Contents lists available at ScienceDirect



Palaeogeography, Palaeoclimatology, Palaeoecology

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A spike of woody plant biomarkers in the deep-sea iridium layer at the Cretaceous/Paleogene boundary

the result of an asteroid impact.



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A R T I C L E I N F O

Received in revised form 11 July 2014

Received 11 November 2013

Available online 12 August 2014

Accepted 28 July 2014

Planktonic foraminifera

Cretaceous-Paleogene

Article history:

Kevwords:

Biomarker

Plant Mass extinction

Anoxia

ABSTRACT

At the Cretaceous/Paleogene (K/Pg) boundary, 66 million years ago, the Chixulub impact resulted in significant environmental changes and a mass extinction of dinosaurs and marine invertebrates such as ammonites. Here, we report that accumulation of woody plant biomarkers in the deep water occurred in the iridium anomaly at ~700 km from the impact crater. The results reveal that the concentration of terrestrial organic molecules derived from woody plants, namely biphenyl and dibenzofuran, shows synchronized changes and increases abruptly in the red layer (fine ejecta), which has an iridium spike, above tsunami-like coarse deposits indicating a significant increase in the influx of woody plant fragments into the ocean a few years after the impact. Long-chain *n*-alkanes and cadalene derived from land vegetation in the tsunami-like coarse deposits prior to the transportation of trees were also transported to the deep sea. This implies that transportation of grass to the deep sea started within a few days of the bolide impact. Transportation of trees then began a few years later. A rapid increase in the concentration of dibenzothiophenes also occurs in the red layer, indicating that low-dissolved-oxygen conditions had expanded in the bathypelagic zone over the seafloor. An increase in the influx of terrestrial organic matter into the deep ocean could have resulted in the low-dissolved-oxygen conditions. Furthermore, the stratigraphic

distribution of planktonic foraminifera at Beloc shows that Cretaceous planktonic foraminifera became extinct as

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1. Introduction

The K/Pg mass extinction, which is one of the five largest mass extinctions in Earth's history (Raup and Sepkoski, 1982), was likely triggered by the impact of an extraterrestrial body (e.g., Alvarez et al., 1980; Schulte et al., 2010) because extinction of Cretaceous planktonic foraminifera coincided with a bolide impact at the K/Pg boundary (Kaiho and Lamolda, 1999; Norris et al., 1999). It is proposed that the impact resulted in abrupt environmental changes, such as a global dust cloud (darkness and cooling), sulfate aerosols (darkness and cooling) and acid rain (e.g., Sigurdsson et al., 1992; Pope et al., 1994; Hildebrand, 2007). These environmental changes caused land vegetation destruction at the K/Pg boundary (e.g., Wolfe and Upchurch, 1986; Arinobu et al., 2005; Mizukami et al., 2013). In North America, palynological and megafloral paleobotanical studies have demonstrated that vegetation, consisting mainly of angiosperms, collapsed in coincidence with the iridium anomaly (Tschudy et al., 1984; Wolfe and Upchurch, 1986; Pillmore et al., 1999). In New Zealand, an abrupt decrease in gymnosperms and a disappearance of angiosperms at the K/Pg boundary have been reported (Vajda et al., 2001; Ferrow et al., 2011). Vajda and McLoughlin (2004) demonstrated a dramatic decrease in angiosperms and gymnosperms followed by vegetation succession, as indicated by an increase in fern spores (fern spike) after fungal dominance. Saito et al. (1986) have shown a fern spike and an abrupt decrease in angiosperms and gymnosperms in Kawaruppu, Japan. This fern spike, which is evidence of vegetation destruction, has been identified only in North America, New Zealand, and Japan. Nichols and Johnson (2008) have concluded that the change in land vegetation across the K/Pg boundary remains almost unknown, except for North America.

The impact resulted in environmental changes not only on land but also in the ocean. Dysoxic conditions in the mesopelagic zone expanded across the K/Pg boundary in the ocean. Kajiwara and Kaiho (1992) have indicated low-oxygen conditions in the earliest Danian intermediate water by sulfur isotope analysis of whole rock sulfide in the Kawaruppu section, Japan. Intermediate water oxygen minima during the earliest Danian at Stevns Klint in Denmark were reported based on sulfur isotope analysis of pyrite (Schmitz et al., 1988; Kajiwara and Kaiho, 1992). At Flaxbourne River in New Zealand and Caravaca in Spain, low-oxygen conditions have been demonstrated by changes in benthic foraminiferal assemblages (Strong et al., 1987; Coccioni and Galeotti, 1994). Dysoxic conditions at Caravaca have also been shown, as evidenced by the benthic foraminiferal oxygen index (BFOI), total organic carbon (TOC), the ratio of thick-walled oxic foraminifera relative to all oxic foraminifera, the hydrogen index, the oxygen index, Mn content,

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and $\Delta \delta^{34}$ S_{sulfide} – sulfate (Kaiho et al., 1999). Mo, U, and V richness at the impact layer of Caravaca demonstrates euxinic conditions (De Oca et al., 2013). Low-oxygen conditions were detected by the benthic foraminiferal oxygen index (BFOI; Kaiho, 1994, 1999) in the basal part of the *Guembelitria cretacea* zone at Agost, Spain (Algret and Thomas, 2005). Here, we report as one of the results of this study the dissolved oxygen conditions at Beloc, Haiti. The Caravaca, Agost, and Beloc sections all consist of pelagic pale-gray marls with abundant microfossils (Maurasse and Sen, 1991; Algret and Thomas, 2005).

Organic geochemical studies of the K/Pg boundary sediments have been conducted to some extent. The quick resurgence of algal primary productivity less than 1 kyr after the impact has been demonstrated, as evidenced by stable isotopes of carbon and nitrogen and the abundances of algal steranes and bacterial hopanes in Stevns Klint (Sepúlveda et al., 2009). An abrupt increase in terrestrial organic matter caused by land vegetation destruction resulted in low-dissolved-oxygen conditions across the K/Pg boundary in Caravaca according to the distribution of sedimentary organic molecules such as long-chain *n*-alkanes and dibenzothiophenes (Mizukami et al., 2013).

In this report, we provide a planktonic foraminiferal biostratigraphy and high-resolution profiles of the changes in the distribution of biomarkers, indicating changes in soil erosion and oceanic redox, across the K/Pg boundary, at Beloc, Haiti.

2. Geologic setting and samples

The Beloc K/Pg section is located in southern Haiti (Fig. 1). Haiti was located approximately 700 km south of Chixulub at the end-Cretaceous (Olsson et al., 1997). In this study, we analyzed the stratotype section in Beloc, Haiti (Maurasse and Sen, 1991). In the K/Pg section at Beloc, coarse ejecta, which include spherules and impact glasses, directly overlies uppermost Maastrichtian marlstones, which contain many large planktonic foraminifera (Fig. 2). The coarse ejecta reveal no consistent vertical size gradation. Maurasse and Sen (1991) suggested that this sedimentological feature is due to a tsunami effect. This layer is about 60 cm thick and overlain by very fine sandstones and marls, which are about 13 cm and 10 cm thick, respectively. Within the marls, a 1–2-cm rust-orange clay layer, referred to as the red layer (or fine ejecta), contains the iridium (Ir) anomaly (Maurasse and Sen, 1991). These coarse ejecta, sandstones, marls, and the red layer are collectively referred to as the K/Pg sandstone complex (Smit et al., 1996). Smit (1999) has defined

the K/Pg boundary as the base of the coarse ejecta because the K/Pg sandstone complex was produced by the impact. The upper part of the marls is overlain by Danian limestones, which contain small planktonic foraminifera (Fig. 2). In this paper, the base of the coarse ejecta (K/Pg boundary) is set to 0 cm, with the heights of lower and upper strata described relative to it. Maurasse and Sen (1991) have reported on the planktonic foraminiferal biostratigraphy at the Beloc stratotype section. They identified *Globigerina eugubina*, a Paleogene species, below the red layer.

The paleowater depth of the Beloc section has been estimated as >2000 m (Maurasse and Sen, 1991). However, in contrast, Keller et al. (2001) showed that the Beloc section represents a paleowater depth of 1000–1500 m. At the very least, the depositional environments of Beloc were in the bathypelagic zone in deep water.

The sandstone complex may be the result of disturbance by the tsunami. Therefore, the sandstone beds record events of one day starting from the impact. The red layer showing the Ir anomaly should have been deposited in approximately one year or a few years due to material remaining in the stratosphere.

The sandstones are poorly sorted, and the matrix is composed of pale-gray marl. Therefore, the preservation of organic molecules in the sandstones is thought to be similar to that in the marlstones. The matrix also contains calcareous nanoplankton and planktonic foraminifera, but few benthic foraminifera. The sandstone complex does not contain terrestrial plant remains or shallow carbonate fossils. It is composed mostly of marine source matrix and ejecta that include microspherules. The marine sediments were redeposited in the ocean and mixed with the ejecta.

3. Methods

3.1. Analysis of planktonic foraminifera

We used a total of 21 marl, sandstone, or siltstone samples from 10 cm below to 91 cm above the base of the K/Pg sandstone complex. We disaggregated 50 g, 25 g, and 12.5 g of each sample in 5% hydrogen peroxide, washed them through a 32-µm screen, and dried them, obtaining about 200 specimens from each. When 200 specimens could not be obtained, we collected as many specimens as possible. However, planktonic foraminifera could not be quantified because Danian marl-stones could not be disaggregated by standard processing techniques



Fig. 1. Paleomap showing the studied section (Beloc) and locations mentioned in this paper.

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