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Three Hypotheses for the Causes of the Paleocene-Eocene Thermal Maximum: A Fifty-Five Million Year Old Mystery

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Introduction

Fifty-five million years ago, the Earth warmed 4-5°C in a blink of geologic time. A new source of carbon into the atmosphere induced greenhouse warming that rapidly changed the climate. On land, mammals became more numerous and migrated across the continents. In the oceans, acidity rose and 30% of the microscopic benthic foraminifera that lived on the sea floor went extinct. Life changed, but went on, leaving a record of its passing in the elemental composition of the shells of dead foraminifera in the ocean sediment.

This event, known as the Paleocene Eocene Thermal Maximum (PETM), was global in nature, with evidence appearing in every ocean basin and in many terrestrial locations. It was the warmest period of the Cenozoic and an abrupt deviation from the gradual warming of the late Paleocene and early Eocene. Global temperatures derived from oxygen isotope records were about 8°C warmer than today at the onset of the PETM, which then peaked at a blistering 4-5°C warmer before returning to pre-PETM conditions.

While the body of data surrounding the effects of this rapid climate change continues to grow, what triggered the event in the first place is still unknown. In a world facing the growing threat of global warming, understanding the past is key to understanding the present. Over the last ten years, scientists have proposed three hypotheses concerning the source of the carbon that entered the oceans and atmosphere: the release of methane hydrates from the sea floor, carbon dioxide degassing of the North Atlantic Igneous Province, and a meteor impact. Each hypothesis has its strengths and weaknesses, and by examining them we come to a better understanding of the Earth, the PETM, and what the future may hold.
Background

Reconstructing the Past

Marine sediment records are commonly used for reconstructing past oceanic and climatic events. Marine sediment accumulates over millions of years ocean detritus, including input from rivers, particles that result from bacteria and phytoplankton life cycles, and the shells of dead foraminifera and other microfauna. Within these components are the elements that form them, such as oxygen and carbon, which in turn are comprised of the various isotopic forms that come exist in seawater, $^{18}\text{O}$, $^{16}\text{O}$, $^{13}\text{C}$ and $^{12}\text{C}$. Environmental conditions such as temperature dictate which isotopes are in greater abundance, and therefore ocean sediment cores give us a record of past seawater conditions.

Isotope fractionation, the preferential use one isotopic form of an element over another, occurs in biological processes and ice formation. To illustrate, I will use the oxygen isotope ratios that measure indirectly, or proxy for, changes in temperature due to ice formation. Ice preferentially forms from $\text{H}_2\text{O}$ with $^{16}\text{O}$, leaving the seawater enriched in $\text{H}_2\text{O}$ made from $^{18}\text{O}$. Thus a colder ocean that is forming ice has more $^{18}\text{O}$ compared to $^{16}\text{O}$, as opposed to a warmer ocean that has a lower ratio of $^{18}\text{O}/^{16}\text{O}$. Foraminifera living in this colder ocean use seawater oxygen that is enriched in $^{18}\text{O}$ to form their shells of calcium carbonate, $\text{CaCO}_3$.

In order to compare isotopic ratios between foraminifera species and ocean basins, the $^{18}\text{O}/^{16}\text{O}$ ratio needs to be standardized. Standard Mean Ocean Water (SMOW) and its successor, Vienna Standard Mean Ocean Water (VSMOW), are samples of modern seawater taken for this purpose. The notation after standardization ($[^{18}\text{O}/^{16}\text{O}_{\text{sample}} - ^{18}\text{O}/^{16}\text{O}_{\text{standard}}] / ^{18}\text{O}/^{16}\text{O}_{\text{standard}}$) is $^{18}\text{O}$ and is reported in parts per thousand. Isotopically heavier samples are
enriched in $^{18}$O relative to the standard and have a positive $^{18}$O. Isotopically lighter samples have relatively more $^{16}$O and are negative.

The simple example stated above encompasses the basic principles of isotope fractionation. However, the oceans are complex integrated systems of organic and inorganic chemistry such that no one proxy perfectly reflects what it is measuring. Imbedded in the calculations are assumptions and corrections for complicating factors. In the case of $^{18}$O, other influences on the ratio of seawater include 1) the oxygen isotopic ratios of precipitation, 2) fractionation due to evaporation, or 3) salinity. These continuously mix and confound the $^{18}$O signal due to temperature. When measured in foraminifera, these other sources of fractionation must be taken into account when interpreting the paleotemperature. Modern analogues are often used to approximate paleoceanic conditions such as precipitation and evaporation.

To compensate for the drawbacks of one proxy, often several different ones are used to measure the same parameter, such as temperature. Multiple proxies for the same samples validate each other and show that the changes in the isotopic record over time are real. Together the results are robust. Sediment cores have been taken in every ocean basin, and the patterns that emerge both across proxies and between different measurements (temperature, carbon source, or export productivity, for instance) show global trends in the oceans that often translate into global trends in climate.

*The Paleocene Eocene Thermal Maximum*

The Paleocene Eocene Thermal Maximum was first seen in the oxygen and carbon isotopic records of marine sediment from the Indian Ocean (Barrera and Huber, 1991 *in*
Dickens et al., 1995). Since then, the event has been observed in every ocean basin and on land, indicating that this was a global event (Katz et al., 1999; Zachos et al. 2001; Zachos et al., 2005). Approximately fifty-five million years ago, the $^{18}$O record indicates that temperatures rose 4-5°C over a period of 10,000 years (Dickens et al., 1995), maximizing 30,000 years after the onset (Zachos et al., 2005), and sustained for approximately 200,000 years before recovery to pre-PETM conditions (Figure 1; Zachos et al., 2001).

At the same time, the $^{13}$C decreased by 2-3‰ over about 20,000 years, with a recovery period again on the order of 200,000 years (Figure 1; Zachos et al. 2005). This is known as the carbon isotope excursion (CIE). The change in carbon isotopic composition indicates that there was a change in the source of the carbon into the oceans and, because of their close relationship, the atmosphere. The influx of a new source of carbon and the rise in temperature suggest that greenhouse forcing from CO$_2$ or CH$_4$ was in effect.

Other research verifies that the PETM was a global climatic event. Immediately following the event, many species of benthic foraminifera that reside on the ocean floor went extinct (Kennett and Stott, 1991). Reconstructed deep sea circulation patterns show a change
from Southern Hemisphere overturning to Northern Hemisphere overturning due to warming (Tripati and Elderfield, 2005; Nunes and Norris, 2006), and reconstructed calcite compensation depths (CCD) show that they shallowed by two kilometers over 10 000 years, indicating acidification of the ocean consistent with increased levels of dissolved carbon (Zachos et al., 2005). On land, the $^{13}\text{C}$ decrease by 2-3‰ was also observed (Harrington et al., 2005). In addition, during the PETM there was widespread plant migration and the radiation of mammals (Zachos et al. 2001).

**Causes of the PETM**

What is so striking about the PETM is the rapidity with which the climate system altered due to a change in the carbon cycle. Ten thousand years is not a long time, geologically speaking, even for systems changing naturally. Given the rate of anthropogenic input of CO$_2$ into the atmosphere, understanding the causes of and feedbacks to the PETM are very important for understanding what may be in store for humans in the coming centuries.

There are three hypotheses for the causes of the PETM. The first and most widely accepted is the release of methane hydrates from continental shelves. The two other hypotheses I will discuss are the injection of carbon into the atmosphere from volcanism in the North Atlantic Igneous Province and the effects of a meteor impact on the Earth.

**Release of Methane Hydrates**

Methane hydrates, also called methane clathrates, are crystalline structures of water that trap methane (CH$_4$). They occur in modern oceans within the upper depth zone of the
sediment column along the continental margins, where they are stable depending on water temperature, pressure, salinity, and trace gas composition (Figure 2; Dickens et al., 1995; Dickens, 2003). Their formation depends on a sufficient concentration of available methane in the pore waters, usually provided by the bacterial processing of organic matter (Dickens, 2003).

The $^{13}$C isotopic signature of methane hydrates is -60‰. A global decrease of 2-3‰ in seawater $^{13}$C would require a large influx of isotopically lighter carbon, such as the methane hydrates. Dickens (1999) suggests that between 1000-2000 Gt of carbon (Gt = $10^{15}$ g; the US emitted 173 Gt of carbon in 2002) is necessary to reduce the $^{13}$C isotopic signal globally. This is feasible on the assumption that the reservoir of methane hydrates in the late Paleocene was similar in size and distribution to that of the modern ocean, which may or may not be valid (Figure 3).

Figure 2: Diagram of Gas Hydrate Stability Zone on the continental slope. Dickens, 2003.
In the modern oceans, the gas hydrate reservoir is shaped like a lens, thickening under deeper water (Figure 2). The current estimate for the global reservoir size is between 1000 to 22,000 Gt C, with most estimates around 10,000 Gt (Dickens, 2003). The estimates are made from integrated estimates of pore space at the temperature and pressure range of stable methane hydrates, in which 1-10% is assumed to actually contain hydrates (Dickens, 2003). These numbers assume consistency across continental slopes around the globe and are broad ranges.

The question of how the methane hydrates are released is one with a few hypotheses of its own. The two triggering mechanisms proposed are thermal dissolution and slumping on continental slopes. Thermal dissolution is tied to changing patterns of ocean circulation. In this model, initial warming from an uncertain source causes a rapid change in ocean circulation such that deep water forms in the North Pacific instead of the Southern Ocean.
The change in circulation causes a rise in intermediate water temperatures that affects the stability field of the methane hydrates, destabilizing them and releasing them to the surface (Tripati and Elderfield, 2005). Slumping of the continental slope has been interpreted from analysis of the stratigraphic lithology in the sub-tropical North Atlantic, where the release of hydrates was likely (Figure 4). A mud clast layer immediately preceding the CIE shows evidence of having been transported from upslope (Katz et al. 1999).

Figure 4: Release of methane hydrates due to sediment slumping. Katz et al. 1999.

While the methane hydrates hypothesis sufficiently explains the negative shift in $^{13}$C, it does not adequately explain the rise in temperature. The estimated methane release to account for the carbon excursion is insufficient to raise the global seawater temperature 4-5$^\circ$C by greenhouse forcing (Tripati and Elderfield, 2005; Zachos et al. 2005). Moreover, the degree of acidification of the oceans at the PETM due to an increase in dissolved CO$_2$ and thus an increase in carbonic acid implies that approximately 4500 Gt C was released into the ocean. This value is a model result from Zachos et al. (2005) based on work done in the Southern Ocean. The mass of carbon necessary here exceeds the ~2000 Gt C the methane hydrate hypothesis calls on for the change in $^{13}$C (Table 1). These results suggest that the
methane hydrates are not the only source of carbon that drives the climate change at the PETM.

<table>
<thead>
<tr>
<th>Estimated Gt C necessary</th>
<th>Temperature</th>
<th>$^{13}$C</th>
<th>pH</th>
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<tbody>
<tr>
<td></td>
<td>$&gt;2000$; $\sim 2000 \Rightarrow 1^\circ$C</td>
<td>1000-2000</td>
<td>4500</td>
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<tr>
<td></td>
<td>Tripati and Elderfield, 2005</td>
<td>Dickens, 1995</td>
<td>Zachos, 2005</td>
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Table 1: Comparison of estimates of methane release necessary to match observations of oceanic temperature, $^{13}$C, and pH.

Recent research in the Gulf of Mexico further indicates that methane hydrates are not the only answer. Research by Milkov et al. (2003) on two sites and a wider sample size of methane hydrate bearing sediments suggests that previous estimates of global methane hydrates are too large. Instead, the authors propose that modern reservoir contains 2100–3600 Gt C, an amount that barely covers that necessary for the $^{13}$C reduction. Further reducing the estimate of available methane for greenhouse forcing is the oxidation in the water column of methane that is released. Bacteria and archea oxidize methane and reprecipitate it as carbonate depleted in $^{13}$C (Milkov and Sassen, 2003). Thus not all of the methane released reaches the surface.

A final objection to the methane hydrate theory is the soundness of the assumption that there were methane hydrates in the Paleocene and Eocene. Higher than modern temperatures prevailed during this time, which in turn begs the question of whether it was cold enough for the methane to become trapped in the water clathrate structure at all (Zachos et al., 2001)

The methane hydrate hypothesis is not a perfect solution to the mystery of the PETM. Constraints on the amount of methane necessary for the observed changes in temperature, $^{13}$C, and pH conflict, as do estimates of the modern reservoir size upon which the argument
is founded. Problems with the theory have prompted study of other influences that may have contributed to the CIE and the rise in global temperature.

*North Atlantic Igneous Province Volcanism*

The North Atlantic Igneous Province (NAIP) comprises the rift zone that separated Greenland from Northern Europe and Canada (Figure 5). The volcanism is associated with the initiation of the Iceland plume that instigated seafloor spreading, splitting the continental masses (Thomas and Bralower, 2005). There are two periods of volcanism. The first was from ~60-62 Ma and resulted in basalts along the western and southeastern edges of Greenland and Scotland and Ireland, accompanied by silicic ash (Sinton and Duncan, 1998). The second period was from ~57-58 Ma, two million years before the onset of the PETM. Basalt was produced again on Greenland’s eastern margin and along Great Britain’s western margin (Sinton and Duncan, 1998). Evidence from drill cores shows that the volcanism of this second period occurred subaerially or in shallow water. Thus CO₂ degassing occurred directly into the atmosphere (Thomas and Bralower, 2005).

The timing of the NAIP volcanism coincided with the general warming trend of the late Paleocene and early Eocene (Figure 6). There are different opinions on how much the influx of CO₂ directly impacted the climate, however. Svensen (2004) argued that hydrothermal vents off the coast of Norway were ancient conduits of hot methane that originated in the crust that warmed ocean water in addition to reaching the surface and contributed to greenhouse forcing. The methane is purported to have exploded in plumes
Figure 5: North Atlantic Igneous Province in the Paleocene and Eocene. The NAIP was active in the formation of the northern Mid Atlantic Ridge and the opening of the North Atlantic basin. Thomas and Bralower, 2005.

Figure 6: North Atlantic Igneous Province volcanic events compared to the timing of the PETM. On the right, the bars represent volcanic events at locations varying from left to right. Adapted from Thomas and Bralower, 2005.
that protected the majority of it from oxidation or dissolution in the ocean. Since thermogenic methane has a $^{13}\text{C}$ of -20 to -30‰, it could account for some of the CIE (Zachos, 2005). More importantly, the hydrothermal venting warms the regional bottom water and thus destabilizes the methane hydrates along the shelf, which then release into the atmosphere (Svensen 2004).

In a more southern location of the NAIP (Figure 5), Thomas and Balower (2005) looked at trace metals as a proxy for hydrothermal activity. Plumes from submarine volcanism often carry trace metals leached from the surrounding basalts and deposit them in the sediment downstream. Thomas and Balower found that the sediment cores they analyzed did not support hydrothermal warming consistent with Svensen’s interpretation. Instead they agreed with the previous work that the NAIP was subaerial with little influence on the PETM, if any. The authors express caution, citing Eldholm and Thomas’s (2003) conclusions that the PETM warming and CIE occurred too rapidly to have been directly caused by the NAIP volcanic activity. Ambiguity lies in tying the extended volcanic events with the specific timing of the PETM but does not preclude the possibility.

**Meteor Impact**

The meteor impact scenario proposed by Cramer and Kent (2005) tries to address many of the problems found with previous hypotheses. They use a simplified model to show the effects of a 9 km-diameter meteor impact. The meteor is assumed to have ~150 Gt of carbon with a $^{13}\text{C}$ signature of -45‰ to partially account for the CIE. As it enters the atmosphere, the carbon would burn off and enter the atmospheric carbon reservoir, both adding to the greenhouse gases and lowering the global $^{13}\text{C}$ signal. The impact would also
contribute to raised temperatures and the CIE by 1) superheating the atmosphere from the shock wave, 2) creating a tsunami that would destabilize and cause slumping along continental shelves, thus releasing methane hydrates, 3) vaporizing the meteor and surrounding rock if on land, and 4) releasing deep water CO₂ due to warming if an oceanic impact (Cramer and Kent, 2005).

Other data they interpret as evidence for a meteoric impact includes the magnetization of sediments off the New Jersey coast. At the layer concurrent with the PETM, the magnetization is abnormally higher than the layers above and below, suggesting an increased concentration of magnetic nanoparticles (Kent et al. 2003). The authors argue that the nanoparticles are inconsistent with continental detritus and that similar particles had been found at the Cretaceous/Tertiary (K/T) boundary.

A small layer of iridium was found in Spain coincident with the onset of the CIE (Kent et al., 2003). Because the majority of iridium on Earth comes from meteors, it is an indication of an extraterrestrial impact, as was shown by its association with the K/T impact (Alvarez, 1990).

Certain points of the argument for an extraterrestrial impact can be interpreted in different ways that both support and undermine the hypothesis. In comment and reply responses to Kent et al. (2003), the interpretation of the magnetic nanoparticles, iridium layer, and biologic turnover are contested and defended. Dickens and Francis (2003) argue that they are results of increased terrigenous input due to increased weathering from warmer temperatures, while Kent et al. (2003) maintain that they could be due to a meteor impact. There is no conclusive evidence for an impact, and no crater has been found. The meteor
impact hypothesis is speculative, and the model used in Cramer and Kent (2005) is very simple. As in any model, the results are only as good as the data set available for inputs.

**Concluding Remarks**

In summary, the three main hypotheses for the causes of the PETM do not universally fit the data sets currently available. Accounting for both the $^{13}$C and temperature rise with a plausible trigger mechanism is difficult. The methane hydrate hypothesis does not sufficiently constrain the reservoir size available or necessary to account for all observations, the NAIP hypothesis depends on uncertain bottom water warming, and the meteor impact scenario is based on contestable data.

A fourth hypothesis recently proposed but not yet published suggests that widespread and long-lasting fires caused the CIE and onset of the PETM (Finkelstein 3/7/06). The basic idea is that the higher atmospheric CO$_2$ levels of the early Cenozoic result in a higher frequency of lightning strikes due to the higher electrical conductivity of CO$_2$. Fires burning unchecked for a century could potentially burn enough biomass to cause the CIE and subsequent rise in temperature. This hypothesis has yet to be fully developed, and it will be interesting to see where it leads.

The Paleocene Eocene Thermal Maximum remains a partial mystery. No one hypothesis explains the causes for this remarkable climate change event, but perhaps a more integrated approach of all the hypotheses will stand up to scrutiny. In particular, the methane hydrate hypothesis rests on the assumption that there is another trigger for the destabilization of the hydrates, likely a temperature warming threshold that once crossed resulted in a climate altering release of greenhouse gas.
The research conducted in the pursuit of finding the origins has illuminated and expanded our understanding of the effects of the feedbacks between the oceans, atmosphere, and land in the wake of the influx of a new carbon source to the global carbon cycle. These same feedback mechanisms, such as the warming of bottom waters or the acidification of the oceans, will come into play in the future as anthropogenic carbon release to the atmosphere continues on a much shorter timescale. Zachos et al. (2005) estimate that the same change in oceanic pH that occurred during the PETM over 10 000 years can be achieved by humans in 300 from the burning of fossil fuels. The Earth will regain its equilibrium as it did after the PETM, but even that recovery took the time equivalent of human existence. Understanding the causes and effects of this rapid climate change will hopefully give us insight to the present and help us plan for the future.
References


