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High-resolution carbon isotope record for the Paleocene-Eocene thermal maximum from the Nanyang Basin, Central China

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The Paleocene-Eocene thermal maximum (PETM) was a transient episode of global warming, associated with massive atmospheric greenhouse gas input that occurred at the Paleocene/Eocene boundary. Biostratigraphic and isotope stratigraphic studies indicate that the PETM event is well documented in the marl deposits of the Yuhuangding section in the Nanyang Basin, Central China, with a carbon isotope negative excursion of ~6.1‰ within 19-m-thick marl deposits. This is the highest resolution record of the PETM so far found in the world. The PETM event was triggered within 2-cm-thick marl sediments, with a decrease of $\delta^{13}C$ (stable carbon isotope ratio) from –3.2‰ to –5.2‰, suggesting a massive methane hydrate release for a transient period that was possibly caused by a catastrophic event. A comparison between marine and terrestrial records indicates a "Three-Phase Model" for the PETM event. Initially there is a rapid negative excursion in the $\delta^{13}C$ record, followed by a slowly decreasing trend, and then a gradual positive recovery, corresponding respectively to a rapid dissociation of oceanic methane hydrate, followed by a slow release of methane and then the consumption of the released methane.

PETM, carbon isotope, greenhouse gases, Nanyang Basin

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The Paleocene-Eocene thermal maximum (PETM) was a transient global warming event occurring at the Paleocene/Eocene boundary. This warming was accompanied by a prominent negative carbon isotope excursion (CIE) that affected all parts of the global exogenic carbon cycle, indicating that the PETM was caused by the rapid injection of a large amount of isotopically light carbon into the ocean/atmosphere system. Possible sources of large amounts of carbon include: (1) a catastrophic release of methane (CH_4) hydrate from the continental slope seafloor [1], (2) the production of thermogenic CH_4 and carbon dioxide (CO_2) during contact metamorphism associated with the intrusion of a large igneous province into organic rich sediments [2], (3) a global conflagration of Paleocene peatlands [3], and (4) bacterial respiration of organic matter from a desiccated epicontinental seaway [4]. Currently, it is widely accepted that the PETM was caused mainly by the dissociation of massive amounts of methane hydrate preserved in continental shelves. It is estimated that ~2800–5000 Gt biogenic carbon ($\delta^{13}C$ = –60‰) was rapidly released into the ocean/atmosphere system during the initial phase of the PETM [4], leading to a large carbon isotope excursion (CIE). Despite its short duration (120–200 ka), the PETM had catastrophic effects on both the climate and ecosystem,

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e.g. global warming [5], mass extinction of benthic foraminifera [6], rapid diversification of planktonic foraminifera [7], continental faunal migration [8], and rapid acidification of the ocean [9].

Because the PETM was triggered by a rapid greenhouse gas release, a process similar to the increase in atmospheric CO_2 since pre-industrial times, there is a fear of a catastrophic release of methane hydrate from the continental slope under future global warming scenarios. In this regard, the PETM can be used to posit an analog for future greenhouse warming and has thus attracted much attention. Despite many studies, confusion still exists about the mechanism of greenhouse gas emission [1], the release process [10] and amount of carbon, and the removal of excess carbon from the atmosphere, partly due to the lack of high-resolution PETM records, especially terrestrial records. To date, most of the PETM records have come from marine sediments, and are documented in sediments with a thickness of only 1–2 m, with some even suffering from sedimentary disturbances. In the terrestrial PETM records, only four sections have been studied so far: Bighorn Basin in Wyoming, USA [11], Williston Basin in North Dakota, USA [12], Hengyang Basin, China [13], and Erlian Basin, China [14]. The PETM records from the Hengyang and Erlian basins are based on sparse carbonate nodules with low resolution. The record from the Williston Basin still needs further verification; while the stable carbon isotope ratio (δ^{13}C) record of the Bighorn Basin also comes from discrete carbonate nodules, although systematic paleontological studies have been conducted. Therefore, more high-resolution terrestrial records are needed to improve our understanding of the PETM.

The extensive Cenozoic deposits in China have considerable potential to provide a detailed record of the PETM. Here we present a high-resolution δ^{13}C record of continuous marl sediments from the western Nanyang Basin, with the objective of identifying the PETM event and addressing the above issues.

1 Geological setting

The Nanyang Basin is a depression area that has been subsiding since the late Cretaceous [15]. The terrigenous detrital sediments from the late Cretaceous to late Eocene can be subdivided into Hugang, Baiying, and Yuhuangding formations. In the 1970s, fragments of dinosaur eggs were found in the reddish sandstone of Hugang Formation, and hence this formation was assigned a late Cretaceous age [16]. Baiying Formation, consisting of thick lacustrine marls, was placed during the Paleocene, as it contains *Hanomys malcolmi* [17]. Yuhuangding Formation is characterized by grayish-pink lacustrine marl with interbedded reddish silty mudstone and calcareous mudstone. The mammal fossils from the Yuhuangding Formation are grouped into three assemblages [18]. The lower fossil assemblage contains *Asiocoryphodon conicus* and *Manteodon flerowi*, and is assigned to the Early Eocene age; the middle assemblage is in the Late Early Eocene age, represented by *Rhombomylus* cf. *turpanensis*, *Advenimus hubeiensis* and cf. *Heptodon* sp.; the upper assemblage contains abundant *Gobiatherium minutus*, *Eomoropus Zhanggouensis*, *Lophialetes Primus*, *Yimengia* sp. and *Forstercooperia* sp., indicating an age of Middle to Late Eocene. Therefore, the upper Baiying and the lower Yuhuangding formations are the focus here for identifying the PETM.

2 Carbon isotope record

At Yuhuangding (Figure 1), 270-m-thick marl sediments from the upper Baiying and the lower Yuhuangding Formation were sampled at 2–10 cm intervals, with the top of the studied portion being ~100 m below the overlying Dacangfang Formation The δ^{13}C values for samples at 1 m intervals were measured first to identify the CIE. Then the δ^{13}C values of 60-m-thick sediments around the CIE were measured at 2–10 cm intervals. In total, 534 samples were analyzed. For isotope analysis, ~150 μg samples of powder were drilled from micrite in bulk marl samples under a microscope. Samples were reacted with 100% phosphoric acid at 72°C for 1 h in a GasBench II carbonate preparation device interfaced with a MAT253 isotope ratio mass spectrometer. Results were calibrated to Pee Dee belemnite (V-PDB) and are reported as per million (‰) with analytical precision less than 0.15‰.

From 0 to 30 m (Figure 2), the δ^{13}C values fluctuate slightly around –3.2‰, while they have a slight negative trend from 30 to 182 m. At 182 m, the δ^{13}C values decrease rapidly from –3.2‰ to –5.2‰ within a 2 cm interval. From 182 to 188.8 m, the δ^{13}C values decrease gradually, and then exhibit an abrupt negative shift (~2.5‰) at 188.8 m, followed by a rapid return from –8.9‰ to –6‰. Subsequently, the δ^{13}C values gradually decline again and reach as low as –9.3‰ at 195 m, and then increase gradually and finally stabilize around –6‰ at 200 m and above. In addition, there are several small carbon isotope excursions prior to the CIE (below 182 m). For example, one of the most notable negative excursions (~2‰) occurs between 165 and 170 m.

3 Comparison of the PETM records

The carbon isotope record shows that the entire PETM event is well documented in the marl sediments between 182 and 201 m in the Yuhuangding section, Nanyang Basin. Comparisons of the PETM records (Figure 3) among the Nanyang Basin, the Ocean Drilling Program in the western North Atlantic (ODP 690B) and the Bighorn Basin show apparent similarities for the CIE: a rapid negative shift

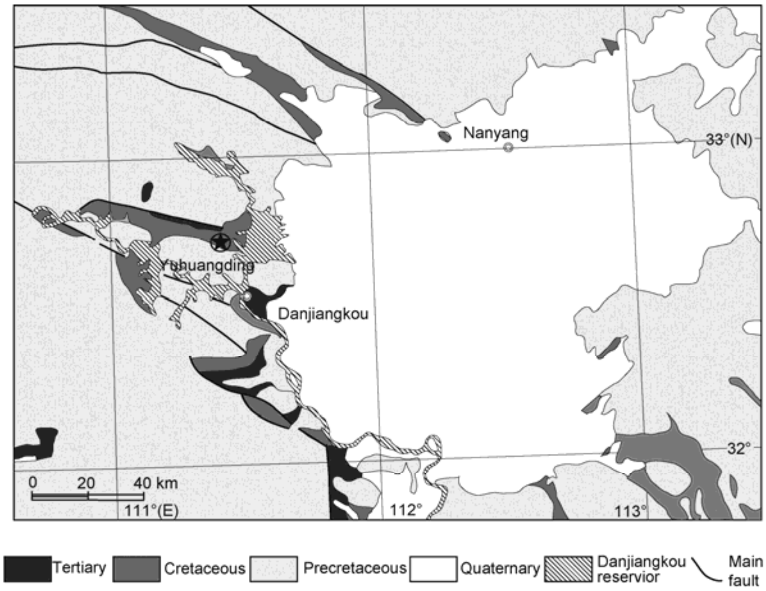

Figure 1 Geological sketch map of the Nanyang Basin.

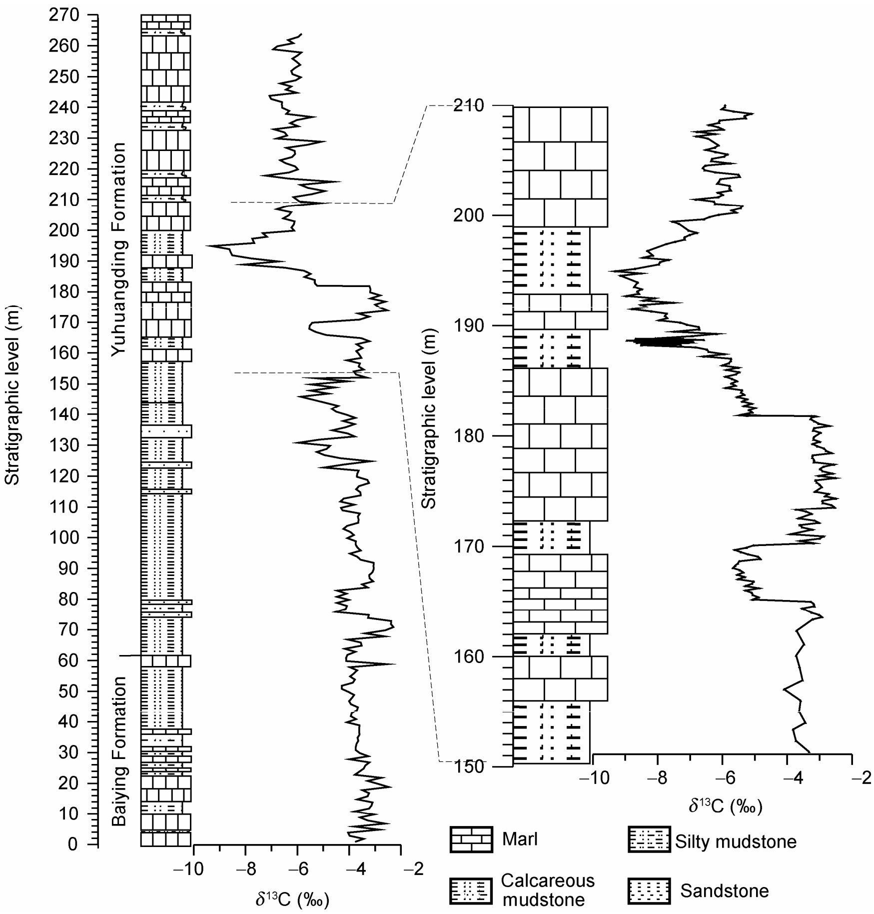

Figure 2 Lithostratigraphic column and carbon isotope record of the Yuhuangding section.

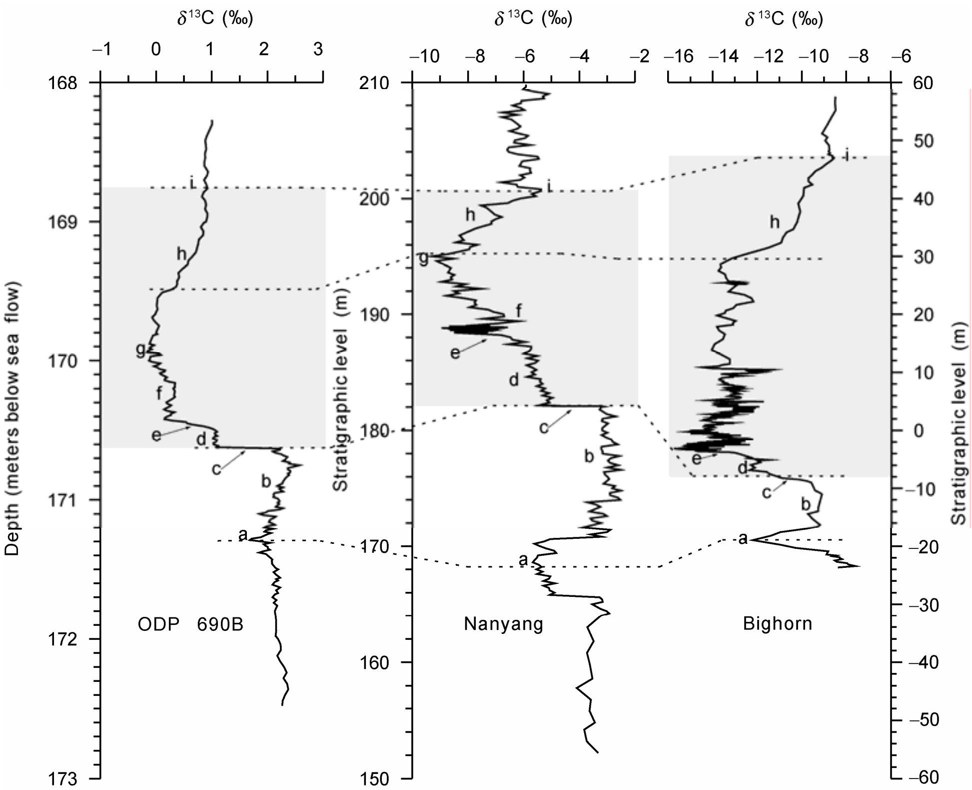

Figure 3 Correlation of δ^{13}C records between ODP 690B [10], Nanyang Basin, and Bighorn Basin [19]. ODP 690B data are from bulk carbonates, and are plotted against depth as meters below the seafloor. Bighorn Basin data are derived from pedogenic carbonate nodules. Shaded areas indicate the PETM event.

in δ^{13}C records, followed by a further drop, and subsequent gradual positive trend. However, significant differences are also observed. Firstly, the total magnitudes of the δ^{13}C excursions in the Nanyang and Bighorn Basins are ~6.1‰ and ~8‰, respectively; much greater than the marine δ^{13}C excursion (~2.5‰). Secondly, the δ^{13}C record from ODP 690B in Figure 3 shows two rapid negative excursions (c, e) and a third gradual negative excursion (g), with a transient plateau (d) between the first two negative excursions. The δ^{13}C curve from the Bighorn Basin in Figure 3 exhibits only two rapid negative excursions (c, e). The δ^{13}C record from the Nanyang Basin (Figure 3) has an initial rapid excursion (c), followed by a gradual negative excursion (d), then a second rapid excursion (e), followed by a short stage return (f), and a third gradual excursion (g). Thirdly, there are several small isotope excursions (~2‰) in the Nanyang δ^{13}C record prior to the CIE. The one closest to the CIE (a) can also be found in the Bighorn record but is not evident in the record from ODP 690B. In summary, the δ^{13}C record from the Nanyang Basin is similar to that from ODP 690B, but the thick marl sediments in the Nanyang Basin provide more detailed features of the PETM event. Therefore, we suggest a "Three-Phase Model" for the PETM event: an initial rapid negative δ^{13}C excursion, followed by a gradual decrease, and then a gradual positive recovery. These three phases correspond to a rapid emission of oceanic methane hydrate, a slow release of methane, and then a gradual removal of the released carbon.

4 Discussion

Until now, an absolute age constraint is lacking for the duration of the PETM. For the Yuhuangding section, the magnetostratigraphic record has been difficult to establish due to the weak magnetic signal of the marl sediments. The orbital tuning of geochemical records from marine sediments has yielded a 120–200 ka for the PETM event [20–22]. If we accept this estimate and assume a constant sedimentation rate for the Yuhuangding section, our PETM record yields a sedimentation rate of 9.5–15.8 cm/ka, which is much higher than that of the marine records (0.9–1.5 cm/ka). Despite the ~55-m-thick sediment for the PETM in the Bighorn Basin, the time resolution of its δ^{13}C record is largely limited by the discrete pedogenic carbonate nodules. The δ^{13}C record from the Nanyang Basin thus represents the highest resolution PETM record available to date, thus facilitating detailed investigations into the PETM event.

In the Nanyang record, the PETM was triggered within a

2 cm interval, indicating that its onset occurred in less than 210 years. This favors the hypothesis that the PETM was caused by a massive release of methane hydrate (δ^{13}C = –60‰) from the continental slope. Other hypotheses for carbon release, such as decomposition of rich organic sediments, burning of peat land and tectonic processes, would have led to a slow carbon release rather than a rapid emission. At present, there are two hypotheses for methane hydrate release. One is that global warming during the Late Paleocene ultimately caused the dissociation of methane hydrate from sediments on the continental slope [1]. The other is related to geological events that triggered the release of methane, e.g. continental slope failure, an earthquake in the deep sea, and an intrusion of a larger igneous province [2,23]. The global warming hypothesis deserves special attention because it may serve as an analog for current global warming. However, it is evident that our record favors a catastrophic release mechanism. After the CIE onset, the δ^{13}C values further gradually decreased by ~4.1‰ during 82–137 ka (estimates from sedimentation rates). Obviously, this latter process cannot be explained by the catastrophic release of methane. A possible mechanism is as follows. The global warming driven by the initial release of methane could have induced positive feedback, whereby accumulations of methane hydrate degassed into the ocean and atmosphere, as thermal stability regimes altered.

So, how much methane hydrate was released during the PETM? And how much carbon remained in the atmosphere? These questions can only be answered by invoking some assumptions. The ocean inorganic reservoir in the Late Paleocene is uncertain and thus has been assigned a pre-industrial value of 38000 Gt C [24], with a mean δ^{13}C value of 0; thereby, 1652 Gt C as methane would have to be added to the ocean carbon reservoir to explain a ~2.5‰ excursion of the δ^{13}C in marine records. Considering that the carbon distribution between ocean and atmosphere is 6:4 during a carbon perturbation [25], the mass of carbon added to the atmosphere should be around 1101 Gt. Given a concentration of 1000 ppmv (1 ppmv = 2.12 Gt C) [26] for atmospheric CO_2 before the PETM, the amount of carbon in the atmosphere should be 2120 Gt. Assuming a pre-industrial δ^{13}C value (–6.5‰) for atmospheric CO_2 prior to the PETM, a –6.1‰ excursion in the Nanyang δ^{13}C record indicates 268 Gt C remaining in the atmosphere, comparable with the increased amount of carbon in the atmosphere since the industrial revolution. The rest, 833 Gt C, would have been sequestrated by the terrestrial ecosystem and silicate weathering within 38–63 ka (estimates from sedimentation rates). The amount of the removed carbon (833 Gt C) is a minimum estimate because we did not consider a shift in the ocean-atmosphere exchange equilibrium due to terrestrial ecosystem feedback and the carbonate-compensation effect. Despite the warmer climate during the PETM, the total amount of global methane hydrate in the Paleocene is comparable with that of today (~10000 Gt C) [1,27]. Our estimate indicates that global warming during the PETM did not cause a total collapse of the methane hydrate reservoir. This situation may be explained by the enhanced carbon fixation by terrestrial and oceanic ecosystems, as well as the increased consumption of atmospheric CO_2 by silicate weathering.

5 Conclusions

Biostratigraphic and isotope stratigraphic studies indicate that the entire PETM event is well documented in the marl deposits of the Yuhuangding section in the Nanyang Basin, with a negative carbon isotope excursion of ~6.1‰ within 19-m-thick marl deposits. This is the highest resolution record of the PETM so far found in the world. The carbon isotope record from the Nanyang Basin shows that the PETM event was triggered within 2-cm-thick marl sediments, with a decrease of δ^{13}C from –3.2‰ to –5.2‰, suggesting a massive methane hydrate release during a transient period, possibly caused by a catastrophic event.

A comparison between marine and terrestrial records suggests a “Three-Phase Model” for the PETM event: an initial rapid dissociation of massive oceanic methane hydrate, followed by a slow release of methane and then the consumption of the released methane by the earth’s surface system. Large amounts of methane were further released after the onset of the PETM event, which may have been a result of positive feedback induced by an increase in temperature, i.e., the deep water warming caused a shift in the methane hydrate-seawater equilibrium and hence a further release of methane. However, the methane hydrate preserved in the continental slope was only partly released despite the positive feedback effect, and the cause remains unknown. In addition, most of the released methane was withdrawn in 38–63 ka by marine-atmosphere-terrestrial ecosystems.

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