Warming the Fuel for the Fire: Evidence for the thermal dissociation of methane hydrate during the Paleocene-Eocene thermal maximum

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Abstract

Dramatic warming and upheaval of the carbon system at the end of the Paleocene Epoch have been linked to massive dissociation of sedimentary methane hydrate. However, testing the Paleocene-Eocene thermal maximum (PETM) hydrate dissociation hypothesis has been hindered by the inability of available proxy records to resolve the intial sequence of events. The cause of the PETM carbon isotope excursion remains speculative, primarily due to uncertainties in the timing and duration of the PETM. We present new high-resolution stable isotope records based on analyses of single planktonic and benthic foraminiferal shells from Ocean Drilling Program Site 690 (Weddell Sea, Southern Ocean), demonstrating that the initial carbon isotope excursion was geologically instantaneous and

was preceded by a brief period of gradual surface water warming. Both of these findings support the thermal dissociation of methane hydrate as the cause of the PETM carbon isotope excursion. Furthermore, the data reveal that the methane-derived carbon was slowly mixed from the surface ocean downward, suggesting that a significant fraction of the initial dissociated hydrate methane reached the atmosphere prior to oxidation.

Introduction

At the close of the Paleocene epoch ~55 million years ago, the Earth experienced one of the most dramatic global warming events in the geologic record - the Paleocene-Eocene thermal maximum (PETM). Within a few thousand years, sea surface temperatures warmed ~4 to 8°C and deep ocean temperatures increased by ~5°C (Figure 1; e.g., Kennett and Stott, 1991). The short-lived warming event (~210 kyr; Röhl et al., 2000) induced a host of biotic responses, including mass extinction of benthic foraminifera, rapid diversification of planktonic foraminifera and terrestrial mammals, and blooms of dinoflagellates (e.g., Tjalsma and Lohmann, 1983; Kelly et al., 1996; Hooker, 1996; Clyde and Gingerich, 1998; Crouch et al., 2001).

The PETM corresponds to an abrupt negative 3-4 ‰ carbon isotope excursion (CIE) in marine and terrestrial sedimentary sections (Figure 1; e.g., Kennett and Stott, 1991; Koch et al., 1992), a feature with major diagnostic significance. This excursion implies a massive and rapid addition of isotopically light carbon to the oceans and atmosphere. Possible explanations for this input have focused on enhanced mantle CO_2 outgassing during North Atlantic Igneous Province emplacement (Eldholm and Thomas, 1993), dissociation of massive quantities of methane hydrates along continental slopes (Dickens et al., 1995), and impact of a carbonaceous bolide

(Deming, 1999; Kent et al., 2001). The apparent rate and magnitude of the CIE are consistent with both seafloor methane and a carbonaceous impactor as the carbon sources. However, the available data cannot distinguish between these two sources of light carbon, or whether the carbon (methane or otherwise) was added first to the oceans or atmosphere. The fundamental problem is that temporal relationships between warming and carbon input in different environments cannot be resolved with published stable isotope records.

We present new stable isotope data from Ocean Drilling Program Site 690 (Weddell Sea, Southern Ocean) that indicate that the onset of the CIE was geologically instantaneous, consistent with the hydrate dissociation hypothesis or impact-related carbon release. However, the data also demonstrate that the CIE at Site 690 was preceded by a brief period of gradual surface water warming. Thus the most coherent explanation for the entire data set is that gradual sea-surface warming led to the thermal dissociation of sedimentary methane hydrate. In addition, our data suggest that a substantial amount of the methane released was oxidized in the atmosphere.

Methods

We generated stable isotope records based on analyses of individual foraminiferal shells, a strategy used in two previous PETM investigations (Stott, 1992; Kelly et al., 1996). Site 690 (Figure 2) was selected because it is the most expanded and complete deep-sea PETM section recovered to date (Röhl et al., 2000). A continuous U-channel across the onset of the PETM was cut into 1 cm samples; above this we sampled the core every 5 cm. We conducted stable isotope analyses on 483 well-preserved specimens (Thomas et al., 1999) of the surface-dwelling, photosymbiont-bearing genus *Acarinina* and the thermocline-dwelling genus *Subbotina*

(D'Hondt and Zachos, 1993) over a 121 cm interval, and on 7 individual and 5 multi-specimen benthic foraminiferal samples over a 7 cm interval (ending 4 cm below the benthic foraminiferal extinction). Measurements of individual benthic foraminifera *N. truempyi* were limited because specimens large enough (>5 μg) for analysis were extremely rare, especially close to the onset of the benthic foraminiferal extinction (BFE). All stable isotope analyses were conducted at UC Santa Cruz with a precision better than 0.1‰ for $\delta^{13}C$ and $\delta^{18}O$.

Results

Several key features emerge from the single-specimen stable isotope data (Figure 3). Specimens of surface- and thermocline-dwelling planktonic foraminifera record only pre-excursion or excursion $\delta^{13}C$ values across the onset of the event. The onset of excursion $\delta^{13}C$ values within specimens of both groups occurs within a span of 1 cm, and coincides with individuals that still record pre-CIE values. In contrast to the bimodal planktonic carbon isotope distribution, both the surface- and thermocline-dwelling foraminiferal $\delta^{18}O$ records contain intermediate values, marking a more gradual transition from pre-PETM to PETM $\delta^{18}O$ values. Transitional $\delta^{18}O$ values are expressed by the *same individual specimens* that contain pre-PETM $\delta^{13}C$ values.

Shifts in stable isotope values of different groups of foraminifera also show a stratigraphic sequence of events (Figure 3). From bottom to top: 1) $\delta^{18}O$ values of surface-dwelling planktonics decrease by ~1.5‰ between 170.81 mbsf (Level 1) and 170.78 mbsf (Level 2). 2) Level 2 also corresponds to the initial decrease in $\delta^{18}O$ values of thermocline-dwelling planktonics and the ~4‰ decrease in $\delta^{13}C$ values of surface-dwelling specimens. 3) At 170.70 mbsf (Level 3), $\delta^{13}C$ values of thermocline dwellers decrease by ~2.5‰. 4) Peak-PETM $\delta^{18}O$

values of thermocline dwellers (~-2‰) occur at Level 4 (170.67 mbsf). Level 4 also marks a slight decrease in $\delta^{13}C$ (~1.5‰) and $\delta^{18}O$ values (~1‰) of two benthic individuals. New multi- and single-specimen benthic analyses above these two individuals indicate reworking based on pre-PETM $\delta^{13}C$ and $\delta^{18}O$ values.

Above a brief convergence at the onset of the PETM (from 170.70 to 170.42 mbsf), the trends in planktonic stable isotope values begin to diverge. Oxygen isotope values of thermocline dwellers remain at ~-1.5‰ up to 170.42 mbsf, then begin to gradually increase. However, $\delta^{13}C$ values of thermocline dwellers remain low throughout the interval studied (to 169.84 mbsf). Oxygen isotope values of surface dwellers are ~-1.5 ‰ from 170.78 to 170.42 mbsf, decrease from ~-1.5 to –2.5 ‰ at 170.37 mbsf, and remain at ~-2.5 ‰ for the remainder of the record. Carbon isotope values of surface dwellers begin to increase at 170.37 mbsf.

Discussion

Our combined carbon and oxygen single-specimen isotopic data (Figure 3) provide a detailed chronology of rapid changes in Southern Ocean thermal and carbon isotope depth gradients during the onset and initial recovery of the PETM. While Kennett and Stott (1991) first recognized the stable isotope excursions at Site 690, their multi-specimen analyses lacked the resolution to unravel the timing relationships between warming and carbon input. Multi-specimen records also average out the environmental variability that the single-specimen strategy exploits. As a result, we are now able to resolve the onset and evolution of the thermal and carbon anomalies. Our data supports a warming-induced carbon input such as thermal dissociation of methane hydrates.

Evidence for the "Blast of Gas": The bimodal distribution of single-specimen carbon isotope values at the onset of the CIE suggests that the initial input of isotopically light carbon occurred in a geologic instant. We can discount the argument that the sharp base of the CIE resulted from dissolution or a hiatus (Dickens, 1998), because the very planktonic foraminifera that record only pre- or peak excursion $\delta^{13}C$ values record a *gradual decrease* in the corresponding $\delta^{18}O$ values. The geologically instantaneous onset of the CIE precludes the North Atlantic Igneous Province as the source of light carbon, because the $\delta^{13}C$ value of mantle CO_2 is only ~-6 per mil. The stratigraphic and hydrographic sequence of the first excursion $\delta^{13}C$ values from surface to thermocline to benthic dwellers implies that the carbon isotope anomaly gradually propagated *downward* from the sea surface to the bottom waters.

Triggering the Blast: The stratigraphic progression of single-specimen stable isotope changes, with the decrease in surface water $\delta^{18}O$ values preceding the decrease in $\delta^{13}C$ values, enables us to rule out several possible explanations of PETM carbon input. The onset of the CIE would have preceded the decrease in $\delta^{18}O$ values if the PETM had resulted from erosion-induced hydrate dissociation (e.g., Katz et al., 2001) or from a carbonaceous impactor (e.g., Kent et al., 2001). Explosive volcanism (e.g., Bralower et al., 1997) would have resulted in an increase or no change in $\delta^{18}O$ values at a high-latitude site. Thus, the only plausible mechanism to consider is the thermal dissociation of methane hydrates.

The occurrence of specimens of surface-dwelling foraminifera that record transitional $\delta^{18}O$ values and pre-CIE $\delta^{13}C$ values (Level 1, Figure 3) suggests a ~2˚C warming of surface waters *prior to the onset* of the CIE. This finding conflicts with that of Bains et al. (1999) who found no evidence for pre-PETM sea surface warming on the basis of bulk sedimentary oxygen

isotope analyses. We argue that the discrepancy results from the different analytical techniques, as changes in bulk stable isotopes at Site 690 during the PETM interval reflect changes in the assemblage of calcareous nannofossils (Bralower, in press). The cause of this warming is not known, although long-term outgassing of CO_2 from the North Atlantic Igneous Province is a distinct possibility. With the onset of the CIE (Level 2, Figure 3) surface mixed-layer temperatures eventually warmed an additional 4˚C. Transitional $\delta^{18}O$ values recorded by thermocline dwellers occur above the $\delta^{18}O$ decrease in surface dwellers (Level 2, Figure 3), indicating a distinct delay in the warming of the thermocline waters (several hundred meters depth). Moreover, the high degree of scatter in the "transitional" thermocline-dweller $\delta^{18}O$ data is consistent with the notion that thermocline structure changed, prompting shifts in foraminiferal depth habitats as the intermediate and deep ocean began to warm.

Pathway of Hydrate Carbon: The top-down progression of the onset of the CIE suggests that a significant proportion of the methane from dissociated hydrates was rapidly transferred to the atmosphere and surface ocean. In order for calcifying organisms to record a methane-derived $\delta^{13}C$ anomaly, the isotopically light methane must first be oxidized into CO_2 and incorporated into the HCO_3^- pool from which calcification occurs. Because the pattern of CIE propagation proceeded downward from surface waters, oxidation of methane must have taken place within the atmosphere/surface ocean. Had the initial release of methane been more gradual (enabling oxidation within the deep ocean), Site 690 planktonic foraminifera would have recorded transitional $\delta^{13}C$ values at the onset of the event, and benthic individuals would have recorded the excursion prior to the planktonics.

At Site 690, progression of the initial $\delta^{18}O$ decrease also occurs from surface waters downward. Heat may have been mixed vertically down to the thermocline, while warmer intermediate and deep waters may have been advected into the study region after sufficient warming in their respective source areas. The onset of peak thermocline warming (lowest $\delta^{18}O$ values) coincides with the onset of the CIE in surface waters. This implies that hydrate dissociation did not occur at Site 690, otherwise thermocline and deeper-water warming would have preceded the onset of the CIE.

The more gradual transition to excursion $\delta^{13}C$ values in the benthic foraminiferal record can be understood by considering the dynamics of mixing and the vast size of the deep-sea inorganic C reservoir. As indicated by the bimodal planktonic $\delta^{13}C$ data, the mean $\delta^{13}C$ of the relatively small and well-mixed atmosphere and surface ocean carbon reservoirs should have responded immediately to the initial release of methane. In contrast, because of the large mass of carbon and the slower mixing time of the deep ocean (~1,500 years), it should take several thousands of years for the full magnitude of the CIE to be manifested in the deep sea. Thus, the delay in the thermocline and benthic $\delta^{13}C$ decrease reflects the additional time required to mix the carbon anomaly throughout the deep-sea carbon reservoir. The lack of benthic individuals available for analysis (during the decline and extinction of benthic foraminifera) may also bias the timing of environmental change in the deep-sea.

We note that the top-down progression in carbon input observed at the PETM is strikingly similar to the recent changes in the atmospheric and surface ocean carbon reservoirs in response to release of anthropogenic CO_2. In the last century, the $\delta^{13}C$ of atmospheric and surface-ocean CO_2 has decreased by ~1.2‰ (e.g., Joos and Bruno, 1998), while the deep ocean has yet to show detectable change.

PETM Recovery: Increasing surface-dwelling planktonic $\delta^{13}C$ values suggest that initial recovery of surface-water dissolved inorganic carbon (DIC) began even while thermocline and benthic foraminifera still recorded CIE values. The smaller, surface-ocean carbon reservoir should have recovered from the isotopic perturbation more rapidly than the larger deeper-oceanic reservoirs. But the fact that the surface dwellers do not record any subsequent $\delta^{13}C$ decrease after the initial onset of the CIE implies that all of the hydrate dissociation may have occurred in one major event. Additional hydrate dissociation should have resulted in further decrease of surface-water DIC $\delta^{13}C$ values. Alternatively, subsequent gradual hydrate may have occurred but the methane-derived carbon remained within the deep-ocean reservoir.

The thermal structure of the Southern Ocean water column changed markedly during the several tens of thousands years following the onset of the PETM. After an initial convergence of surface and thermocline $\delta^{18}O$ values at the onset of the warming (as noted by Kennett and Stott, 1991), thermal stratification resumed. Coincident with the initial recovery in surface water $\delta^{13}C$ values, surface water $\delta^{18}O$ values decreased by another ~1 ‰ possibly as a consequence of enhanced greenhouse warming. These trends suggest a re-establishment of local thermal and chemical stratification.

Proposed Causal Scenario for the PETM

We propose the following scenario to explain the stratigraphic sequence of events in the new stable isotope data. Gradual warming occurred first in surface waters, then in waters at thermocline and intermediate depths. Subduction or downwelling of warmer intermediate waters in the region of water mass formation led to thermal dissociation of methane hydrates at a

location with a significant sedimentary hydrate content. Methane gas from the dissociated hydrates reached the atmosphere prior to widespread oxidation. The thermocline/intermediate water thermal anomaly likely reached the Southern Ocean via a combination of advection from a distal source region and vertical diffusion. The propagation of the carbon anomaly proceeded rapidly throughout the atmosphere and surface ocean, then more slowly downward into the thermocline and then bottom waters.

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Figure Captions

1. Carbon and oxygen isotope records from Ocean Drilling Program Site 690 (data from Kennett and Stott, 1991) showing the PETM stable isotope excursions.
2. Paleogeographic reconstruction of the late Paleocene showing the location of Site 690 (from the Ocean Drilling Stratigraphic Network).
3. Single-specimen carbon and oxygen isotope data. Previously published benthic foraminiferal data are from Kennett and Stott (1991) and Thomas and Shackleton (1996). The gray arrow denotes the onset of the benthic foraminiferal extinction (BFE). Orange dashed lines indicate the stratigraphic sequence of events at the onset of the PETM. High-resolution samples derived from the archive-half U-channel of Hole 690B, Section 19-3 extend from 170.40 to

171.11 meters below sea floor (mbsf). Above and below the U-channel (169.84 to 171.73 mbsf), samples were taken from the archive half at 2 to 5 cm intervals. Individuals from the genera *Acarinina* and *Subbotina* were handpicked from the >250 μm size fraction.

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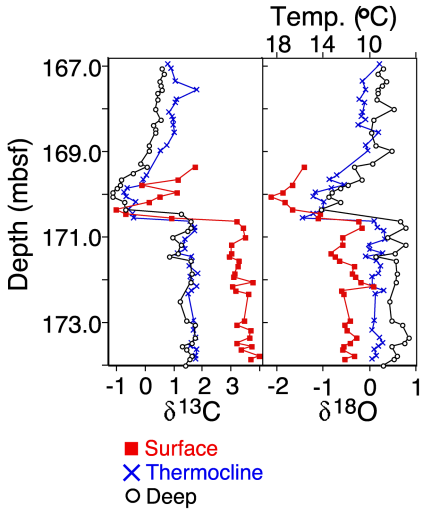
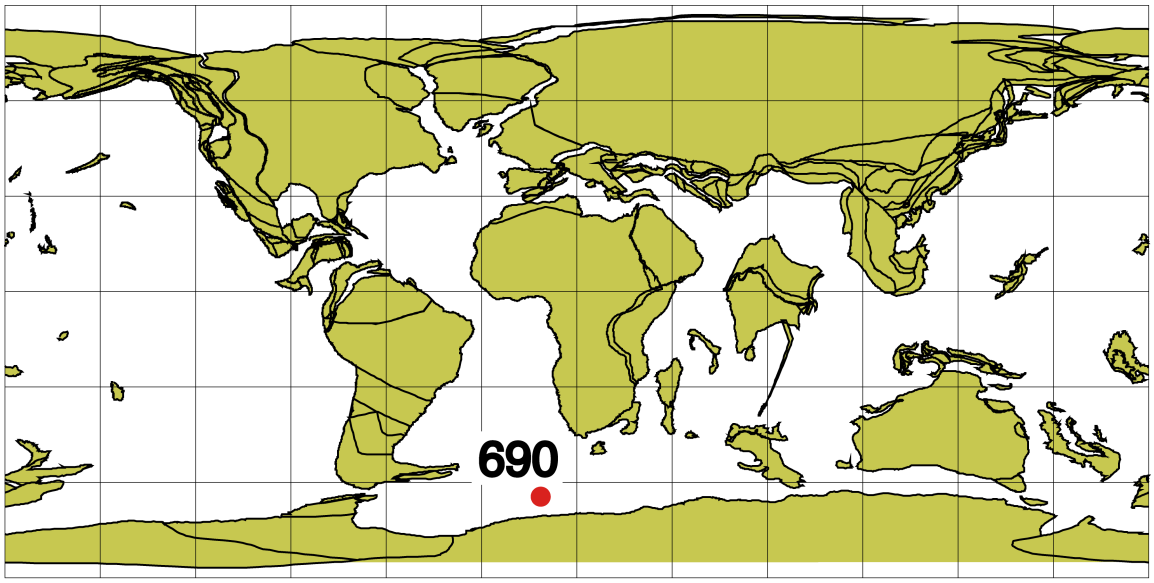
D. Thomas et al., Figure 1





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