Paleoceanographic changes across the Cretaceous-Tertiary boundary: carbon and nitrogen isotope stratigraphy at the Agost section, Spain

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Introduction

The catastrophic events at the Cretaceous-Tertiary (K/T) boundary caused major biogeochemical disturbances, which affected the world's oceans on a global scale. Numerous carbon isotope studies of deep-sea carbonates from widely distributed locations document these changes, but only limited data for the carbon and nitrogen isotopic composition of the syngenetic organic matter are available. In this paper, we combine the inorganic C with organic C and N isotope stratigraphy at the Agost section (SE Spain) to illustrate the biogeochemical and paleoceanographic changes across the K/T boundary.

Results

The $\delta^{13}C$ value of bulk carbonate shows an abrupt negative shift of 1.9‰ at the K/T boundary and a gradual increase towards pre-excursion values over the next 40 cm (Fig. 1). The $\delta^{13}C$ value of the benthic foraminifera shows only a slight positive shift of approximately 0.2‰ across the boundary. Prior to the boundary, the benthic $\delta^{13}C$ values are less than the planktic producing a normal marine surface-to-bottom water carbon isotope gradient. After the boundary, the gradient is inverted. The $\delta^{13}C$ values of the kerogen shows a negative shift of 1.6‰ at 1.5 cm above the boundary followed by a positive anomaly over the next 30 cm. The $\delta^{15}N$ values of the kerogen, in contrast, remain relatively constant across the boundary.

Discussion

A negative carbon isotope shift in the carbonate has been observed in many K/T boundary sequences, reflecting a globally synchronous phenomenon. This shift has been attributed to decreased productivity after the boundary, which led to a relative increase in the abundance of ^{12}C in the dissolved inorganic carbon (DIC) reservoir of surface waters. Where benthic isotope data are available, the shift is usually associated with a collapse in the surface-to-bottom water carbon isotope gradient. At Agost, however, the carbon isotope anomaly is synchronous with an inverted carbon isotope gradient with the $\delta^{13}C$ value of benthic foraminifera being greater than for the bulk carbonate. An inverted gradient was also recorded at El Kef (Tunisia) section, which like Agost was located in the Tethys Ocean. A normal gradient is produced by a combination of photosynthetic activity in the surface waters and respiration of sinking organic matter in the underlying waters. A possible change in the food chain during the earliest Tertiary, whereby bacteria occupied ecological niches previously reserved for the now extinct zooplankton becoming the dominant surface-water 'grazers', could have produced such an inverted gradient (Hsü and McKenzie, 1990). In modern oceans, most organic matter leaving the surface waters sinks locked up in fecal pellets. In the earliest Tertiary, fecal pellet producers had been decimated, and we propose that most of the photosynthesized organic matter remained in the upper water masses. As a result, microbial respiration in the surface waters increased greatly producing the observed enrichment of ^{12}C in surface waters relative to the bottom waters. This phenomenon has be called a 'respiring ocean' to denote the enhanced role of bacteria after the mass mortality at the K/T boundary (Hsü and McKenzie, 1990). At Agost, the inverted gradient persists for some time even as primary productivity recovered, as indicated by a return to pre-boundary $\delta^{13}C$ values for the surface water DIC.

The significant decrease in the $\delta^{13}C$ value of the kerogen immediately above the boundary could be a reservoir affect recording the drastic decrease in photosynthetic removal of ^{12}C with mass mortality. But, this decrease is quickly followed by increased $\delta^{13}C$ values in the kerogen associated with decreased $\Delta^{13}C$(carb.-kero.) values (Fig. 1).

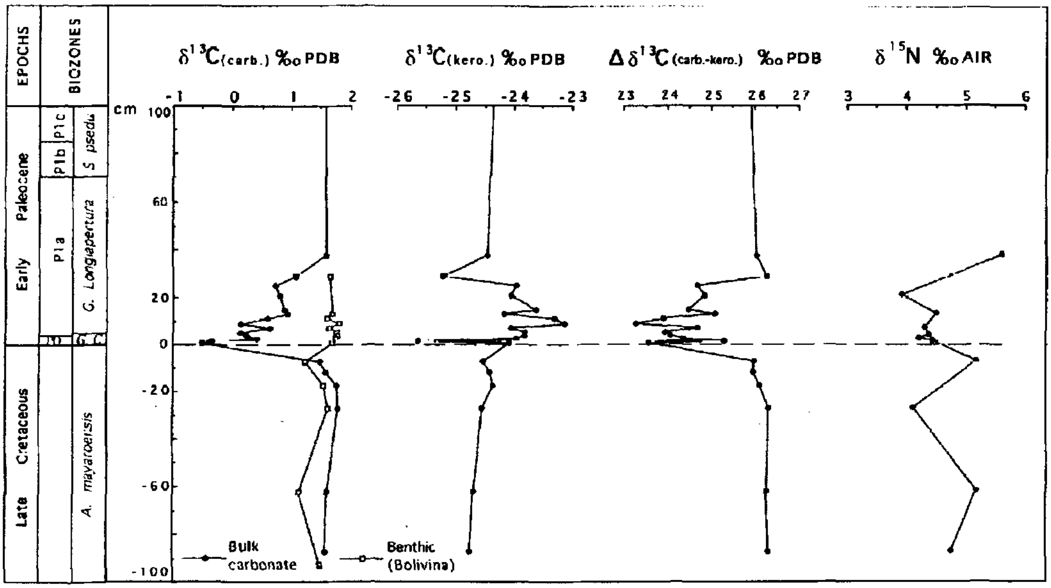

FIG. 1.

These trends were interpreted as being caused by a decrease in dissolved CO_2 in surface waters resulting from unusual nannoplankton blooms at the beginning of the Tertiary (Hollander *et al.*, 1993). The $\delta^{15}N$ values of the kerogen, however, do not support this hypothesis, as a positive shift would be expected due to the high nitrate consumption which is normally observed during phytoplankton blooms (Altabet and Francois, 1994). In fact, the lack of significant changes in the $\delta^{15}N$ values of the kerogen may reflect that nitrate, which is normally the limiting nutrient in modern oceans, was never significantly depleted in the water column after the K/T boundary event, implying low rates of productivity.

A second explanation for the observed trends could be related to small changes in the pH of surface waters with the proposed increased bacterial respiration. Recent work by Hinga *et al.* (1994) has shown a large pH dependence (2.7‰/0.1 pH unit) in the fractionation between DIC and phytoplankton organic matter produced. The observed decrease of 1 to 1.5‰ in $\delta^{13}C$ values at Agost would represent a decrease of about 0.05 pH units. Thus, a small change in sea water pH after the K/T boundary, rather than increased productivity, could have caused the decrease in $\Delta^{13}C$ (carb.-kero.) observed in the studied samples.

References

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