

**PHYSIOLOGY OF PHOTOAUTOTROPHS AND PALEOENVIRONMENT DURING THE CRETACEOUS OCEAN ANOXIC EVENTS BASED ON NITROGEN AND CARBON ISOTOPE ANALYSES OF INDIVIDUAL SEDIMENTARY PORPHYRINS**

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Sedimentary porphyrins are tetrapyrrole molecules with alkyl chains derived from chlorophylls, heme, and other biomolecules (e.g., Treibs, 1936; Baker and Louda, 1986; Callot and Ocampo, 2000). In particular, structures of deoxophylloerythroetioporphyrin (DPEP) and its analogues strongly suggest them to be originated from chloropigments. Thus, stable isotopic compositions of nitrogen and carbon of these porphyrins should directly reflect those of the chloropigments (e.g., Hayes et al., 1987; Chicarelli et al., 1993). We analysed nitrogen and carbon isotopes of various individual porphyrins extracted from sequential samples from the Livello Bonarelli black shale (uppermost Cenomanian, Italy) to elucidate the physiology of photoautotrophs and paleoenvironment during the Cretaceous OAE.

Based on the isotopic relationship between tetrapyrrole portion of chlorophylls and cells of the photoautotroph (the former 4.8‰ depleted in <sup>15</sup>N and 1.8‰ enriched in <sup>13</sup>C relative to the latter; Ohkouchi et al., 2006; Ohkouchi et al., in prep.), nitrogen isotopic compositions of the entire photoautotrophic community is estimated to be -2 to 0‰ based on δ<sup>15</sup>N of Ni DPEP (-6.6 to -4.8‰) and Cu DPEP (-5.7 to -5.1‰). These values strongly suggest that the nitrogen assimilated during phototrophic primary production was largely supplied *via* N<sub>2</sub>-fixation. Meanwhile, carbon isotopic compositions of Ni DPEP (-20.5 to -17.9‰) and Cu DPEP (-20.1 to -16.3‰) suggest that of the entire photoautotrophic community being approximately -22 to -18‰. Thus, the estimated isotopic fractionation associated with carbon fixation in the Bonarelli paleoenvironment was strikingly small (-15 to -13‰) compared to those of the simulated *ordinary* photoautotrophic community in each paleoenvironments, namely, -20 to -14‰ and -23 to -20‰, respectively. The result suggests rapid growth rates for these photoautotrophs in an intense bloom conditions that perhaps had associated active transport of carbon substrates and/or a significant rate of β-carboxylation. Therefore, both nitrogen and carbon isotopic signatures of the porphyrins suggest considerable contribution of diazotrophic cyanobacteria in the primary production.

Moreover, all samples from the Livello Bonarelli black shale contain trace amounts of porphyrins with more than 34 carbon atoms that should have derived from

bacteriochlorophylls *c*, *d*, and *e* of the obligate anaerobic photoautotroph, green sulfur bacteria. It thus suggests presence of reduced, anaerobic water mass within the photic zone ( $0 < 200\text{m}$ ) in a strongly stratified water column. In fact, the dominance of diazotrophic cyanobacteria in primary production should be an inevitable consequence of water column stratification due to diminished supply of dissolved inorganic nitrogen to the surface water.

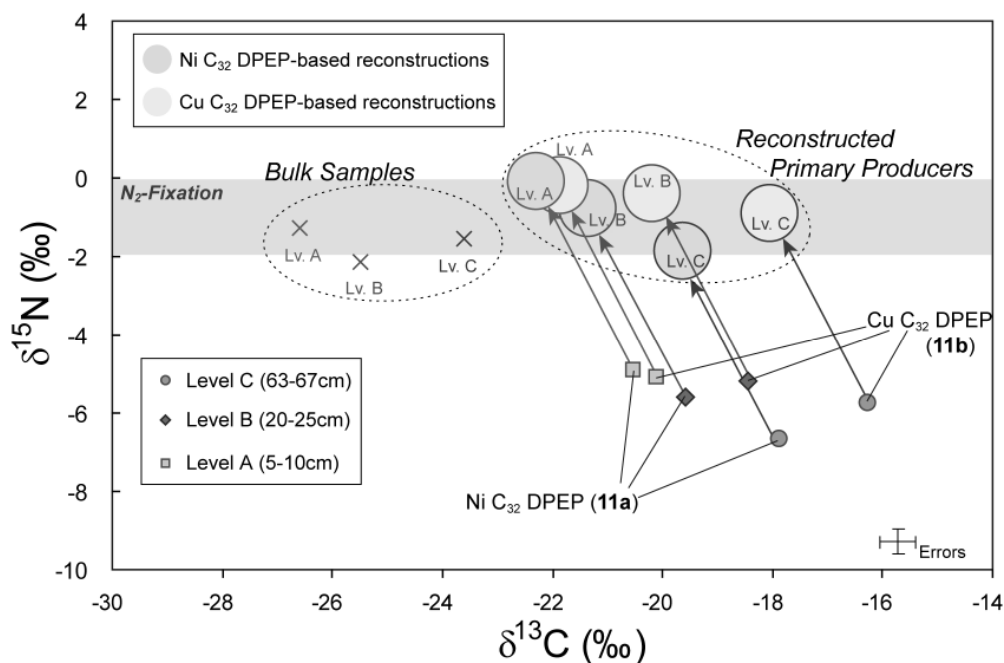


Figure 1. Reconstructed  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  values of photoautotrophic cells from the Livello Bonarelli black shale. Circles indicate approximate ranges of mean isotopic compositions for the photoautotrophic community reconstructed from by Ni and Cu  $\text{C}_{32}$  DPEPs for each stratigraphic level.  $\delta^{15}\text{N}$  for diazotrophic photoautotrophs is expected to be  $-2$  to  $0$ ‰. Isotopic compositions of bulk organic matters are plotted as well.

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## HOW LARGE WAS THE “TRUE” CARBON ISOTOPE EXCURSIONS AT THE PETM?

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The Paleocene-Eocene Thermal Maximum (PETM) is a period of extreme and abrupt global warming that coincides with a pronounced negative carbon isotope excursion (CIE) in both terrestrial and marine carbonate and organic matter. Although the cause of the CIE is debated, all proposed mechanisms call for the rapid addition of <sup>13</sup>C-depleted carbon to the ocean-atmosphere-biosphere system. If processes that fractionate carbon isotopes operated in the same way during the PETM as before and after, then terrestrial and marine reservoirs should show a uniform shift in values of the same magnitude. Instead, terrestrial leaf wax lipids demonstrate a CIE of 5-6‰ or more, whereas the marine carbonate CIE is only 3-4‰.

One hypothesis is that the marine carbonates have been isotopically altered, and that the leaf wax lipid record demonstrates the true magnitude of the CIE (5-6‰) (Pagani et al., 2006). Ocean acidification during the PETM would have led to non-deposition and dissolution of carbonate preventing the accumulation of marine carbonate at the base of the PETM (Zachos et al., 2005). In addition, reduced pH and carbonate concentrations at the base of the PETM would have led to more positive carbon isotope ratios of marine carbonate, reducing the magnitude of the excursion by up to 0.5‰ until pH rebounded (Bowen *et al.*, 2004).

Here we examine this hypothesis by assuming that our leaf wax lipid record from the Bighorn Basin, WY, USA, represents the true magnitude of the CIE (5‰). We estimate the expected marine carbonate CIE by first calculating the carbon isotope signature of atmospheric CO<sub>2</sub> and then calculating the δ<sup>13</sup>C values for calcite in equilibrium with atmospheric CO<sub>2</sub> (via dissolved inorganic carbon). Because the equilibrium fractionation factor between calcite and CO<sub>2</sub> is temperature-dependant, the warmer PETM causes the estimated marine carbonate CIE to be 6‰, even larger than that observed in leaf waxes. The largest CIE observed in marine carbonate is 4‰ (Fig. 1). If the leaf wax CIE represents the true CIE, the marine record would have to be enriched in <sup>13</sup>C by 2‰ throughout the entire PETM.

To date, no mechanism has been presented that can cause a sustained 2‰ enrichment in marine carbonates throughout the PETM. The effects of ocean carbonate and acidification would be concentrated at the beginning of the PETM and are estimated at 0.5‰. Therefore, we support the alternative hypothesis, that the leaf wax CIE is amplified relative to the true CIE through changes in carbon isotope discrimination by plants. Although the true CIE, meaning the net isotopic change in the combined ocean-atmosphere-biosphere reservoir, need not be that of marine carbonates (3-4‰), we have shown that it is even less likely to be that of leaf wax lipids (5-6‰) and is most likely somewhere in-between.

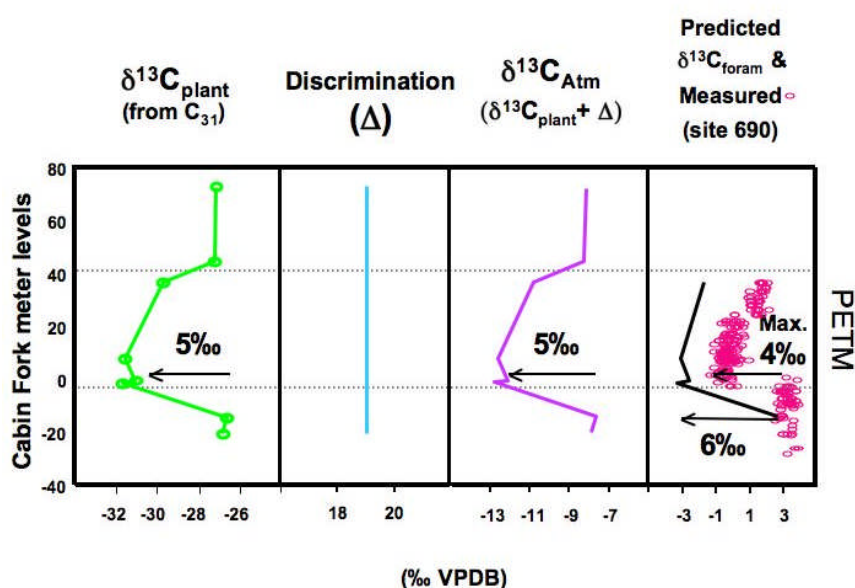


Figure 1 A)  $\delta^{13}\text{C}$  of total plant tissue calculated from  $\text{C}_{31}$   $n$ -alkane measured in the Bighorn Basin, WY, USA using  $\epsilon = 4.94$  ‰. B)  $^{13}\text{C}$ -discrimination assumed. C) Predicted atmospheric  $\text{CO}_2$   $\delta^{13}\text{C}$ . D) Predicted  $\delta^{13}\text{C}$  values for marine calcite (solid line) precipitated in equilibrium with atmospheric  $\text{CO}_2$  following. Measured values from planktonic forams from site 690 (ovals) (Thomas et al., 2002). CIE magnitude indicated by arrows.

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## BIOMARKERS AND ISOTOPIC RECORDS OF CLIMATE CHANGE ACROSS THE PALEOCENE-EOCENE THERMAL MAXIMUM

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The Paleocene-Eocene Thermal Maximum (PETM), a period of abrupt and significant global warming, is one of the most dramatic climate events in the history of our planet. It is characterised by a rapid negative shift in the  $\delta^{13}\text{C}$  values of marine and terrestrial carbon, a change attributed to a massive release of methane from gas hydrates. Carbon isotopic records have been obtained from terrestrial settings and used to estimate the magnitude of the shift in atmospheric  $\text{CO}_2$   $\delta^{13}\text{C}$  values. Unfortunately, such records are limited in number and resolution. In an attempt to address this issue, we have studied two PETM sedimentary sequences dominated by terrestrial organic matter: a Kumara section (New Zealand), deposited in deltaic to nearshore marine sediments and one from Tanzanian continental margin sediments. Analyses of the distribution of higher plant and bacterial biomarkers and their carbon isotopic composition provide direct records of changes in higher plant vegetation, sedimentary redox conditions and atmospheric  $\text{CO}_2$ .

In the Kumara section, the organic matter is dominated by terrestrial biomarkers derived from either higher plants (e.g. *n*-alkanes with a strong odd-over-even predominance) or bacteria (hopanes), consistent with deposition in a riverine or deltaic setting. *N*-alkane  $\delta^{13}\text{C}$  values were measured and a 4.5‰ negative shift recorded, suggesting the studied interval spans the PETM. Interestingly, the negative isotope excursion is associated with a remarkable change in biomarker assemblages over this interval. First, pristane and phytane (derived from algal chlorophyll) and low-molecular-weight *n*-alkanes become more abundant, indicating a shift to marine dominated conditions. Second, a variety of biomarker proxies suggest that bottom waters and sediments became more reducing. Third, the abundance of oleananes, angiosperm biomarkers, increases dramatically, possibly reflecting a dramatic change in the higher plant assemblage. These shifts in depositional setting coincide with a lithologic transition and provide direct evidence for sea level rise associated with the PETM.

In the Tanzania section, similar terrestrial biomarkers abound, but in addition to *n*-alkanes and hopanes other functionalised biomolecules were also identified: *n*-alkanols and *n*-alkanoic acids (with an even-over-odd predominance) derived from higher plants and bacterially-derived hopanoids. Hopane and hopanoid abundances and distributions vary through the section, with a significant decrease in the abundances of all hopanoids just below the PETM boundary, whereas the *n*-alkanoic acid distribution switches from a short-over-long-chain predominance to a predominance of long chain components at the PETM and then back again after the event. Lower molecular weight *n*-alkanoic acids are typically derived from bacteria whereas higher plants are the primary source for their higher molecular weight homologues; therefore, these trends suggest a change in the organic matter source during the PETM, possibly driven by an increase in terrestrial runoff. The  $\delta^{13}\text{C}$  values derived from *n*-alkanes reveal a negative shift of  $\sim 6.5\text{‰}$  over the PETM interval. The magnitude of this shift is much greater than the value of  $3\text{‰}$  quoted in most of the existing literature and based on planktonic foraminifera<sup>1</sup>.

Although these large terrestrial shifts could be the result of changes in humidity or plant distribution, it is also possible that these terrestrial records better represent the true magnitude of the carbon isotope excursion. This has implications for the quantity and source of the  $^{13}\text{C}$ -depleted carbon, and other sources, besides methane hydrates, should be considered.

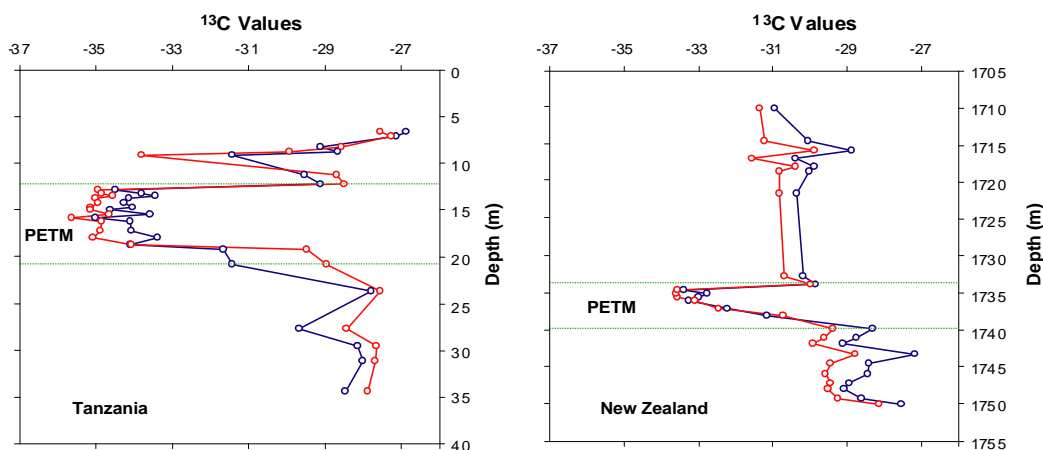


Figure 1.  $\delta^{13}\text{C}$  values of higher plant derived  $\text{C}_{27}$  and  $\text{C}_{29}$  *n*-alkanes through the PETM, blue and red data points respectively. The Tanzanian setting yields a CIE of  $\sim 6.5\text{‰}$ , whilst the New Zealand section shows a  $4.5\text{‰}$  negative shift. Both values are larger than the traditional  $3\text{‰}$  marine excursion.

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