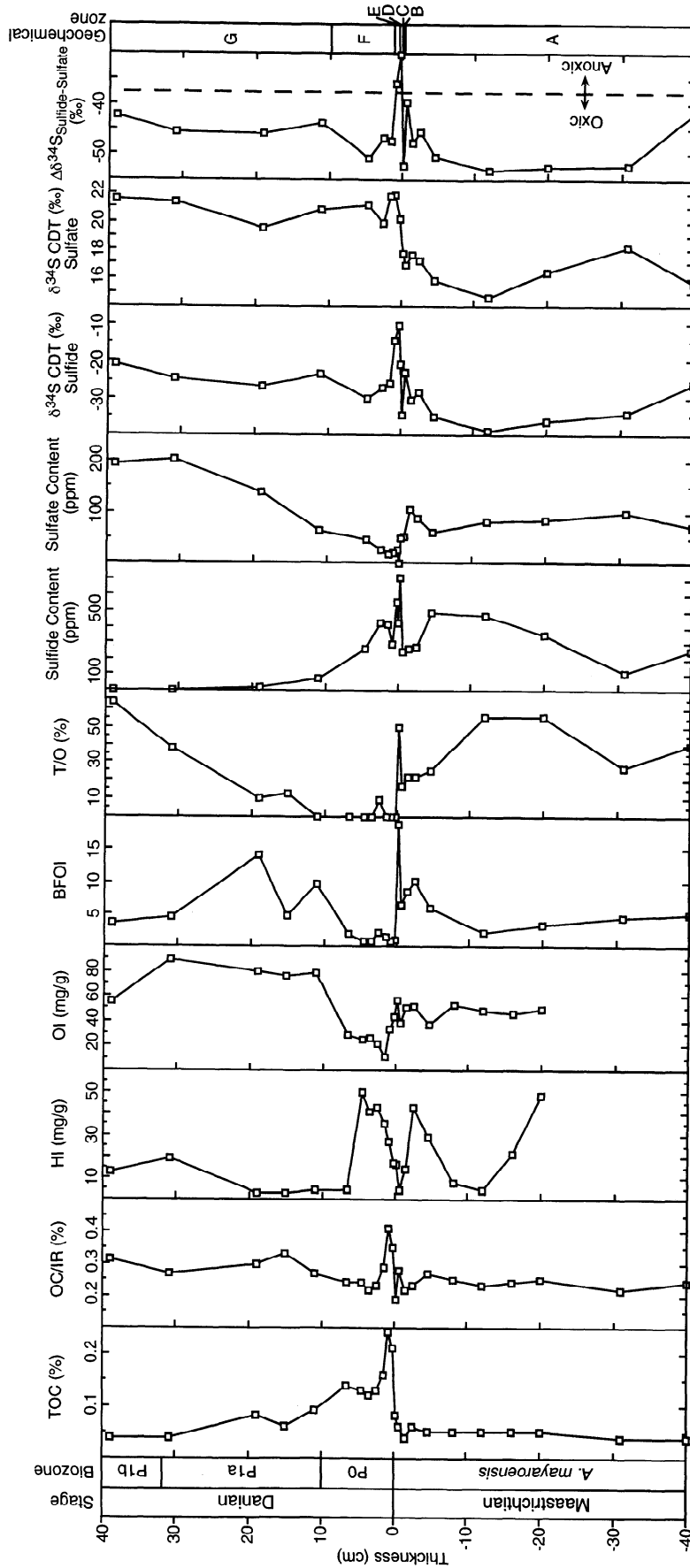


Figure 3. Foraminiferal and geochemical fluctuations between -40 and +40 cm (relative to the K/T boundary designated as 0 cm) through the upper Maastrichtian and lower Danian in the Caravaca Section. T/O is the ratio of thick-walled oxic foraminifera relative to all oxic foraminifera.

0.1-1 cm in thickness were taken continuously from -5 to +7 cm in the section. Thirty-three samples of 2 cm in thickness were taken continuously between -40 and -5 cm and between +10 and +40 cm. Finally, we selected 36 samples at 0-9 cm intervals for measurements (Figures 2 and 3). These strata are divided into four biozones: *Abathomphalus mayaroensis*, P0, P1a, and P1b zones [Smit, 1982] (Figure 2).

2.3. Time scale and Sedimentation Rates

On the basis of an established geomagnetic polarity column of the Caravaca section [Smit, 1982], C30N/C29R and C29R/C29N boundaries correspond to depth of 11.7 m below and 5.1 m above the K/T boundary. The duration of the Maastrichtian and the Paleocene portions of C29R are 377 ± 20 and 296 ± 41 kyr, respectively [Herbert et al., 1995]. Therefore the average sedimentation rates of Maastrichtian and Paleocene portions of C29R are estimated to be 3.1 and 1.7 cm kyr⁻¹, respectively, in the Caravaca section. However, the contents of CaCO₃ are lower in the Caravaca boundary clay layer (P0 zone; average 37.9% weight) relative to the lower Paleocene marly section (P1 zone; average 70.7% weight). Assuming that the depositional flux of the residual mineral matrix is constant, we infer that the average sedimentation rate in the boundary clay layer could have been approximately half that of the marly lithology in Paleocene. The average sedimentation rate in the boundary clay layer is calculated to be 0.8 cm kyr⁻¹, except for the fallout lamina, which is assumed to be instantaneous. Thus the interval from -40 to +40 cm encompasses the last 13.0 kyr of the Cretaceous and the first 29.9 kyr of Tertiary.

2.4. Stable Isotope Ratios

Fifty grams of sediment from each sample were disaggregated in 5% hydrogen peroxide, washed through a 63 μ m screen, and dried at 50°C, yielding abundant foraminifera. Alternatively, 2-3 g samples disaggregated in 5% hydrogen peroxide were left for 5 min after shaking. The upper part of the liquid was siphoned off and dried at 50°C, yielding the fine fraction (<10 μ m).

The stable isotopic ratios of the carbonate fine fraction, benthic foraminiferal tests of *Lenticulina* spp. (250-500 μ m), and planktonic foraminiferal tests of 12 common species were measured in samples collected between -40 and +40 cm. All samples of fine fraction carbonate and foraminifera were analyzed by using a Finnigan Mat Delta-S mass spectrometer. All isotopic values are reported relative to the Peedee belemnite (PDB) standard. The overall uncertainties of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are within 0.03 and 0.06‰, respectively.

Although chambers of foraminifera were entirely filled by diagenetic calcite, fine pores and wall structures were generally preserved. We measured the stable isotope ratio of tests filled by diagenetic calcite because it is impossible to separate calcite from tests. There is no apparent correlation between the amount of cement in a given test and stable isotope values ($R^2 = 0.17$ for $\delta^{13}\text{C}$ and $R^2 = 0.03$ for $\delta^{18}\text{O}$) measured in broken specimens of a planktonic foraminifera (*Globotruncanita stuarti*) from the basal Danian at Caravaca [Kaiho and Lamolda, 1999]. This suggests that the stable isotope composition of the cement is similar to that of the original biogenic calcite. The similarity suggests that $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the

cement are ~ 2.0 and -2.0 ‰, respectively. Both stable isotope ratios of pristine benthic foraminiferal test can be estimated on the basis of an assumption of stable values of cements for species and through the stratigraphic interval (-40 to +40 cm).

Original $\delta^{13}\text{C}$ will remain essentially unchanged by diagenesis in sediments with low organic carbon content [Barrera and Keller, 1990]. Carbonate is high (32-73%) and organic carbon low (0.04-0.24%) in the Caravaca section (Figures 2 and 3), indicating that both have not affected isotopic values of the fine fraction and foraminiferal carbonate.

The Caravaca isotope data yield expected trends, that is, paleotemperature differences between benthic foraminifera, planktonic foraminifera, and fine fraction carbonate as well as meridional paleotemperature differences with ODP site 750 [Zachos et al., 1992] in the case of $\delta^{18}\text{O}$ values and paleodepth differences between Caravaca and DSDP 577 [Zachos et al., 1989a] in the case of both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Figure 4) [Kaiho and Lamolda, 1999]. Such trends support the interpretation that the isotopic values are robust at the Caravaca section and little affected by diagenetic alteration.

Stable carbon isotope ratios for kerogen in insoluble residues remaining after HCl treatment and extraction of bitumen were measured with a Finnigan MAT delta-S mass spectrometer on CO₂ prepared by combustion of kerogen. The kerogen was placed in a thin quartz tube (6 mm ϕ OD x 70 mm) for analysis. The quartz tube was then placed in another large quartz tube (9 mm ϕ OD x 70 mm) where 0.7 g of Cu had been placed in the bottom, and 2.0 g of CuO was added. A small amount of thin Ag film was used to cover the top of the thin quartz tube. After evacuation the outer quartz tube was sealed. The tube was first heated in a furnace at 500°C for 30 min and then at 800°C for 2 hours to induce complete oxidation of the kerogen. The CO₂ produced was purified cryogenically using a dry ice-ethanol trap and liquid nitrogen traps. The results reported herein are expressed in the standard δ notation with respect to the PDB standard with the precision for isotope analysis within 0.06‰. The ³⁴S values of the sulfide sulfur and the sulfate sulfur from the rock samples were examined by combining the Kiba reagent method [Sasaki et al. 1979] with some chemical separation techniques and analyzed using a Finnigan Mat delta-E mass spectrometer [Kajiwara et al., 1997].

2.5. Elemental and Carbonate Analysis

Samples were crushed to a fine powder after drying at 40 to 50°C and split into several subsamples for elemental analyses. The analyses of major and minor trace elements of bulk sediments were performed by ion coupled plasma spectrometry (ICP). In the ICP method, 100 mg of powdered sample were decomposed using 5 mL of ultrapure hydrofluoric acid (HF), 3 mL of ultrapure HNO₃ and ultrapure hydrochloric acid (HCl) two times. The solution is diluted with 5 mL of concentrated ultrapure nitric acid (HNO₃) and double-distilled MILLI-Q water to adjust the total volume to exactly 100 mL. The prepared solution was subsequently analyzed by ICP and atomic emission spectrometry at the Geological Survey of Japan. Precision estimated from replicate analyses is within 3%. Solutions prepared from pure chemicals and JB-2, JB-3, JA-1, JA-2, JG-1, and JG-2 from Geological Survey of Japan were used for standards. The reproducibility of these measurements was better than 2%. For measurements of weight percentages of

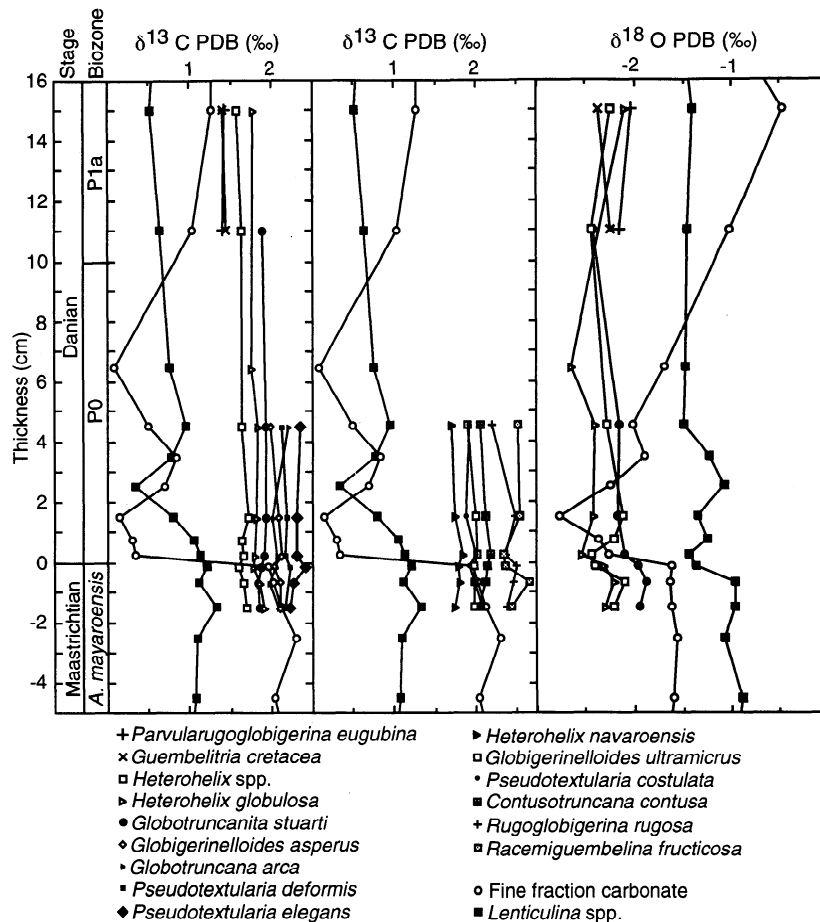


Figure 4. Carbon and oxygen isotopic data of planktonic foraminiferal tests, fine fraction carbonate, and *Lenticulina* spp. between -5 and +15 cm (relative to the K/T boundary designated as 0 cm) in the upper Maastrichtian and lower Danian in the Caravaca Section.

carbonates, concentrated CH_3COOH was used to remove carbonate from powdered samples.

2.6. Clay minerals

For clay mineral analyses the $<2 \mu\text{m}$ fraction of each sample was separated and analyzed by the preferred orientation method on a Rigaku Rint 1200 System X-ray diffractometer using Cu K α radiation at an accelerating voltage of 40 kV and 30 mA. Ethylene glycol was used to saturate the $<2 \mu\text{m}$ oriented clay specimens. Percentage evaluations of clay minerals were based on peak intensity by using 001 reflections of smectite (17 Å), illite (10 Å), and kaolinite (7 Å) on ethylene glycolated samples. The clay indices, smectite/illite, kaolinite/illite, and kaolinite/smectite, were obtained from ratios of illite, kaolinite, and smectite percentages [Robert and Chamley, 1991, 1992; Robert and Kennett, 1992, 1994; Diester-Haass et al., 1993].

2.7. Organic Carbon

Samples were crushed and ground into powder ($<75 \mu\text{m}$) for TOC and rock-eval pyrolysis. Carbonate was removed with cold and then hot (60°C) 6N HCl. Following HCl treatment,

20 mg portions of each sample were analyzed for their organic carbon content using a Yanaco MT-3 CHN analyzer. Approximately 100 mg of the powdered samples were subjected to rock-eval pyrolysis using a Delsi rock-eval II analyzer.

Organic petrography was used to identify organic particles with preparation of organic concentrates obtained through HCl and HF treatment. Using a combination of transmitted low-voltage light and reflected ultraviolet fluorescent light, organic matter was microscopically classified into five main maceral groups using the classification of Sawata and Akiyama [1994].

2.8. Benthic Foraminiferal Oxygen Index

BFOI values were obtained for 30 samples by employing the index described by Kaiho [1994a], which is based on Holocene assemblages from bathyal and abyssal environments and dissolved oxygen values in immediately overlying waters. Variations in oceanic primary productivity, flux of organic carbon to the sediments, and dissolved oxygen levels in the water column are thought to be important in the control of benthic foraminiferal test size, wall thickness, morphology, and species composition of assemblages by many foraminiferal paleontologists. Aspects of these processes should be re-

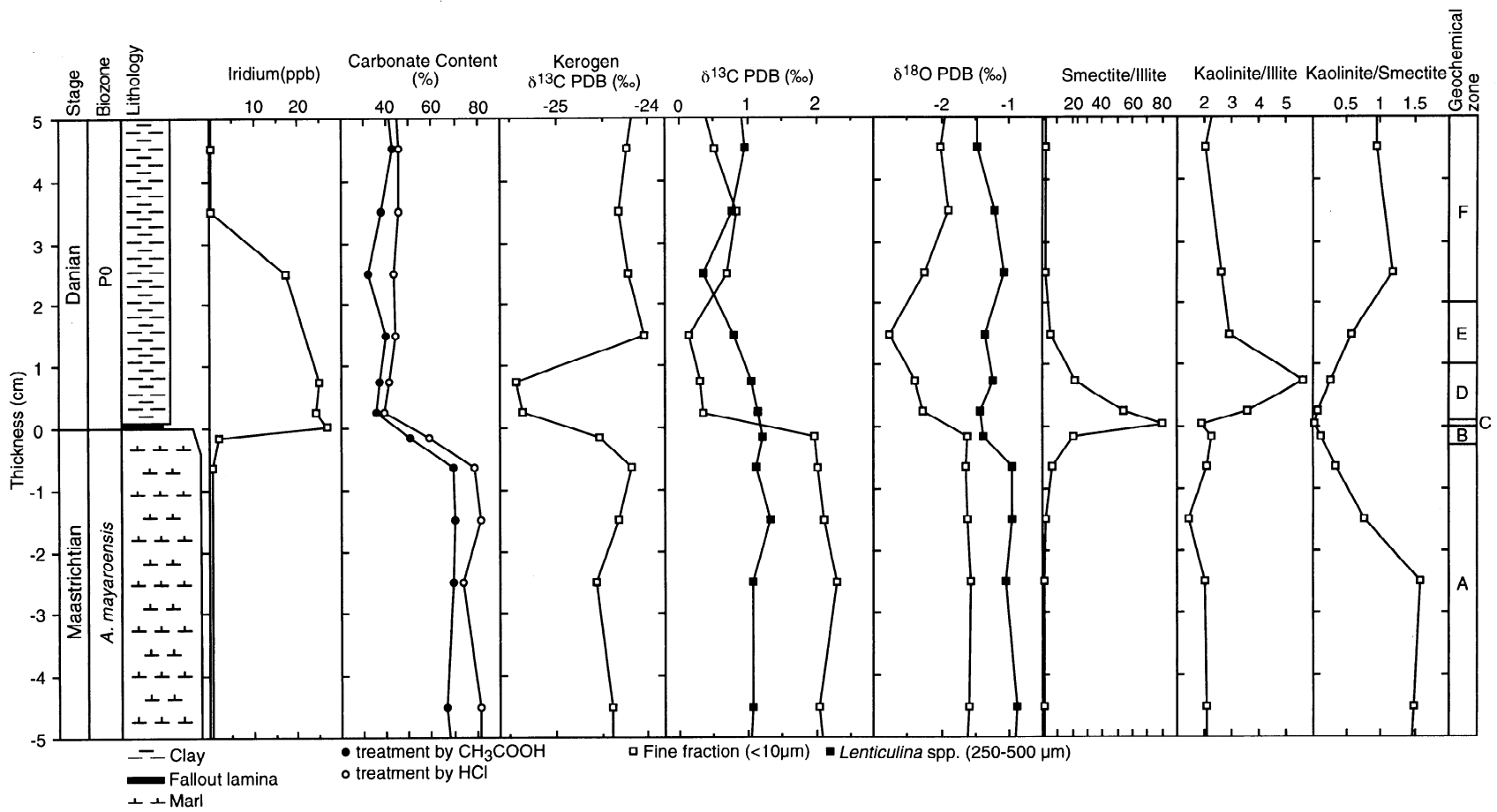


Figure 5. Lithology and geochemical fluctuations between -5 and +5 cm (relative to the K/T boundary designated as 0 cm) in the upper Maastrichtian and lower Danian in the Caravaca section. Ir data are after Smit and Hertogen [1980].

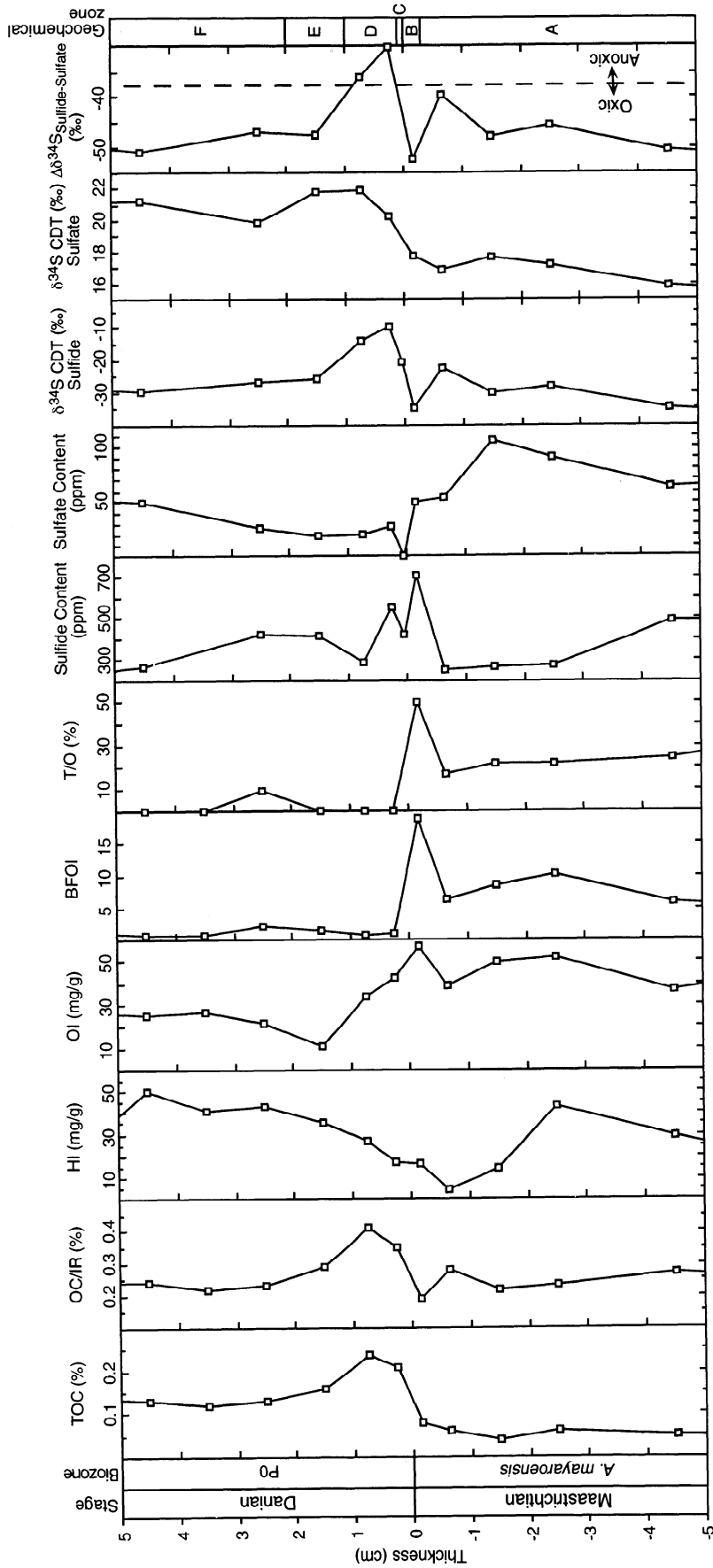


Figure 6. Foraminiferal and geochemical fluctuations between -5 and +5 cm (relative to the K/T boundary designated as 0 cm) in the upper Maastrichtian and lower Danian in the Caravaca section.

flected by the BFOI based on these foraminiferal characteristics. However, analyses indicate that the BFOI correlates most strongly with dissolved oxygen levels in overlying water ($R^2 = 0.81$), weakly with oceanic primary productivity ($R^2 = 0.55$), and weakly with organic carbon flux to the sediments ($R^2 = 0.51$). Although both dissolved oxygen and organic carbon flux are main controlling factors for benthic foraminiferal assemblages, the BFOI is a useful indicator extracted from benthic foraminiferal assemblages for estimating the condition of dissolved oxygen in Cretaceous and Cenozoic oceans [Kaiho, 1999]. Because thick-walled benthic foraminifera dominate the assemblages under more oxic conditions [Kaiho, 1994a], we also analyzed T/O to estimate dissolved oxygen conditions.

3. Results and Discussion

3.1. Geochemical and Foraminiferal Stratigraphy

Geochemical and foraminiferal data are presented on two different scales between -40 and +40 cm (-13 and +30 kyr) and between -5 and +5 cm (-2 and +6 kyr) (Figures 2, 3, and 5-7). This 80 cm thick interval can be subdivided into 7 intervals on the basis of these data.

Strata between -40 and -0.3 cm (A zone) are characterized by (1) high carbonate content, (2) high $\delta^{13}\text{C}$ values of fine fraction carbonate (FFC) and kerogen, (3) high $\delta^{18}\text{O}_{\text{FFC}}$ values, (4) low kaolinite/illite ratios, (5) low TOC and OC/IR, (6) medium OI, (7) medium to high BFOI and T/O, (8) medium sulfide and sulfate contents, (9) low $\delta^{34}\text{S}$ of sulfide and sulfate, (10) low difference values between $\delta^{34}\text{S}$ sulfide and $\delta^{34}\text{S}$ sulfate ($\Delta\delta^{34}\text{S}_{\text{sulfide} - \text{sulfate}}$), (11) relatively low abundance of Fe, Ti, Zn, Ni, V, Mg, Al, Na, and Li, and (12) relatively high abundance of P, Mn, Ca, Sr, Ba, and Y. Strata between -0.3 cm to 0 cm below the K/T boundary (B zone) differ from A zone in having intermediate values between A and D zones in carbonate content, higher sulfide content, higher BFOI, and all of the above mentioned elements. The basal 1 mm of the Danian (C zone), the so-called fallout lamina, is characterized by a reddish brown color; significant concentrations of smectite, Fe, Ti, Zn, Ni, V, Sr, and Ir recording the K/T boundary impact event (Figures 2 and 7) [Smit, 1982]; increases in Mg and Al; and decreases in P, Mn, Ca, Ba, and Y (Figure 7).

The unit between +0.1 and +1 cm (D zone) is distinguished from A and B zones by 32 events including the following: low carbonate content, negative excursion of $\delta^{13}\text{C}_{\text{FFC}}$ (1.8‰ reduction) and $\delta^{13}\text{C}$ of kerogen (0.9‰ reduction); low $\delta^{18}\text{O}_{\text{FFC}}$ values (0.8‰ reduction); a striking decrease in the gradient between $\delta^{13}\text{C}_{\text{FFC}}$ and $\delta^{13}\text{C}$ (*Lenticulina*) ($\Delta\delta^{13}\text{C}_{\text{FFC-BFT}}$); increasing kaolinite/illite and kaolinite/smectite ratios; decreasing smectite/illite ratios; high TOC and OC/IR; increasing HI; decreasing OI; low BFOI; low T/O; high sulfide content (lower part); low sulfate content; high $\delta^{34}\text{S}$ values of sulfide and sulfate; high $\Delta\delta^{34}\text{S}_{\text{sulfide} - \text{sulfate}}$; high abundance in Mg, Al, Na, Li, Fe, Ti, Zn, Ni, and V; and low abundance in P, Mn, Ca, Sr, Ba, and Y. There are no significant changes in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of *Lenticulina* spp., which clearly survived the end of the Cretaceous [Kaiho and Lamolda, 1999], within these samples.

The E zone (+1 to +2 cm) is characterized by minimum values of $\delta^{13}\text{C}_{\text{FFC}}$ and $\delta^{18}\text{O}_{\text{FFC}}$; increasing $\delta^{13}\text{C}$ of kerogen,

kaolinite/smectite and HI; decreasing smectite/illite ratio, kaolinite/illite ratio, TOC, OC/IR, OI, $\Delta\delta^{34}\text{S}_{\text{sulfide} - \text{sulfate}}$; and similar values in the elements except for increasing Y. The F zone (+2 cm to +10 cm) differs from E zone in having higher HI, OI, and $\delta^{18}\text{O}_{\text{FFC}}$ values and lower TOC and OC/IR. A minimum $\delta^{13}\text{C}$ value of *Lenticulina* spp. was recorded in the basal F zone. Medium $\delta^{13}\text{C}_{\text{FFC}}$ and high $\delta^{18}\text{O}_{\text{FFC}}$ values, positive $\Delta\delta^{13}\text{C}_{\text{FFC-BFT}}$, low TOC, decreasing sulfide content, increasing sulfate content, medium BFOI, increasing T/O, low HI, high OI, and recoveries of most elements characterize the G zone (+10 to +40 cm).

3.2. Elemental Analyses

Elements can be divided into three groups on the basis of our analyses: group 1 elements concentrated in the fallout lamina: these include Fe, Ti, Zn, Ni, and V; group 2 elements showed higher contents in the foraminiferal P0 zone and include Li, Na, Mg, and Al; and group 3 elements showed low contents in the P0 zone and include P, Ca, Ba, Mn, Sr, and Y (Figure 7). P, Ca, Ba, Mn, and Y are not concentrated in the fallout layer, but Sr is.

The six elements (Fe, Ti, Zn, Ni, V, and Sr) concentrated in the fallout lamina are heavier (atomic weights are 47.9-87.6) than the group 2 elements (Li, Na, Mg, and Al; atomic weights are 6.9-27.0). The heavier elements are thought to have been introduced with Ir by the impact event at the K/T boundary because they display stratigraphic fluctuations similar to Ir (Figure 7). Mg and Al have maxima in the fallout lamina and intermediate characteristics between the six heavier elements (Fe, Ti, Zn, Ni, V, and Sr) and two lighter elements (Na and Li). Concentrations of four elements (Ca, P, Ba, and Sr) in the group 3 probably correlate with biomass because Ca, P, and Ba are contained in organisms, P is an element controlling oceanic biomass, and Sr has chemical characteristics similar to Ba. The high concentration of Sr in the fallout lamina is due to impact, and low values in the P0 zone are due to the mass extinction at the K/T boundary. Because Mn is accumulated in oxic conditions and is not precipitated in anoxic bottomwater conditions, the content of Mn probably correlates with the dissolved oxygen conditions of bottom waters [Bernier, 1980]. Higher contents in groups 1 and 2 in the P0 zone reflected low contents of Ca in the P0 zone.

Similar changes across the K/T boundary were recognized in the Flaxbourne River section, New Zealand, for Zn, Fe, Mg, Al, Mn, and Sr [Strong et al., 1987] and in Stevns Klint, Denmark, for Fe, Ti, Zn, and Ni [Alvarez et al., 1980]. These latter analyses were not carried out at high stratigraphic resolution.

3.3. Primary Productivity

Five fluorescent visual macerals were observed in the organic concentrates from selected samples (Figure 8). One type, woody/coaly kerogen, is of terrestrial origin and accounts for 40-58% of the kerogens present; the origin of the others cannot be identified. The occurrence of similar percentages of the five maceral groups in all samples may suggest that there was no major change in the origin of kerogens throughout the zones analyzed, but the macerals contain many unknown elements. However, woody/coaly kerogen slightly increase in the E zone.

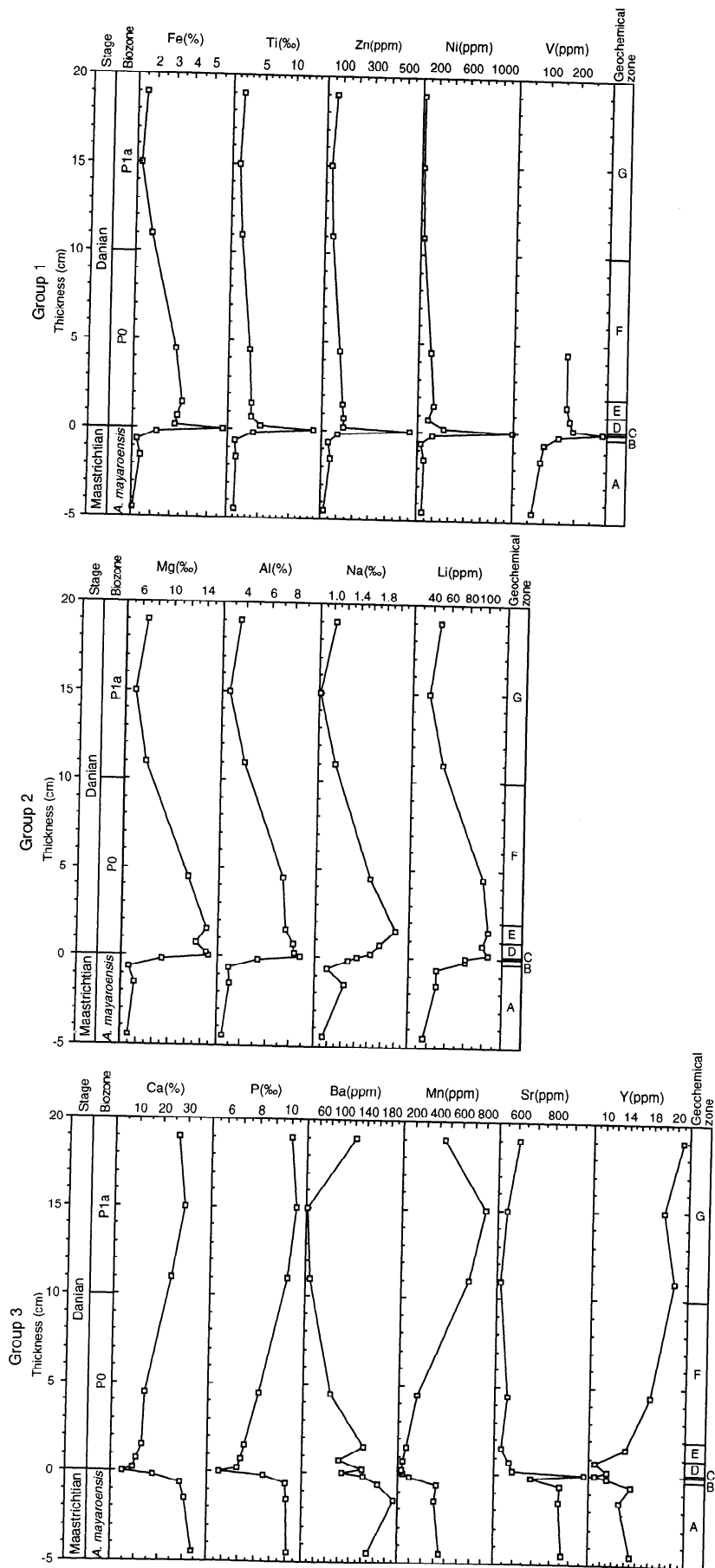


Figure 7. Elemental abundance between -5 and +5 cm in the upper Maastrichtian and lower Danian in the Caravaca section.

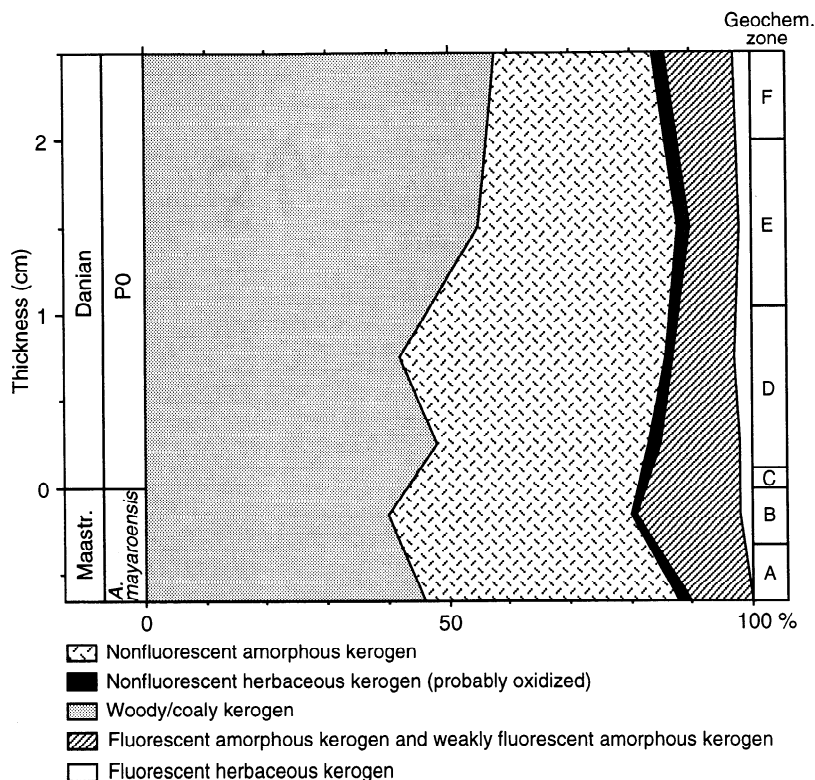


Figure 8. Maceral composition by fluorescent visual kerogen analysis between -1 and +3 cm in the upper Maastrichtian and lower Danian in the Caravaca section.

The negative excursion of $\delta^{13}\text{C}_{\text{FFC}}$ in the D zone is not due to diagenetic effects based on the occurrence of a coincidental negative shift of $\delta^{13}\text{C}$ of kerogen and the constant component of maceral groups. In fact, the negative excursion is a global phenomenon [Perch-Nielsen *et al.*, 1982; Smit, 1982; Zachos and Arthur, 1986; Margolis *et al.*, 1987; Keller and Lindinger, 1989; Zachos *et al.*, 1989a, 1992] probably caused by the mass mortality and the combustion of terrestrial biomass, with subsequent transfer of isotopically light carbon to surface waters [Wolbach *et al.*, 1985; Venkatesan and Dahl, 1989; Ivany and Salawitch, 1993]. Alternatively, there is no rapid reduction of $\delta^{13}\text{C}$ analyzed in *Lenticulina* spp. in the D zone, likely because of the significant reduction of the organic carbon (C_{org}) flux from surface waters to sediments. Positive values of $\Delta\delta^{13}\text{C}_{\text{FFC-BFT}}$ should be observed in a normal ocean because of selective absorption of ^{12}C by phytoplankton and organic carbon flux to sediments. Positive values of $\Delta\delta^{13}\text{C}_{\text{FFC-BFT}}$ ($\sim 1\%$) in the upper Maastrichtian (A and B zones) imply the presence of a normal biological pump supplying C_{org} to sediments (Figure 2). However, the Danian D and E zones and upper part of the F zone are characterized by negative $\Delta\delta^{13}\text{C}_{\text{FFC-BFT}}$ values (-0.8 to -0.7%). The lower part of the F zone has similar values in $\delta^{13}\text{C}_{\text{FFC}}$ and $\delta^{13}\text{C}_{\text{BFT}}$ ($\Delta\delta^{13}\text{C}_{\text{FFC-BFT}} = -0.5$ to -0.3%) because of a gradual decrease in $\delta^{13}\text{C}_{\text{BFT}}$ from the D zone to the lower part of the F zone. Original $\delta^{13}\text{C}$ values of *Lenticulina* tests may be $\sim 1\%$ lower than the measured values because of higher $\delta^{13}\text{C}$ values of cements ($\sim 2.0\%$) relative to the *Lenticulina* test. In this case the upper Maastrichtian strata (A and B

zones) have positive values of $\Delta\delta^{13}\text{C}_{\text{FFC-BFT}}$ ($\sim 2\%$) and the Danian D and E zones and upper part of the F zone are characterized by similar values in $\delta^{13}\text{C}_{\text{FFC}}$ and $\delta^{13}\text{C}_{\text{BFT}}$. The lower part of the F zone has positive values of $\Delta\delta^{13}\text{C}_{\text{FFC-BFT}}$ ($\sim 1\%$). The rapid reduction in $\Delta\delta^{13}\text{C}_{\text{FFC-BFT}}$ at the K/T boundary implies a rapid decrease in the pelagic biomass and significant reduction of C_{org} flux to sediments.

Recovery of $\Delta\delta^{13}\text{C}_{\text{FFC-BFT}}$ and carbonate content started at the base of the planktonic foraminiferal zone P1a or G zone, suggesting increases in primary productivity and C_{org} flux to sediments at this time. Similar changes of $\Delta\delta^{13}\text{C}_{\text{FFC-BFT}}$ (actually bulk samples instead of FFC) are also observed in the K/T boundary section at DSDP sites 577 and 750 [Zachos *et al.*, 1989a, 1992]. The negative excursion of $\delta^{13}\text{C}$ values in *Lenticulina* spp. occurred at 2-3 cm above the negative excursion of $\delta^{13}\text{C}_{\text{FFC}}$. A possible cause of this delay is a time lag for transportation of carbon from surface waters to intermediate waters because of significant reduction of C_{org} flux to sediments. The time lag is estimated as ~ 3 kyr because *Lenticulina* spp. are believed to have inhabited the top 1-2 cm surface sediment [e.g., Kaiho, 1994a]. Other potential reasons for the time lag are diagenesis in one or the other and reworking of benthic foraminifera.

Decreases in Ca, P, and Ba contents at the K/T boundary and low values in the P0 zone also indicate that oceanic primary productivity decreased at the K/T boundary. Recoveries of Ca and P at the base of the P1a zone also imply increases in primary productivity at 13 kyr after the K/T boundary.

3.4. Dissolved Oxygen Changes

The application of the foraminiferal indices BFOI and T/O shows that a rapid decrease in dissolved oxygen levels occurred in the D zone (Figures 3 and 5). BFOI values show a rapid decrease in dissolved oxygen levels from low to medium oxic ($1.5\text{--}3.0\text{ mL L}^{-1}\text{ O}_2$) to low oxic ($1.5\text{--}2.0\text{ mL L}^{-1}\text{ O}_2$) just after the K/T boundary event. The recovery of BFOI and T/O values occurred ~ 13 and $\sim 18\text{--}25$ kyr after the K/T boundary event, respectively.

Marked increases in TOC and OC/IR, increasing HI, and decreasing OI and Mn content in the C or D zones support the hypothesis that dissolved oxygen levels decreased rapidly to a low oxic state during earliest Danian time. Higher HI values in the E and F zones relative to those in the D zone suggest a better state of preservation of organic matter [Demaison and Moore, 1980].

The $\delta^{34}\text{S}$ values of sulfate, with respect to the international standard Canyon Diablo Troilite (CDT), measured during this study range from $15\text{--}18\text{‰}$ in upper Maastrichtian sediments and from $20\text{--}22\text{‰}$ in lower Danian samples. The $\delta^{34}\text{S}$ values of sulfide range from -15 to -10‰ in the basal 1 cm of the Danian (D zone) and from -40 to -20‰ in upper Maastrichtian sediments (A and B zones) and the remaining lower Danian (E to G zones). Therefore the apparent extent of fractionation of sulfides, with respect to the contemporaneous oceanic sulfate ($\Delta\delta^{34}\text{S}_{\text{sulfide-sulfate}}$), during the earliest Danian, is estimated to be in the range of -30 to -36‰ , suggesting that the earliest Danian intermediate waters were anoxic [Kajiwara and Kaiho, 1992]. Alternatively, larger differences of -39 to -53‰ during the late Maastrichtian and the later early Danian interval indicate that the intermediate waters were oxic.

All eight indicators, including BFOI, T/O, TOC, OC/IR, HI, OI, Mn, and $\Delta\delta^{34}\text{S}_{\text{sulfide-sulfate}}$, indicate a rapid decrease in dissolved oxygen levels at the K/T boundary. The subsequent low BFOI, low T/O, higher TOC and OC/IR, higher HI, and low OI indicate that low oxic conditions ($1\text{--}2\text{ mL L}^{-1}\text{ O}_2$) in intermediate waters lasted for ~ 13 kyr after the K/T boundary event. However, the low $\Delta\delta^{34}\text{S}_{\text{sulfide-sulfate}}$ values in the D zone indicate anoxic conditions prevailed for ~ 1 kyr after the K/T boundary event. A similar discrepancy was also recognized in the K/T boundary section at Kawaruppu, Japan, between $\Delta\delta^{34}\text{S}_{\text{sulfide-sulfate}}$ and benthic foraminiferal assemblages [Kaiho, 1992; Kajiwara and Kaiho, 1992]. Although the reason for this discrepancy is unknown, it is possible that short-term or periodic fluctuations of dissolved oxygen conditions may be responsible. There are other possibilities (1) that one or more of the records might be biased by other factors than O_2 or (2) that the various proxies may vary in their sensitivity to O_2 levels.

A coincidental minimum in intermediate water dissolved oxygen levels during the earliest Danian was reported at Kawaruppu, Japan, as evidenced by sulfur isotope ratios [Kajiwara and Kaiho, 1992]. Benthic foraminiferal assemblages from the basal Danian at Caravaca [Coccioni and Galeotti, 1994] and Flaxbourne River Section in New Zealand [Strong et al., 1987] are composed of low oxygen species characterized by thin-walled, flattened, or tapered morphotypes (C. P. Strong, personal communication, 1994). The low oxygen event in intermediate waters immediately after the K/T event was probably a global event. A possible cause of low dis-

solved oxygen conditions just after the K/T event may have been increased oxygen consumption in the intermediate waters in response to an increase in supply of organic matter from terrestrial biomass and sediments redistributed to continental shelves and slopes. Recovery of the TOC, HI, OI, BFOI, T/O, and Mn content occurred ~ 13 kyr after the K/T boundary event (G zone), indicating an increase in dissolved oxygen levels in the intermediate water.

3.5. Climate Changes

The oxygen isotope ratio of FFC decreased 1.2‰ in the basal 2 cm of Danian strata (D-E zone). This indicates that gradual warming occurred in the surface water ~ 1 kyr after the K/T boundary event as marked by the Ir anomaly. If diagenetic effects were causes of the decrease in $\delta^{18}\text{O}_{\text{FFC}}$ values, $\delta^{18}\text{O}$ values of reworked planktonic foraminiferal species in the boundary clay should also have decreased. However, there is no distinct shift in $\delta^{18}\text{O}$ values of reworked planktonic foraminiferal species (Figure 4). This suggests that $\delta^{18}\text{O}_{\text{FFC}}$ values imply paleotemperature in the seawaters.

Kaolinite typically develops in tropical soils on well-drained surfaces of diverse rock types in areas of high precipitation, and its formation requires a minimum soil temperature of $\sim 15^\circ\text{C}$ [Gaucher, 1981]. The ratios of kaolinite to illite and kaolinite to smectite in marine sediments are good indices for estimation of climate changes [e.g., Robert and Kennett, 1994]. Major increases in kaolinite indicate increases in temperature and rainfall. Although the kaolinite/smectite ratio cannot be used for estimation of climate changes between -1 and $+2$ cm because of smectite concentration in the fallout lamina, the kaolinite/illite ratio is a useful proxy. A threefold increase in the kaolinite/illite ratio is recorded in the D zone (Figure 5).

These data suggest that a gradual increase in atmospheric temperature and rainfall occurred in the low latitude Northern Hemisphere beginning between 0 and ~ 0.4 kyr after the boundary and lasted over ~ 3 kyr. Two spikes in the kaolinite/illite ratio in the G zone do not imply a significant warming because of the coincident and relatively constant kaolinite/smectite ratio and high $\delta^{18}\text{O}_{\text{FFC}}$.

Indications of earliest Danian warming were also reported at Caravaca [Romein and Smit, 1981], Agost [Smit, 1990], and Zumaya, Spain [Mount et al., 1986; Margolis et al., 1987], and at El Kef, Tunisia [Perch-Nielsen et al., 1982], as evidenced by a decrease in $\delta^{18}\text{O}$ of FFC or bulk samples in the lower part of the boundary clays. However, a pronounced warming following the boundary has never been documented in detail, although various records show one-point spikes (usually in fine fraction or bulk carbonate) at the boundary or no change at all in the deep sea [Zachos et al., 1992]. It would be difficult to discover evidences of the warming episode because of much lower sedimentation rates in the deep sea than in the continental margins; the P0 zone is especially very thin in the deep sea. This warming would have been a result of the impact-induced release of CO_2 from the carbonate shelf and the ocean's photic zone [O'Keefe and Ahrens, 1989], reduction of primary productivity, and burning of the above-ground biomass. O'Keefe and Ahrens calculated a worldwide increase in temperature from 2 to 10°C for periods of $10^4\text{--}10^5$ years using the impact-induced release of CO_2 from the carbonate shelf and the

ocean's photic zone. Our $\delta^{18}\text{O}_{\text{FFC}}$ data imply an $\sim 5^\circ\text{C}$ warming for periods of 10^2 - 10^3 years.

The very short-term warming of surface water at the K/T boundary did not lead to distinct warming in the intermediate water as evidenced by $\delta^{18}\text{O}$ values in *Lenticulina* spp. Instead, a cooling (recovery of temperature) in the atmosphere and the surface water occurred between 3 and 16 kyr after the K/T boundary event as indicated by an increase in $\delta^{18}\text{O}_{\text{FFC}}$ in the F and G zones and a decrease in kaolinite/illite ratio in the F zone.

4. Conclusions

Fluctuations in HI in the A Zone are probably due to variations in preservation or statistical error associated with low values since five indices (TOC, OC/IR, BFOI, T/O, and $\Delta\delta^{34}\text{S}_{\text{sulfide - sulfate}}$) of dissolved oxygen show no significant changes in the A Zone. Increasing HI, maximum sulfide content, a slight decrease in $\delta^{18}\text{O}$ in *Lenticulina* spp., and intermediate values of 12 elements, carbonate content, and smectite content in the B zone would have been a reflection of the Danian seawater environments because the sediments of the B zone (0.3 cm in thickness) were exposed to Danian seawater. Therefore there is no evidence of pre-events before the K/T boundary event. High concentrations of Fe, Ti, Zn, Ni, V, Ir,

and smectite in the fallout layer are interpreted as due to the bolide impact at the K/T boundary.

A rapid decrease in $\delta^{13}\text{C}_{\text{FFC}}$ and $\delta^{13}\text{C}_{\text{org}}$ values at the K/T boundary was probably caused by combustion of terrestrial biomass and mass mortality. Coincidental rapid reductions in $\Delta\delta^{13}\text{C}_{\text{FFC-BFT}}$, Ca, P, and Ba at the K/T boundary imply rapid mass mortality in the pelagic ecosystem and a significant reduction of C_{org} flux to underlying sediments. Low dissolved oxygen conditions were coincidentally and globally developed in intermediate waters. Although a cause cannot be cited for this latter event, it was likely related to an increase in supply of organic matter from terrestrial biomass and sediments to intermediate waters following the mass mortality event. Global warming occurred with a time lag of 0-3 kyr as a function of the impact-induced release of CO_2 from carbonate sediments, dissolution from the ocean surface, burning of the above-ground biomass, and reduction of primary productivity. Recovery of the calcareous planktonic biomass led to the recovery of the carbonate and P contents and $\Delta\delta^{13}\text{C}_{\text{FFC-BFT}} \sim 13$ kyr after the K/T boundary impact event.

Acknowledgments. We thank K. Minoshima for measurement of elements, T. Yamada for maintenance of a mass spectrometer at Tohoku University, J. C. Ingle for comments on an earlier draft, and R. D. Norris and R. M. Leckie for reviews. This work was partly supported by a grant-in-aid for scientific research from the Ministry of Education, Science and Culture of Japan.

References

- Alvarez, L. W., W. Alvarez, F. Asaro, and H. Michel, Extraterrestrial cause for the Cretaceous-Tertiary extinction, *Science*, 208, 1095-1108, 1980.
- Barreira, E., and G. Keller, Stable isotope evidence for gradual environmental changes and species survivorship across the Cretaceous/Tertiary boundary, *Paleoceanography*, 5, 867-890, 1990.
- Berner, R. A., *Early Diagenesis: A Theoretical Approach*, Princeton Univ. Press, Princeton, N.J., 1980.
- Bhandari, N., P. N. Shukla, and G. C. Castagnoli, Geochemistry of some K/T sections in India, *Palaeoogeogr. Palaeoecol.*, 104, 199-211, 1993.
- Boersma, A., and N. J. Shackleton, Oxygen- and carbon-isotope variations and planktonic-foraminifer depth habitats, Late Cretaceous to Paleocene, Central Pacific, Deep Sea Drilling Project sites 463 and 465, *Initial Rep. Deep Sea Drill. Proj.*, 62, 513-526, 1981.
- Brinkhuis, H., and W. J. Zachariasse, Dinoflagellate cysts, sea level changes and planktonic foraminifers across the Cretaceous-Tertiary boundary at El Haria, northwest Tunisia, *Mar. Micropaleontol.*, 13, 153-191, 1988.
- Canudo, J. I., El Kef blind test I results, *Mar. Micropaleontol.*, 29, 73-76, 1997.
- Canudo, J. I., G. Keller, and E. Molina, Cretaceous/Tertiary boundary extinction pattern and faunal turnover at Agost and Caravaca, S.E. Spain, *Mar. Micropaleontol.*, 17, 319-341, 1991.
- Coccioni, R., and S. Galeotti, K/T boundary extinction: Geologically instantaneous or gradual event? Evidence from deep-sea benthic foraminifera, *Geology*, 22, 779-782, 1994.
- Demaison, G. J., and G. T. Moore, Anoxic environments and oil source bed genesis, *AAPG Bull.*, 64, 1179-1209, 1980.
- D'Hondt, S., and G. Keller, Some patterns of planktonic foraminiferal assemblage turnover at the Cretaceous-Tertiary boundary, *Mar. Micropaleontol.*, 17, 77-118, 1991.
- D'Hondt, S., P. Donaghay, J. C. Zachos, D. Luttenberg, and M. Lindinger, Organic carbon fluxes and ecological recovery from the Cretaceous-Tertiary mass extinction, *Science*, 282, 276-279, 1998.
- Diester-Haass, L., C. Robert, and H. Chamley, Paleocceanographic and paleoclimatic evolution in the Weddell Sea (Antarctica) during the middle Eocene-late Oligocene, from a coarse sediment fraction and clay mineral data (ODP site 689), *Mar. Geol.*, 114, 233-250, 1993.
- Dolenc, T., and J. Pavsic, Elemental and stable isotope variations in the Cretaceous-Tertiary boundary sediments from the Soca Valley, NW Slovenia, *Terra Nova*, 7, 630-635, 1995.
- Elliot, D. H., R. A. Askin, F. T. Kyte, and W. J. Zinsmeister, Iridium and dinocysts at the Cretaceous-Tertiary boundary on Seymour Island, Antarctica: Implications for the K-T event, *Geology*, 22, 675-678, 1994.
- Gaucher, G., *Les Facteurs de la Pedogenese*, 730 pp., G. Lelotte, Dison, Belgium, 1981.
- Ginsburg, R. N., Perspectives on the blind test, *Mar. Micropaleontol.*, 29, 101-103, 1997.
- Herbert, T. D., I. P. Silva, E. Erba, and A. G. Fischer, Orbital chronology of Cretaceous-Paleocene marine sediments, in *Time Scales and Global Stratigraphic Correlations*, vol. 54, edited by W. A. Berggren, et al., pp. 81-93, Soc. of Econ. Paleontol. and Mineral., Tulsa, Oklahoma, 1995.
- Hsü, K. J., and J. A. McKenzie, Carbon-isotope anomalies at era boundaries: Global catastrophes and their ultimate cause, *Geol. Soc. Am. Spec. Pap.*, 247, 61-70, 1990.
- Hsü, K. J., J. A. McKenzie, and Q. X. He, Terminal Cretaceous environmental and evolutionary changes, *Geol. Soc. Am. Spec. Pap.*, 190, 317-327, 1982.
- Huber, B. T., Evidence of planktonic foraminifer working versus survivorship across the Cretaceous-Tertiary boundary at high latitudes, *Geol. Soc. Am. Spec. Pap.*, 307, 319-334, 1996.
- Ivany, L. C., and R. J. Salawitch, Carbon isotopic evidence for biomass burning at the K-T boundary, *Geology*, 21, 487-490, 1993.
- Kaiho, K., A low extinction rate of intermediate-water benthic foraminifera at the Cretaceous/Tertiary boundary, *Mar. Micropaleontol.*, 18, 229-259, 1992.
- Kaiho, K., Benthic foraminiferal dissolved oxygen index and dissolved oxygen levels in the modern ocean, *Geology*, 22, 719-722, 1994a.
- Kaiho, K., Planktonic and benthic foraminiferal extinction events during the last 100 m.y., *Palaeoogeogr. Palaeoecol.*, 111, 45-71, 1994b.
- Kaiho, K., Effect of organic carbon flux and dissolved oxygen on the benthic foraminiferal oxygen index (BFOI), *Mar. Micropaleontol.*, in press, 1999.
- Kaiho, K. and M. A. Lamolda, Catastrophic extinction of planktonic foraminifera at the Cretaceous/Tertiary boundary evidenced by carbon and oxygen isotopes at Caravaca, Spain, *Geology*, 27, 355-358, 1999.
- Kajiwara, Y., and K. Kaiho, Oceanic anoxia at the Cretaceous/Tertiary boundary supported by the sulfur isotopic record, *Palaeoogeogr. Palaeoecol.*, 99, 151-162, 1992.
- Kajiwara, Y., K. Kaiho, and N. Ohkouchi, An invitation to the sulfur isotope study of marine sediments: implications and constraints for the exogenic sulfur cycle, *Annu. Rep. Inst. Geosci. Univ. Tsukuba*, 23, 69-74, 1997.
- Kaminski, M. A., and B. A. Malmgren, Stable isotope and trace element stratigraphy across the Cretaceous/Tertiary boundary in Denmark, *Geol. Föeren. Stockholm Foerh.*, 111, 305-312, 1989.
- Keller, G., Extinction, survivorship and evolution of planktonic foraminifera across the Cretaceous/Tertiary boundary at El Kef, Tunisia, *Mar. Micropaleontol.*, 13, 239-263, 1988.
- Keller, G., Extended period of extinctions across the Cretaceous/Tertiary boundary in planktonic

- foraminifera of continental-shelf sections: Implications for impact and volcanism theories, *Geol. Soc. Am. Bull.* 101, 1408-1419, 1989.
- Keller, G., and M. Lindinger, Stable isotope, TOC and CaCO₃ record across the Cretaceous/Tertiary boundary at El Kef, Tunisia, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 67, 243-265, 1989.
- Kyte, F. T., Z. Zhou, and J. T. Wasson, Siderophile-enriched sediments from the Cretaceous-Tertiary boundary, *Nature*, 288, 651-656, 1980.
- MacLeod, N., and G. Keller, Comparative biogeographic analysis of planktic foraminiferal survivorship across the Cretaceous/Tertiary (K/T) boundary, *Paleobiology*, 20, 143-177, 1994.
- Margolis, S. V., J. F. Mount, E. Doehne, W. Showers, and P. Ward, The Cretaceous/Tertiary boundary carbon and oxygen isotope stratigraphy at Zumaya, Spain, *Paleoceanography*, 2, 361-377, 1987.
- Mount, J. F., S. V. Margolis, W. Showers, and P. Ward, Carbon and oxygen isotope stratigraphy of the upper Maastrichtian, Zumaya, Spain: A record of oceanographic and biologic changes at the end of the Cretaceous Period, *Palaios*, 1, 87-92, 1986.
- O'Keefe, J. D., and T. J. Ahrens, Impact production of CO₂ by the Cretaceous/Tertiary extinction bolide and the resultant heating of the Earth, *Nature*, 338, 247-249, 1989.
- Olsson, R. K., El Kef blind test III results, *Mar. Micropaleontol.*, 29, 80-84, 1997.
- Perch-Nielsen, K., J. Mckenzie, and Q. He, Biostratigraphy and isotope stratigraphy and the "catastrophic" extinction of calcareous nannoplankton at the Cretaceous/Tertiary boundary, *Geol. Soc. Am. Spec. Pap.*, 190, 353-371, 1982.
- Robert, C., and H. Chamley, Paleoenvironmental significance of clay mineral associations at the Cretaceous-Tertiary passage, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 79, 205-219, 1990.
- Robert, C., and H. Chamley, Development of early Eocene warm climates, as inferred from clay mineral variations in oceanic sediments, *Global Planet. Change*, 89, 315-331, 1991.
- Robert, C., and H. Chamley, Late Eocene-early Oligocene evolution of climate and marine circulation: Deep-sea clay mineral evidence, in *The Antarctic Paleoenvironment: A Perspective on Global Change*, Antarct. Res. Ser., vol. 56, edited by J. P. Kennett, and D. A. Warnke, pp. 97-117, AGU, Washington, D. C., 1992.
- Robert, C., and J. P. Kennett, Paleocene and Eocene kaolinite distribution in the South Atlantic and Southern Ocean: Antarctic climatic and paleoceanographic implications, *Mar. Geol.*, 103, 99-110, 1992.
- Robert, C., and J. P. Kennett, Antarctic subtropical humid episode at the Paleocene-Eocene boundary: Clay-mineral evidence, *Geology*, 22, 211-214, 1994.
- Romein, A. J. T., and J. Smit, The Cretaceous/Tertiary boundary: Calcareous nannofossils and stable isotopes, *Proc. K. Ned. Akad. Wet., Ser. B*, 84, 295-314, 1981.
- Sarkar, S. K., P. N. Bhattacharya, P. N. Shukla, N. Bhandari, and D. P. Naidin, High-resolution profile of stable isotopes and indium across a K/T boundary section from Koshak Hill, Mangyshlak, Kazakhstan, *Terra Nova*, 4, 585-590, 1992.
- Sasaki, A., Y. Anikawa, and R. E. Folinsbee, Kiba reagent method of sulfur extraction applied to isotopic work, *Bull. Geol. Surv. Jpn.*, 30, 241-245, 1979.
- Sawata, K., and M. Akiyama, Carbon isotope composition of macerals separated from various kerogens by density separation method (in Japanese with English abstract), *J. Jpn. Assoc. Pet. Technol.*, 59, 244-255, 1994.
- Schmitz, B., G. Keller, and O. Stenvall, Stable isotope and foraminiferal changes across the Cretaceous-Tertiary boundary at Stevns Klint, Denmark: Arguments for long-term oceanic instability before and after bolide-impact event, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 96, 233-260, 1992.
- Smit, J., Extinction and evolution of planktonic foraminifera after a major impact at the Cretaceous/Tertiary boundary, *Geol. Soc. Am. Spec. Pap.*, 190, 329-352, 1982.
- Smit, J., Meteorite impact, extinctions and the Cretaceous-Tertiary boundary, *Geologie en Mijnbouw*, 69, 187-204, 1990.
- Smit, J., and J. Hertogen, An extraterrestrial event at the Cretaceous-Tertiary boundary, *Nature*, 285, 198-200, 1980.
- Smit, J., and A. J. Nederbragt, Analysis of the El Kef blind test II, *Mar. Micropaleontol.*, 29, 94-100, 1997.
- Smit, J., and A. J. T. Romein, A sequence of events across the Cretaceous-Tertiary boundary, *Earth Planet. Sci. Lett.*, 74, 155-170, 1985.
- Smith, A. G., A. M. Hurley, and J. C. Briden, *Phanerozoic Paleogeographic World Maps*, 102 pp., Cambridge Univ. Press, New York, 1981.
- Stott, L. D., and J. P. Kennett, The paleoceanographic and paleoclimatic signature of the Cretaceous/Tertiary boundary in the Antarctic: Stable isotopic results from ODP Leg 113, *Proc. Ocean Drill. Program Sci. Results*, 113, 829-848, 1990.
- Strong, C. P., R. R. Brooks, S. M. Wilson, R. D. Reeves, C. J. Orth, X.-Y. Mao, L. R. Quintana, and E. Anders, A new Cretaceous-Tertiary boundary site at Flaxbourne River, New Zealand: Biostratigraphy and geochemistry, *Geochim. Cosmochim. Acta*, 51, 2769-2777, 1987.
- Tredoux, M., M. J. De Wit, R. J. Hart, N. M. Lindsay, B. Verhagen, and J. P. F. Sellschop, Chemostratigraphy across the Cretaceous-Tertiary boundary and a critical assessment of the iridium anomaly, *J. Geol.*, 97, 585-605, 1989.
- Venkatesan, M. I., and J. Dahl, Organic geochemical evidence for global fires at Cretaceous/Tertiary boundary, *Nature*, 338, 57-60, 1989.
- Wolbach, W. S., R. S. Lewis, and E. Anders, Cretaceous extinctions: Evidence for wildfires and search for meteoric material, *Science*, 230, 167-170, 1985.
- Zachos, J. C., and M. A. Arthur, Paleocyanography of the Cretaceous/Tertiary boundary event: Inferences from stable isotopic and other data, *Paleoceanography*, 1, 5-26, 1986.
- Zachos, J. C., M. A. Arthur, and W. E. Dean, Geochemical evidence for suppression of pelagic marine productivity at the Cretaceous/Tertiary boundary, *Nature*, 337, 61-64, 1989a.
- Zachos, J. C., M. A. Arthur, and W. E. Dean, Geochemical and paleoenvironmental variations across the Cretaceous/Tertiary boundary, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 69, 245-266, 1989b.
- Zachos, J. C., M.-P. Aubry, W. A. Berggren, T. Ehrendorfer, F. Heider, and K. C. Lohmann, Chemobiostratigraphy of the Cretaceous/Paleocene boundary at Site 750, Southern Kerguelen Plateau, *Proc. Ocean Drill. Program Sci. Results*, 120, 961-977, 1992.

T. Arinobu, Mineral and Fuel Resource Department, Geological Survey of Japan, Ibaraki, 305-8567 Japan.

A. Hirai, Technical Research Center, Teikoku Oil Company Limited, Tokyo, 157 Japan.

R. Ishiwatari, Department of Chemistry, Tokyo Metropolitan University, Tokyo, 192-03 Japan.

K. Kaiho, Institute of Geology and Paleontology, Tohoku University, Sendai, 980-8578 Japan. (Kaiho@dges.tohoku.ac.jp)

Y. Kajiwara, Institute of Geoscience, University of Tsukuba, Ibaraki, 305-8571 Japan.

H. Kawahata, Marine Geology Department, Geological Survey of Japan, Ibaraki, 305-8567 Japan.

M. A. Lamolda, Paleontología Facultad de Ciencias, Universidad del País Vasco, Lejona 48940, Spain.

N. Takeda, Japex Research Center, Chiba, 261 Japan.

K. Tazaki and M. Ueshima, Department of Earth Sciences, Kanazawa University, Kanazawa, 920-11 Japan.

(Received August 11, 1998;

revised April 6, 1999;

accepted April 7, 1999.)