An extraterrestrial $^3$He-based timescale for the Paleocene–Eocene thermal maximum (PETM) from Walvis Ridge, IODP Site 1266

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Abstract

In the deep-sea, the Paleocene–Eocene Thermal Maximum (PETM) is often marked by clay-rich condensed intervals caused by dissolution of carbonate sediments, capped by a carbonate-rich interval. Constraining the duration of both the dissolution and subsequent cap-carbonate intervals is essential to computing marine carbon fluxes and thus testing hypotheses for the origin of this event. To this end, we provide new high-resolution helium isotope records spanning the Paleocene–Eocene boundary at ODP Site 1266 in the South Atlantic. The extraterrestrial $^3$He, $^3$He$_{ET}$, concentrations replicate trends observed at ODP Site 690 by Farley and Eltgroth (2003). By assuming a constant flux of $^3$He$_{ET}$ we constrain relative changes in accumulation rates of sediment across the PETM and construct a new age model for the event. In this new chronology the zero carbonate layer represents 35 kyr, some of which reflects clay produced by dissolution of Paleocene (pre-PETM) sediments. Above this layer, carbonate concentrations increase for $\sim$165 kyr and remain higher than in the latest Paleocene until 234 $^{+48/}_{-31}$ kyr above the base of the clay. The new chronology indicates that minimum $\delta^{13}$C values persisted for a maximum of 134 $^{+27/}_{-19}$ kyr and the inflection point previously chosen to designate the end of the CIE recovery occurs at 217 $^{+44/}_{-31}$ kyr. This allocation of time differs from that of the cycle-based age model of Rohl et al. (2007) in that it assigns more time to the clay layer followed by a more gradual recovery of carbonate-rich sedimentation. The new model also suggests a longer sustained $\delta^{13}$C excursion followed by a more rapid recovery to pre-PETM $\delta^{13}$C values. These differences have important implications for constraining the source(s) of carbon and mechanisms for its subsequent sequestration, favoring models that include a sustained release of carbon after an initial pulse.

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1. INTRODUCTION

The gradual warming trend of the early Cenozoic hot-house world is punctuated by several transient extreme global warming events (Zachos et al., 2001; Lourens et al., 2005; Quillévéré et al., 2008) that can serve as examples of the climate system response to rapid greenhouse warming. The most prominent and well studied of these hyperthermal events is the Paleocene–Eocene Thermal Maximum (PETM) with a sea surface warming of 5–9 °C (Kennett and Stott, 1991; Zachos, 2003; Sluijs et al., 2006; Zachos et al., 2006),

global deep-sea warming of 4–5 °C, an $\sim$–3.5‰ carbon isotope excursion (CIE) in marine sections (Pak and Miller, 1992; Thomas and Shackleton, 1996), a $\sim$–4‰ to $\sim$–6‰ CIE in terrestrial sections (Koch et al., 1995), and mass extinction of benthic foraminifera (Thomas and Shackleton, 1996). In the deep-sea, the event is marked by a global carbonate dissolution horizon, a feature that indicates extreme ocean acidification (Zachos et al., 2005).

The leading explanation for these changes is rapid release of a large mass of isotopically light carbon, possibly from methane clathrates (Dickens et al., 1995, 1997; Svensen, 2004) and/or another $^{12}$C-enriched reservoir (Bralower et al., 1997; Kurtz et al., 2003; Svensen, 2004; Storey et al., 2007; Panchuk et al., 2008). Absorption of this carbon by the ocean lowered seawater pH, triggering a shoaling of
the calcite compensation depth (CCD) and buffering of ocean carbonate chemistry by intense dissolution of carbonate sediments. Consequently, the onset of the PETM is truncated or highly condensed in many pelagic sections. Moreover, a recovery layer with relatively high carbonate content often caps the dissolution horizon, possibly recording enhanced carbonate accumulation (Kelly et al., 2005; Zachos et al., 2005). The severity and timing of the chemical erosion and recovery, and associated rapid changes in sedimentation, has posed a particular challenge to developing high-resolution age models from deep-sea sections (Norris and Röhl, 1999; Farley and Eltgroth, 2003; Röhl et al., 2007). Precise and high-resolution age models are essential to understanding the causes and consequences of hyperthermal events and quantifying climate sensitivity (Zeebe et al., 2009). The temporal evolution of the carbon isotopic signal and dissolution event constrain the mass of carbon and its injection rate as well as possible mechanisms involved in its release to and recycling out of the ocean–atmosphere carbon pool (Dickens et al., 1997; Archer et al., 1998; Dickens, 2003; Ridgwell, 2007; Panchuk et al., 2008; Zeebe et al., 2008).

High-resolution age models for the PETM in the deepsea have been developed utilizing one of two methods: by identification of cycles in chemical composition attributed to Milankovitch-paced orbital variability (Röhl et al., 2000, 2007), or by assuming a constant extraterrestrial He flux and inverting measured He concentrations for sedimentation rate (Mukhopadhyay et al., 2001; Farley and Eltgroth, 2003). The two methods are largely independent and have complementary strengths and drawbacks. Astronomical cycle-based models are inherently limited to temporal resolution of about one precession cycle (~21 kyr) and are most reliable over long intervals with gradual changes in sedimentation rate and sufficient lithologic variation so that cycles of multiple orbital frequencies can be confidently identified. The He method provides an instantaneous estimate of sedimentation rate for each sample analyzed so is well suited for intervals with rapid changes in sedimentation rate and/or lithology. It is limited in temporal resolution only by sampling density (in depth) and is most reliable over short intervals of time close to a calibration interval in which the local He flux is determined.

Previous work at Maud Rise (ODP Site 690) and Walvis Ridge (ODP Leg 208) demonstrates some of the advantages and limitations of each method (Röhl et al., 2000, 2007; Farley and Eltgroth, 2003). In intervals adjacent to the PETM with moderately high carbonate content, identification of cycles is fairly straightforward, whereas in the lithologically uniform clay and carbonate-rich intervals, the identification of a cyclic geochemical signal is problematic and subjective (Röhl et al., 2000, 2007). This limitation may be remedied by identifying cycles in the concentrations of multiple minor and trace elements whose fluxes may be orbitally controlled and for which appropriately varying concentrations are detected (Röhl et al., 2007).

The He approach also has limitations and restrictive assumptions. To convert HeET concentrations into sedimentation rates requires determination of the local apparent flux of HeET, F, over a calibration interval where sedimentation rate is well constrained by an independent method. Age models produced using the HeET method are therefore highly sensitive to the precision and accuracy of F and the reliability of the age control used in its determination.

At ODP Site 690 the two methods yield significantly different age models. While both agree that the PETM was very rapid, the overall duration and the rate of recovery of the carbon isotopic anomaly and dissolution event differ between them (Röhl et al., 2000, 2007; Farley and Eltgroth, 2003). These differences yield potentially different interpretations of the PETM and motivate similar studies of additional sites in search of a globally consistent temporal progression.

In this study, we focus on a P–E boundary section recovered during the ODP Leg 208 multi-site depth transect on Walvis Ridge, where coring at five sites recovered complete P–E boundary sections from between 2.4 and 4.8 km water depth. Here, the P–E boundary is marked by pronounced clay layers which increase in thickness from a few cm at the top of ridge to ~30 cm near the basin floor. These stratigraphically uninterrupted pelagic sequences exhibit pronounced lithologic cycles that have been used to develop orbitally tuned age models for the upper Paleocene and lower Eocene (Loureens et al., 2005; Röhl et al., 2007; Westerhold et al., 2007). As such, they afford a unique opportunity to use the HeET method in conjunction with the orbital tuning to evaluate the constant flux hypothesis and to estimate the HeET flux over a calibration interval exceptionally close in space and time to the PETM. Our work also allows a rigorous new comparison of a He-based age model with one based on cyclostratigraphy, and similarly a comparison of both types of age models to their counterparts at ODP Site 690.

For this study, we elected to focus on the mid-water depth Site 1266 (3798 m, ~2600 m paleodepth) where the PETM spans roughly 1.6 m (as defined by the carbon isotope excursion). In addition to helium data, we extended the published carbonate and δ13Cbulk records for this site (Zachos et al., 2005) by several meters above and below the PETM interval.

2. MATERIALS AND METHODS

Samples were collected at intervals of 1–9 cm from 308.54 to 302.00 m composite depth (mcd) with the highest sampling density through the clay layer and recovery interval. Based on the bulk carbon isotope record and correlation to Site 1262 by color reflectance a*, the multi-hole splice of Site 1266 appears to be stratigraphically complete and continuous over this interval with the exception of an interval from 300.36 to 303.3 mcd that may be slightly disturbed. Preparation followed methods previously described by Farley and Eltgroth (2003) and Patterson and Farley (1998). Briefly, this included freeze-drying, homogenization via agate mortar and pestle, and decarbonation with 10% acetic acid solution of 0.5–2.2 g of sediment (depending on carbonate content). The residue, which contains all of the extraterrestrial helium, was isolated by centrifugation.
transferred to a tin sample cup, and baked to ~90 °C to remove adsorbed water. Helium was extracted from the sample by heating to 1500 °C. The evolved He was purified of active gases and other noble gases, cryo-concentrated, and analyzed on a MAP 215-50 noble gas mass spectrometer following standard procedures (Patterson and Farley, 1998). In all cases blank corrections were <10% for both isotopes. Typical analytical precision is better than 5% for 3He and 3% for 4He. However, individual sample 3He concentrations do not reproduce this well due to the “nugget effect” of a small number of extraterrestrial particles (Farley et al., 1997). This issue is discussed more fully below. He in marine sediment is a two-component mixture of relatively light extraterrestrial and heavy terrestrial helium; to determine the fraction of 3He attributable to an extraterrestrial source, we used 3He/4He ratios of 2.1 × 10^{-3} and 4 × 10^{-4} for the terrestrial and extraterrestrial endmembers of the mixing model, respectively (Eq. (1)) (Farley, 2001).

\[
3\text{He}_{ET} = 3\text{He}_{sample} \times \left( \left( \frac{3\text{He}}{4\text{He}} \right)_{sample} - \left( \frac{3\text{He}}{4\text{He}} \right)_{terrestrial} \right) / \left( \left( \frac{3\text{He}}{4\text{He}} \right)_{ET} - \left( \frac{3\text{He}}{4\text{He}} \right)_{terrestrial} \right)
\]

The carbon isotope analyses were carried out at the University of California Santa Cruz using Autocarb acid reaction devices coupled to either an OPTIMA or PRISM IR mass spectrometer. Based on replicate analyses of the Carrara Marble standard, analytical precision is better than ±0.05‰ for C. C isotope ratios are reported relative to the vPDB standard.

%CaCO3 was measured with a total carbon UIC coulometer. In addition to the carbonate content we also report non-carbonate fractions (NCF), i.e., the weight fraction of sediment remaining after the acetic acid leaching of the aliquots analyzed for helium isotopes.

### 3. RESULTS

#### 3.1. Carbonate, NCF, and δ13C records

The new δ13C_{bulk} data are consistent with and extend earlier work (Fig. 1A). Most notably, these data demonstrate that δ13C_{bulk} reaches a local maximum of 1.9‰, at ~303.5 mcd as what appears to be the culmination of the asymptotic recovery from the PETM CIE. The extended %CaCO3 record (Fig. 1A) shows that, once reached after the clay layer, values higher than those observed before the PETM persist for several meters up section before returning to Paleocene values. This chalky layer is characterized by maximum %CaCO3 continuing up to 304.25 mcd, well above the δ13C_{bulk} inflection point previously designated as the ‘end’ of the PETM at 305.21 mcd (Fig. 1A, Table 1, Electronic Annex Tables EA1 and EA2 provide data and previously adopted PETM nomenclature for this site) (Zachos et al., 2005; Röhl et al., 2007).

The non-carbonate fraction (NCF) of the sediment, though operationally different, is comparable to %CaCO3 measurements made by total carbon coulometry. The NCF values are inversely related to those of %CaCO3 (Fig. 1 and Table EA3) but are consistently 3–4% (by weight) greater than (1 – %CaCO3) values for the same depth, including for 14 samples that were used for both analyses. This minor but systematic offset is a result of the different acid digestions used by the two techniques.

#### 3.2. He isotopes: 3He/4He, 3He_{ET}/NCF, 3He_{ET}

3He/4He ratios range between 0.31 × 10^{-6} and 35 × 10^{-6} with a mean of 1.20 × 10^{-6}. These high ratios indicate that almost all of the He (>93% in all samples) derives from an extraterrestrial source and that the deconvolution to compute 3He_{ET} is insensitive to endmember isotopic compositions (Farley, 2001). In order to minimize the effects of rare larger IDPs that induce a biased scatter to the 3He_{ET} record (Farley et al., 1997) two objective filters were applied to the helium data set. First, samples were excluded from further consideration if they were anomalously high (>2.4 times the two immediately adjacent samples) in both 3He_{ET}/NCF and 3He/4He ratio. Such large and rapid temporal fluctuations in either the extraterrestrial He flux or the flux of terrigenous matter seem very unlikely, but are the hallmark of occasional 3He_{ET}-rich grains. Although the exact value of the rejection threshold is somewhat arbitrary, this criterion flagged a reasonable number (18 of 118) samples as anomalous (Table EA3). This number of “high-fliners” is about as expected based on previous work and theoretical modeling of the size distribution of He-bearing IDPs (Farley et al., 1997; Patterson and Farley, 1998; Farley and Eltgroth, 2003). The spatial distribution of anomalous samples appears to be random and includes several samples from the pre-PETM calibration interval. Thus excluding them does not substantially bias the ultimate interpretation of the data (Fig. EA1). Second, to further damp the statistical effects of a finite number of extraterrestrial particles, five-point running means have been drawn through the 3He and 3He/4He data as well as the derived sedimentation rate estimates in Fig. 1.

3He_{ET} values range from ~0.1 to ~2 pcc/g (1 pcc = 10^{-12} cc STP/g) and define a pattern inversely related to carbonate content (Fig. 1C and Table EA3); the highest concentrations correspond to the PETM clay layer. Both below and above this interval (below 306.80 and from 302.00 to 304.10 mcd), 3He_{ET} is in the range of 0.1–0.4 pcc/g with a median value of about 0.18, which we refer to as “baseline”. Within the first centimeter of the clay layer 3He_{ET} increases by about 8-fold above baseline and remains high through the lower half of the clay layer. Moving up section, over the next 50 cm, along with rising carbonate content, 3He_{ET} gradually drops to roughly half of baseline. Values remain low for approximately 2.0 m (from 306.1 to 304.1 mcd) before returning to baseline. This high carbonate content and low He interval terminates 0.51 m above the end of the PETM recovery phase II as defined by an inflection point in the δ13C (Zachos et al., 2005; Röhl et al., 2007). For the sake of consistency with the literature we have designated the end of this “carbonate overshoot” phase as the top of recovery phase III rather than redefining recovery phase II. Refer to Table 1 and Fig. 1 for interval locations and definitions.

3He/4He ratios in the range obtained here essentially reflect the ratio of extraterrestrial 3He in IDPs to terrestrial...
$^3$He in detrital minerals. As shown in Fig. 1B, unlike $^3$He$_{ET}$ concentrations, the $^4$He/$^3$He ratios are nearly constant across the entire studied interval. Similar homogeneity is found when $^3$He$_{ET}$ is normalized to the non-carbonate fraction (mostly clay) in the sample: Fig. 1B shows that $^4$He/NCF ratios vary over a narrow range with no significant trend in depth. Large variations in $^3$He$_{ET}$ without variation in $^4$He/$^3$He and $^3$He$_{ET}$/NCF are not produced by changes in the $^3$He$_{ET}$ flux, but instead are indicative of changes in sedimentation rate (Farley and Eltgroth, 2003).

3.3. Calibration of $^3$He$_{ET}$ flux at ODP Site 1266

To convert $^3$He$_{ET}$ concentrations into sedimentation rates requires an estimate of the local flux, $F$, over a calibration interval of known duration and proximal to the inter-
Table 1
Summary of intervals of interest within the PETM including a comparison of durations indicated by this work and the Röhl et al. (2007) age model.

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<tbody>
<tr>
<td>Clay layer base</td>
<td>Sharp lower contact of dissolution</td>
<td>306.78</td>
<td>0</td>
<td>–</td>
<td>0</td>
<td>–</td>
<td>170.64</td>
<td>0</td>
<td>–</td>
<td>0</td>
<td>–</td>
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<tr>
<td>Clay layer</td>
<td>Interval of carbonate dissolution</td>
<td>306.15</td>
<td>167 $^{+34/-24}$</td>
<td>–</td>
<td>92</td>
<td>–</td>
<td>169.05</td>
<td>99 $^{+17/-13}$</td>
<td>–</td>
<td>94</td>
<td>–</td>
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<tr>
<td>Clay layer top</td>
<td>%CaCO$_3$ recovered to pre-event values</td>
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<tr>
<td>Core base</td>
<td>Onset of CIE</td>
<td>–</td>
<td>21 $^{+/-}$</td>
<td>–</td>
<td>0</td>
<td>–</td>
<td>170.64</td>
<td>0</td>
<td>–</td>
<td>0</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Core</td>
<td>Sustained minimum $\delta^{13}$C values</td>
<td>–</td>
<td>–</td>
<td>113</td>
<td>–</td>
<td>59</td>
<td>–</td>
<td>–</td>
<td>88</td>
<td>–</td>
<td>71</td>
<td>–</td>
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<tr>
<td>Core top/base of recovery</td>
<td>Initial recovery from sustained minimum $\delta^{13}$C inflection point</td>
<td>306.4</td>
<td>134 $^{+27/-19}$</td>
<td>–</td>
<td>59</td>
<td>–</td>
<td>169.56</td>
<td>88 $^{+16/-12}$</td>
<td>–</td>
<td>71</td>
<td>–</td>
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<tr>
<td>Recovery phase I</td>
<td>Initial rapid recovery of CIE</td>
<td>–</td>
<td>–</td>
<td>33</td>
<td>–</td>
<td>30</td>
<td>–</td>
<td>11</td>
<td>–</td>
<td>23</td>
<td>–</td>
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<td></td>
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<tr>
<td>Recovery phase I/II boundary</td>
<td>“Shoulder” $\delta^{13}$C inflection point</td>
<td>306.15</td>
<td>167 $^{+34/-24}$</td>
<td>–</td>
<td>89</td>
<td>–</td>
<td>169.05</td>
<td>99 $^{+17/-13}$</td>
<td>–</td>
<td>94</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Recovery phase II</td>
<td>Gradual recovery of CIE</td>
<td>–</td>
<td>–</td>
<td>50</td>
<td>–</td>
<td>82</td>
<td>–</td>
<td>–</td>
<td>19</td>
<td>–</td>
<td>59</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Recovery phase II top</td>
<td>$\delta^{13}$C inflection point</td>
<td>304.7</td>
<td>217 $^{+44/-31}$</td>
<td>–</td>
<td>171</td>
<td>–</td>
<td>167.12</td>
<td>118 $^{+21/-15}$</td>
<td>–</td>
<td>154</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Recovery phase III</td>
<td>Continued gradual recovery of CIE, with high carbonate deposition</td>
<td>–</td>
<td>–</td>
<td>17</td>
<td>–</td>
<td>18</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Recovery phase III top</td>
<td>End of anomalously high carbonate sedimentation</td>
<td>304.19</td>
<td>234 $^{+48/-34}$</td>
<td>–</td>
<td>189</td>
<td>–</td>
<td>Not recovered</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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val of interest in both space and time. For this study the chosen calibration interval is between 306.92 and 308.54 mcd, just below the onset of the PETM. Six full precession cycles in Fe concentration are clearly defined in this interval by the high-resolution XRF record of (Röhl et al., 2007). The local apparent flux of $^3\text{He}_{\text{ET}}$ in atoms area$^{-1}$ time$^{-1}$, for each of the 15 samples in the calibration interval is calculated by:

$$F = \frac{^3\text{He}_{\text{ET}}}{q} + \rho \times \text{LSR}$$

(2)

where $^3\text{He}_{\text{ET}}$ is the concentration of $^3\text{He}_{\text{ET}}$ in an aliquot of sediment (atoms/mass of sediment) calculated using our mixing model, $\rho$ is the dry bulk density, and LSR is the linear sedimentation rate in cm$^{-1}$ kyr$^{-1}$. Density values for each sample's depth were interpolated from adjacent GRA bulk density measurements made every 2.5 cm and calibrated to onboard dry bulk density measurements (Zachos et al., 2004). Linear sedimentation rates are based on cyclostratigraphy (Röhl et al., 2007) as shown in Fig. 1D and assume a 21 kyr precession period in the Fe concentration data. The mean of 16 flux determinations based on individual samples spanning the calibration interval is $F = 0.37 \pm 0.06$ (2$\sigma$) pcc cm$^{-2}$ kyr$^{-1}$ where the uncertainty is two standard errors of the mean (Table EA4). We observe no temporal trend in the flux estimates through this interval. However, note that this approach (and especially the computation of the uncertainty) implicitly assumes that there are no variations in sedimentation rate at sub-precessional periods. As an alternative approach using the same data, we averaged all 16 $^3\text{He}_{\text{ET}}$ concentrations and then multiplied the result by the mean mass accumulation rate of the entire calibration interval to get a single flux estimate for the entire period. This approach yields $F = 0.38$, in excellent agreement with the first approach.

3.4. He-based sedimentation rates and age model

Helium-based LSR estimates (Table EA3) were made by rearranging Eq. (2) and assuming $F = 0.37$ pcc cm$^{-2}$ kyr$^{-1}$. An age model was constructed by integrating the $^3\text{He}_{\text{ET}}$-based sedimentation rates, with an age of zero assigned to the base of the clay layer. Uncertainty in the $^3\text{He}_{\text{ET}}$-based sedimentation rate and age model is propagated from uncertainty in the flux calibration only. Uncertainty in individual $^3\text{He}_{\text{ET}}$ measurements is conservatively estimated at 20% based on reproducibility, owing primarily to the low abundance of IDPs within the sediment, but averages out in the age model calculations. Possible uncertainty arising from changes in the local $^3\text{He}_{\text{ET}}$ flux over time is fully discussed below.

As shown in Fig. 1D, from the Paleocene baseline of $\sim$1.7 to 2 cm$^{-1}$ kyr$^{-1}$, the model LSR declines to very low values through the clay layer ($\sim$0.2–0.4 cm$^{-1}$ kyr$^{-1}$, 306.78–306.20 mcd) and then rises to rates nearly double the baseline rates through recovery phases II and III ($\sim$306.17–304.18 mcd) before settling back to baseline values.

The age model indicates a duration of $217 ^{\text{234}/31}$ kyr from the base of the clay layer to the minor $\delta^{13}$C inflection point that defines the end of recovery phase II and 234 $^{48}/\text{O}_{\text{PETM}}$ to the end of recovery phase III (Fig. 2). In this model the zero carbonate layer represents 35 kyr and minimum $\delta^{13}$C values were sustained for 134 $^{27}/\text{O}_{\text{PETM}}$ kyr before recovering over the next $\sim$80–120 kyr.

4. DISCUSSION

These data provide a new chronostratigraphic model by which to evaluate the progression of the PETM in the deep sea. In this section, we compare these new data with both previous He-based studies and also cyclostratigraphy-based models for the PETM.

4.1. Evaluating the $^3\text{He}_{\text{ET}}$ flux

Age models and sedimentation rates estimated using the $^3\text{He}_{\text{ET}}$ method are very sensitive to uncertainties in the assumed helium flux, so here we provide evidence supporting the flux we estimated as well as its constancy. The local $^3\text{He}_{\text{ET}}$ flux at Site 1266 of 0.37 ± 0.06 is intermediate to values reported for the same time interval from other locations. A higher flux was reported in the central Pacific ($\sim$0.5 pcc cm$^{-2}$ kyr$^{-1}$ (Farley, 1995)) and at ODP Site 690 in the Southern Ocean (0.69 pcc cm$^{-2}$ kyr$^{-1}$ ± 15% 2$\sigma$ (Farley and Eltgroth, 2003)), and a lower flux in the North Atlantic ODP Site 1051 (0.22 ± 0.03 pcc cm$^{-2}$ kyr$^{-1}$ (Farley and Eltgroth, 2003)). The apparent regional variability in flux, if not a product of inaccurate age models used for calibration, demands the existence of either diffusive/diagenetic or focusing effects and emphasizes the need to use a local rather than a global flux calibration.

The comparison to Site 690 is especially relevant since it forms the basis of the only other complete $^3\text{He}$-based age model for the PETM. To first order the $^3\text{He}_{\text{ET}}$ profiles from the two sites look very similar (Fig. 3). This suggests common influences on sediment accumulation at each site consistent with changes in diillation driven primarily by carbonate sedimentation, or changes in the global accretion of $^3\text{He}$. Considering the timing of inflection points in $^3\text{He}_{\text{ET}}$ relative to $%\text{CaCO}_3$ across the dissolution horizon we argue that it is highly improbable that the $^3\text{He}$ flux first increased, then decreased, with coincident timing to changes in marine carbonate chemistry following an event of global warming. A more parsimonious explanation is that the global flux remained effectively constant. Also, if sediment focusing or winnowing were a dominant influence, such covariance between the sites would be unlikely. Although we cannot completely rule out the possibility of minor redistribution as a source of discrepancy between the He-based age models at these two sites, we believe that both the local flux estimate and resulting age model are superior at Site 1266 compared with Site 690 for the following reasons. Our current method of determining $F$ accounts for any diffusive or diagenetic loss of helium as well as sediment focusing provided they do not vary over the $\sim$7 m interval containing the calibration period and the PETM. The Site 1266 calibration expressly avoids the sources of uncertainty from which the Site 690 flux estimate (and resulting age model) may have suffered (Sluijs et al., 2007). In particular, recovery gaps in the calibration interval were avoided by the
offset multiple-hole drilling strategy used on ODP Leg 208. Furthermore, we used samples collected from the same core (1266C 17H) as most of the interval of interest and an undisputed section of the Röhl et al. (2007) chronology. This avoids possible complications arising from sediment expansion following removal of the overburden. Compared to the calibration of $F$ performed at Site 690, higher sampling density over the calibration interval at Site 1266, as well as the multiple methods of determining $F$, accommodate possible orbital scale variations in sedimentation rates. Finally, the Site 1266 calibration assumes the flux of $^3$He$_{ET}$ remained constant for a much shorter interval; <450 kyr vs. the ~3500 kyr duration of C24r and C25n (Westerhold et al., 2007). This reduces uncertainty due to temporal variability in the local apparent $^3$He flux, which as previously discussed (Farley and Eltgroth, 2003) is probably the largest source of uncertainty in the $^3$He method.

The Site 1266 calibration could still yield an erroneous chronostratigraphy if the $^3$He flux varied through the interval of interest, either due to a global change in extraterrestrial accretion rate, or due to local sedimentary phenomena. Several lines of evidence fail to reveal such complications in the ODP 1266 data set. First, the cycle-based and $^3$He$_{ET}$-based sedimentation rates match not only during the calibration interval (where they were forced to do so) but also where lithologic cycles become readily apparent again, toward the end of our record above 303.6 mcd (Fig. 1D). If a temporal variation in $F$ had occurred, it returned to pre-PETM levels within ~300 kyr of the event, a highly unlikely scenario. Second, large variations in $^3$He$_{ET}$ are observed to occur with minimal variation in $^3$He/$^4$He and $^3$He$_{ET}$/NCF ratios (Fig. 1B) across the entire studied interval. This is suggestive of variations in bulk sedimentation rate (or dissolution) rather than changes in the extraterrestrial accretion rate or in IDP focusing/winnowing.

4.2. Comparison of $^3$He$_{ET}$-based and cyclostratigraphic models for the PETM

The study of Röhl et al. (2007) established a cycle-based chronostratigraphy through the PETM at Site 1266 (Fig. 1D) with which we can compare our results. The sedimentation rate patterns of the two models are generally similar: rates initially drop steeply at the base of the clay layer, then increase to a maximum over the next few meters, then decline back to pre-event levels (Fig. 1D). However, there are prominent differences that are reminiscent of those encountered at Site 690 (Farley and Eltgroth, 2003; Röhl et al., 2007). Just as at Site 690, deviation from the cycle-based rates begins near the top of the CIE core and extends
into the recovery interval. The $^3$He$_{ET}$ model yields relatively lower sedimentation rates through the core and initial recovery (phase I) but higher rates through all of recovery phases II and III, with peak rates in the high carbonate interval (between 304.4 and 305.6 mcd at Site 1266). In comparison the transition to higher rates in the cycle-based model are delayed, with peak values between 303.0 and 304.6 mcd.

Fig. 2 compares $\delta^{13}$C and $\%$CaCO$_3$ plotted against the $^3$He$_{ET}$ and cycle-based age models. Estimates for the total duration of the PETM are roughly similar, but substantial disagreement lies in the allocation of time within the event. Compared to the cycle-based model, the $^3$He$_{ET}$ model indicates up to a 50% longer duration for the clay layer with a more gradual transition to high carbonate content and

Fig. 3. Correlation of ODP Sites 1266 and 690 $\delta^{13}$C$_{bulk}$ and $^3$He$_{ET}$ records. Green tie points after Zachos et al. (2005), purple dashed tie points after Röhl et al. (2007). Similarity in the timing of inflection points in the $^3$He$_{ET}$ curves is consistent with a constant local $^3$He$_{ET}$ flux at each site. The upper extent of low $^3$He$_{ET}$ at Site 690 is poorly constrained due to incomplete recovery during ODP Leg 113. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
nearly double the duration of minimum δ13C values (113 vs. 59 kyr).

It is notable that these discrepancies occur where identification of cyclical variations is least certain. Through the clay layer (~306.5 mcd) and in the high carbonate interval (~305.2 mcd) the minor element variability used in the cycle-based model is of low amplitude and cyclical variations are not readily apparent (e.g., see Supplementary Fig. S1 in Röhl et al. [2007]), hindering recognition of precession cycles. A similar conclusion can be drawn from the Site 690 age models.

An important observation gleaned from the He record of Site 690 is that the highest carbonate interval accumulated at a very rapid rate, higher than indicated from the cycle-based model (Farley and Eltgroth, 2003). The Site 1266 He and cycle chronologies differ in a similar way, although with a smaller magnitude of discrepancy. If the orbital model is correct at Site 1266, the anomalously high sedimentation rates implied by the 3HeET model during this phase would imply that the burial flux of 3He was reduced compared to earlier intervals, possibly by preferential winnowing of the He-bearing particles. This is not supported by the constant 3He/4He and 3HeET/NCF ratios observed in this interval. Furthermore, the carbonate in this rapidly deposited interval at both Walvis Ridge and Maud Rise is dominated by coccolithophores (Zachos et al., 2004; Kelly et al., 2005; Raffi et al., 2009), generally <20 μm, the same size fraction as IDPs and pelagic clays, not coarser grains as would be expected in the case of winnowing. If sufficient winnowing is occurring to disrupt the 3He flux it is happening in such a way as to fractionate the 3HeET from carbonate but not the similar-sized clay fraction. The absence of winnowing effects is also indicated by the percent coarse fraction (>63 μm) data which are essentially identical in the recovery interval at all sites over the 2 km depth transect of Leg 208 (Kelly et al., in press).

Comparison of these results to other PETM sites may resolve these discrepancies, but is hampered by (a) the difficulty of identifying time-synchronous tie points within the PETM for making the comparison, particularly toward the end of the event and (b) the near-certainty that the clay layer at some locations, including Site 1266, is at least partially the product of dissolution of Paleocene (i.e., pre-PETM) sediment. The latter is relevant because the duration of the event as commonly defined includes the time represented by the clay layer.

The 3HeET-based chronology at Site 690 indicates a more rapid event overall than implied by our model for Site 1266. The core of the CIE at Site 690 is suggested to last 88 +16/-12 kyr, vs. 134 +27/−19 kyr at Site 1266. Records of the PETM at Walvis Ridge, unlike Maud Rise, include a substantial horizon (~25 cm) with near zero %CaCO3. The sediment–water interface at Site 1266 is estimated to have migrated down a minimum of 12 cm during the dissolution event (Zeebe and Zachos, 2007), which places the onset of the PETM at Site 1266 approximately 21 kyr within the clay layer. This differential burn-down accounts for at least some of the difference between the 3HeET age models of the two sites. In addition it should be noted that the modeled extent of burn-down is sensitive to poorly known factors including bioturbation and initial porosity.

As discussed in Section 4.1 and by Sluijs et al. (2007), there are reasons to suspect the flux estimate at Site 690. Overestimation of the flux could account for the shorter duration and the faster recovery rate at Site 690 relative to both age models at Site 1266. However, we note that the 3HeET-based sedimentation rates just before the onset of the PETM at Site 690 are in fair agreement with those proposed by Röhl et al. (2007) using cyclostratigraphy. Following our approach at Site 1266 we could compute the flux based on the undisputed pre-PETM cyclostratigraphy; doing so would yield a flux about 10% lower than originally estimated. Thus while some of the discrepancy between the 3HeET-based chronostratigraphy can be resolved by such a revision, the Site 690 model still yields a slightly faster tempo for the PETM. We have no explanation for this relatively modest discrepancy.

Although the exact details remain uncertain, relative to earlier cycle-based models 3HeET-based age models of the PETM imply a comparatively longer δ13C minimum core (~113 kyr) but a more rapid recovery (Table 1). This conclusion is supported by recent work on expanded terrestrial sections in the Bighorn Basin, WY (Aziz et al., 2008) that indicates a duration of 5.5 precession cycles for the core (~115 kyr) and two cycles (~40 kyr) for the recovery. The Bighorn Basin sections as well as our best estimate for the duration of the PETM at Site 1266 (clay layer to the end of Phase II) fall within the allowable 5–7 precession cycles required to maintain the phase of the 405 kyr long eccentricity cycles detected in more regular sediments above and below the PETM at Walvis Ridge (Röhl et al., 2007; Westerhold et al., 2007). One important implication of the extended duration of the low δ13C interval is that it likely requires a sustained release of isotopically light carbon following an initial massive input (Zeebe et al., 2009).

4.3. Recovery Carbonate Cap

A prominent feature of the late recovery phase lithology is the rise in carbonate content that, assuming constant clay flux, implies a >180% increase in the carbonate burial rate over the pre-PETM baseline. This is similar to the approximate doubling of the sedimentation rate implied by 3HeET, suggesting the very high %CaCO3 is the product of an increase in carbonate burial (deposition and/or preservation). Could a decrease in the flux of non-carbonate material contribute to the rise in carbonate content? As the majority of the non-carbonate sediment is terrigenous (Nicolo and Dickens, 2006), a reduction in the terrigenous flux should generate an increase in 3HeET/NCF. Instead, the values of 3HeET/NCF remain constant, supporting the conclusion that the carbonate-rich interval is primarily a consequence of elevated carbonate burial.

An extreme rise in carbonate accumulation and deposition of a carbonate-rich layer or cap during the recovery phase is consistent with a number of proposed mechanisms for the PETM. Unique microfossil assemblages and clay mineralogy found in the cap carbonate at ODP Site 690 suggest enhanced shallow calcite export and terrestrial weathering/runoff during the PETM recovery (Kelly et al., 2005). Such a change to the biologic pump would
accelerate the recovery of the CIE and would enhance carbonate deposition. Furthermore, increased silicate weathering (Ravizza et al., 2001) and buffering of marine carbonate chemistry by the dissolution of deep-sea carbonates is expected to lead to a transient overshoot of the lysocline (Walker and Kasting, 1992; Dickens et al., 1997; Zachos et al., 2005; Zeebe et al., 2009). In this case, a highly over-saturated water column would enhance carbonate preservation, particularly at abyssal depths that are typically close to undersaturation. This is supported by the fact that the carbonate content in the equivalent recovery interval of all the sites in the Walvis depth transect is identical (Zachos et al., 2005).

5. CONCLUSIONS

The pattern in $^3$He$_{ET}$ concentrations across the PETM at ODP Site 1266 from Walvis Ridge, South Atlantic closely resembles observations from ODP Site 690 from Maud Rise, Southern Ocean: elevated concentrations in the clay layer and reduced concentrations in the recovery interval. Observations of the lithology and nearly constant $^4$He/$^3$He and $^3$He$_{ET}$/NCF ratios throughout the interval of study support a constant local flux of $^3$He$_{ET}$ and suggest that effects of sediment focusing and or winnowing on IDP distribution are negligible over the interval of interest. By calibrating the local $^3$He$_{ET}$ flux using an orbital age model over an interval prior to the event, these $^3$He$_{ET}$ concentrations were converted to an age model that implies sedimentation rates through the PETM that are far lower than in the latest Paleocene through the clay layer (306.78–306.2 mcd), but higher in the recovery interval (306.2–304.3 mcd). By ~304 mcd the rates return to those of the latest Paleocene. The interval of high sedimentation is coincident with the interval of very high carbonate content and is similar to the pattern observed at Maud Rise. The upper bound of this interval may record the effective end of the PETM perturbation to marine carbonate chemistry.

This new chronology for the PETM indicates a total duration slightly longer than the recently revised cycle-based estimate of Röhl et al. (2007). However, the greater disagreement lies in the allocation of time within the event. The $^3$He$_{ET}$ concentrations imply a comparatively longer duration for the clay layer followed by a more gradual recovery to carbonate-rich sediments and more sustained minimum δ13C values followed by a more rapid recovery. The high sedimentation rates through the recovery interval are consistent with lithologic observations: an overshoot in carbonate content beyond pre-event values during of the latter stages of recovery. The lengthy duration of the CIE favors models that call upon a sustained flux of carbon following an initial pulse.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2010.03.039.

REFERENCES


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