



Environmental and vegetational changes recorded in sedimentary leaf wax *n*-alkanes across the Cretaceous–Paleogene boundary at Loma Capiro, Central Cuba

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ABSTRACT

The stable carbon isotopic compositions ($\delta^{13}\text{C}$) and chain-length distribution [ACL and $n\text{-C}_{31}/(n\text{-C}_{29} + n\text{-C}_{31})$] of sedimentary leaf wax *n*-alkanes were investigated across the Cretaceous–Paleogene (K–Pg) boundary at Loma Capiro, Central Cuba, to reconstruct paleoenvironmental changes that are recorded in terrestrial higher plants. The stratigraphic profiles of the *n*-alkane $\delta^{13}\text{C}$ values show a negative excursion in the lowermost Paleocene, although its magnitude is much smaller ($\sim 0.3\text{‰}$) than the global signals (1.5 to 2.0‰) in the surface ocean–atmospheric carbon reservoir. Relations between the *n*-alkane $\delta^{13}\text{C}$ values and the $\text{C}_{31}/(\text{C}_{29} + \text{C}_{31})$ ratios exhibit two different trends, suggesting that our $\delta^{13}\text{C}$ records are likely affected by two types of paleoenvironmental factors in addition to the $\delta^{13}\text{C}$ variations in the exogenous carbon reservoir. Rare occurrence of terrigenous organic matter that is usually transported by rivers suggests that the *n*-alkanes at Loma Capiro are likely to have been transported by trade winds, which recorded paleoenvironmental conditions of the northwestern part of the African continent. The *n*-alkane $\delta^{13}\text{C}$ values show a parallel decrease with the ACL and $\text{C}_{31}/(\text{C}_{29} + \text{C}_{31})$ values in the first 37,000 yr following the K–Pg boundary. Such decreases are consistent with plant physiological responses to reduced net evaporation, suggesting a possible influence of the impact-induced warm-humid condition in the early Paleocene. In contrast, the *n*-alkane $\delta^{13}\text{C}$ values are negatively correlated with the $\text{C}_{31}/(\text{C}_{29} + \text{C}_{31})$ ratios from 40,000 to 67,000 yr after the K–Pg boundary. This time period matches well with that required for the recovery of terrestrial floras from the K–Pg mass extinction to those with diversity equivalent to the late Cretaceous, suggesting that the *n*-alkane signals are also likely affected by the plant diversification process after the mass extinction.

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1. Introduction

The mass extinction event at the Cretaceous–Paleogene (K–Pg) boundary is one of the five largest mass extinction events in the Phanerozoic. More than 15% of fossil families went extinct in the ocean (Raup and Sepkoski, 1982), and 15% to 57% of diverse Cretaceous flora abruptly disappeared on land (Orth et al., 1981; Wolfe and Upchurch, 1987; Johnson et al., 1989; Vajda and Raine,

2003; Wilf and Johnson, 2004; Nichols, 2007). The stable carbon isotopic compositions ($\delta^{13}\text{C}$) of the surface ocean (e.g. Hsü et al., 1982; Gilmour et al., 1987; Keller and Lindinger, 1989; Meyers and Simoneit, 1990; Meyers, 1992; Hollander et al., 1993) and terrestrial sedimentary carbon (Schimmelmann and DeNiro, 1984; Arinobu et al., 1999; Arens and Jahren, 2000, 2002) show an abrupt negative excursion at the K–Pg boundary, suggesting a large impact of this mass extinction on global carbon cycles. Combined stratigraphical, micropaleontological, petrological and geochemical data show that this mass extinction was triggered by a large asteroid impact at Chicxulub on Yucatan peninsula, Mexico (Schulte et al., 2010).

The $\delta^{13}\text{C}$ values of terrestrial higher plants are primarily controlled by the isotopic composition of atmospheric CO_2 (Farquhar et al., 1982; Arens et al., 2000). Therefore, stratigraphic records of plant $\delta^{13}\text{C}$ values can provide good constraints on the rate and magnitude of disruption in the global carbon cycles. The $\delta^{13}\text{C}$ excursion in

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sedimentary leaf wax *n*-alkanes implies a loss of at most 24% of the Cretaceous biomass at the boundary (Arinobu et al., 1999).

On the other hand, the $\delta^{13}\text{C}$ values of terrestrial higher plants are also sensitive to isotopic fractionations that reflect ecological and physiological responses to their growing environment (Farquhar et al., 1989; Arens et al., 2000), as well as taxonomic variations within contributing plant communities (Arens and Jahren, 2002). Because abundant evidence suggest a global turnover in vegetation (Vajda and Raine, 2003) and changes in continental climate (Wolfe and Upchurch, 1987; Lehman, 1990; Wolfe, 1990) at the K–Pg boundary, these changes might have affected the $\delta^{13}\text{C}$ values of terrestrial higher plants. In fact, the magnitudes of the $\delta^{13}\text{C}$ excursions recorded in terrigenous organic matter across the K–Pg boundary range from -1.1 to -2.8‰ (Arinobu et al., 1999; Arens and Jahren, 2000, 2002), exhibiting much larger variations than those caused by the plant vital effects ($\sim 0.8\text{‰}$; Arens and Jahren, 2002). However, the causes for these $\delta^{13}\text{C}$ variations still remain unclear.

Several studies have shown that comparison of the $\delta^{13}\text{C}$ fluctuations of terrigenous organic matter with those in the exogenous carbon reservoir, such as marine carbonate, is useful to reconstruct paleoenvironmental signals that are recorded in terrestrial higher plants (e.g. Hasegawa et al., 2003). However, this approach cannot be utilized for K–Pg boundary sequences because the shape and magnitude of the $\delta^{13}\text{C}$ changes of marine carbonates are also affected by changes in calcareous microfossil compositions, size distributions of planktonic foraminiferal species, and local productivity (D'Hondt and Zachos, 1993; Barrera and Keller, 1994).

Long chain (C_{27} to C_{33}) *n*-alkanes with an odd/even carbon number predominance are typical of terrestrial higher plant waxes (Eglinton and Hamilton, 1967). These *n*-alkanes are ubiquitous in marine sediments (Pancost and Boot, 2004), and their chain-length distributions are sensitive to changes in the plant growing environment and the composition of their source vegetation (Hall and Jones, 1961; Poynter et al., 1989; Schefuß et al., 2003; Sachse et al., 2006). Hence, we assess paleoenvironmental conditions that may have been recorded in terrestrial higher plants using two *n*-alkane biomarker proxies based on their chain-length distribution, i.e., the average chain length (ACL_{27-33}) and the $\text{C}_{31}/(\text{C}_{29} + \text{C}_{31})$ ratio. The ACL_{27-33} is the concentration-weighted mean chain length of the C_{27} to C_{33} odd carbon number *n*-alkanes (Poynter et al., 1989), and its variations are generally related to environmental changes such as the temperature and aridity in which their source vegetation grows (Gagosian and Peltzer, 1986; Poynter et al., 1989; Rommerskirchen et al., 2003; Schefuß et al., 2003). In contrast, the $\text{C}_{31}/(\text{C}_{29} + \text{C}_{31})$ ratio is the concentration ratio of the C_{31} *n*-alkanes to the sum of the C_{29} and C_{31} *n*-alkanes (Schefuß et al., 2003), and its variations are more closely related to changes in aridity, than in temperature and vegetation type (Schefuß et al., 2003).

The ultimate objective of this study is to reconstruct the environmental and vegetational changes that may be recorded in the $\delta^{13}\text{C}$ variations across the K–Pg boundary. Here we report the results from the hemipelagic K–Pg sequence at Loma Capiro, central Cuba, in which a published planktonic foraminiferal biostratigraphy (Alegret et al., 2005) and a high sedimentation rate allow us to conduct a stratigraphically well-constrained, high-resolution analysis of this boundary sequence.

2. Setting and stratigraphy of Loma Capiro

Loma Capiro is a small hill of ca. 180 m height in the northeast part of the Santa Clara city, central Cuba (Fig. 1), that provides an excellent exposure of the K–Pg boundary sequence on its southern slope. The K–Pg boundary sequence at Loma Capiro is composed of a hemipelagic sequence of foraminifera-rich massive gray calcareous mudstone and sandstone, and a 10.9 m-thick clastic complex (Fig. 2). These sediments are included in the upper Maastrichtian Santa Clara Formation and the Paleocene Ochoa Formation (Rojas-Consuegra

et al., 2007). Paleogeographic reconstructions suggest that the K–Pg location of the site was about 500 km south of its present position and that its sediment accumulated on the northeastern slope of the Cuban carbonate platform on the south edge of the proto-Caribbean Basin (Fig. 1d; Rojas-Consuegra et al., 2005; Núñez-Cambra and Rojas-Consuegra, 2007; Goto et al., 2008). Benthic foraminiferal assemblages indicate a paleodepth of 700 m to 3000 m (Alegret et al., 2005).

The lithology of uppermost 1.5 m of the Maastrichtian is marked by well-lithified gray calcareous mudstone followed by a continuous upward-fining sequence of the clastic complex with an erosional contact (Fig. 2). The basal 6.5 m of the sequence is characterized by a matrix-supported breccia with siltstone to very fine sandstone matrix and rounded clasts of mudstone, limestone, gabbro and serpentinite. Diameters of these clasts are generally less than 10 cm. Neither imbrication nor changes in grain size are observed. The subsequent 1.5 m of the sequence is upward-fining microbreccia with cross lamination, which is overlain by 65 cm-thick medium to coarse sandstones. The uppermost 2.5 m of the complex is composed of an upward-fining sequence of coarse-medium to medium-fine sandstones with intercalations of 15 cm-thick limestone and 10 cm-thick whitish clay layers.

Similar end-Cretaceous clastic deposits have been widely recognized around the Gulf of Mexico and in the proto-Caribbean Sea (Smit et al., 1996; Tada et al., 2003; Schulte et al., 2006; Goto et al., 2008). Lithologic and paleontologic evidence suggests that these sediments were deposited in a geologically instantaneous period by the collapse of carbonate platforms, gravity flows and large tsunamis that are associated with the K–Pg impact at Chicxulub (Bralower et al., 1998). Likewise, the presence of reworked Cretaceous foraminifera and impact materials in the clastic complex at Loma Capiro suggests its link to the K–Pg impact (Alegret et al., 2005). We therefore placed the K–Pg boundary at the bottom of the clastic complex (= basal 0 in Fig. 2).

The boundary between the clastic complex and the Paleocene mudstone is sharp and marked by light to dark gray mudstone that has a strike of $\text{N}75^\circ\text{E}$ and a northward dip of 56° (Fig. 1c). The lower half of the Paleocene sequence is mainly composed of light gray to brownish gray mudstone with intercalations of sandstone layers. In contrast, the upper half of the sequence is generally characterized by alternating beds of light gray to reddish brown mudstone and 1 to 15 cm-thick light gray fine to medium sandstone. An intercalation of ca. 50 cm-thick fine to medium sandstone is observed at the 454 cm horizon above the clastic complex (Fig. 2).

Three planktonic foraminiferal datums are assigned to the 200 cm, 248.7 cm and 520 to 620 cm horizons above the clastic complex by comparison to the results of Alegret et al. (2005) (Fig. 2). The ages of these datums are 64.9 Ma, 64.5 Ma and 63.0 Ma, respectively (Berggren et al., 1995). Linear sedimentation rates (LSR) of the Paleocene sequence above the clastic complex are therefore calculated as 2.0 cm/kyr for the 0–200 cm, 0.1 cm/kyr for the 200–248.7 cm, and 0.2 cm/kyr for the 248.7–620 cm interval.

3. Materials and methods

3.1. Samples

Samples were obtained from the upper 1.5 m of the Maastrichtian calcareous mudstone and the lower 11 m of the Paleocene mudstone above the clastic complex (Fig. 2). We did not collect samples from the complex because it is mainly composed of reworked Cretaceous materials that the impact left behind, and therefore we put a 0 horizon for the Paleocene sequence at the top of the clastic complex (= top 0 in Fig. 2). We used two slightly separated transects for sampling because the vertical exposure that contained the Maastrichtian section did not allow collection of stratigraphically continuous Paleocene samples. Both transects are well correlated by the upper boundary of the clastic complex. The outcrop was trenched to about

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