Carbonate saturation dynamics during the Paleocene–Eocene thermal maximum: Bathyal constraints from ODP sites 689 and 690 in the Weddell Sea (South Atlantic)

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ABSTRACT

Spatiotemporal patterns of carbonate dissolution provide a critical constraint on carbon input during an ancient (~55.5 Ma) global warming event known as the Paleocene–Eocene thermal maximum (PETM), yet the magnitude of lysocline shoaling in the Southern Ocean is poorly constrained due to limited spatial coverage in the circum-Antarctic region. This shortcoming is partially addressed by comparing patterns of carbonate sedimentation at the Site 690 PETM reference section to those herein reconstructed for nearby Site 689. Biochemosтратigraphic correlation of the two records reveals that the first ~36 ka of the carbon isotope excursion (CIE) signaling PETM conditions is captured by the Site 689 section, while the remainder of the CIE interval and nearly all of the CIE recovery are missing due to a coring gap. A relatively expanded stratigraphy and higher carbonate content at mid-bathyal Site 689 indicate that dissolution was less severe than at Site 690. Thus, the bathymetric transect delimited by these two PETM records indicates that the lysocline shoaled above Site 689 (~1,100 m) while the calcite compensation depth remained below Site 690 (~1,900 m) in the Weddell Sea region. The ensuing recovery of carbonate sedimentation conforms to a bathymetric trend best explained by gradual lysocline deepening as negative feedback mechanisms neutralized ocean acidification. Further, biochemosтратigraphic evidence indicates the tail end of the CIE recovery interval at both sites has been truncated by a hiatus most likely related to vigorous production and advection of intermediate waters.

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1. Introduction

Several key aspects of an ancient (ca. 55.5 Ma) global warming event termed the Paleocene–Eocene thermal maximum (PETM) are considered analogous to those predicted to develop in the coming centuries due to fossil fuel emissions (Intergovernmental Panel on Climate Change, 2005). On geologic timescales, the PETM was a transient (~170 kyr) episode of extraordinary climatic warmth during which global surface temperatures increased by ~5–9 °C (Kennett and Stott, 1991; Zachos et al., 2001, 2003, 2006; Tripati and Elderfield, 2005; Stujs et al., 2006; Kozdon et al., 2011). Detailed study of deep-sea PETM records has shown that this hyperthermal climatic state is closely linked to a negative carbon isotope excursion (CIE) on the order of ~4‰ in marine inorganic carbon as well as pervasive dissolution of deep-sea carbonate sediments (Kennett and Stott, 1991; Thomas and Shackleton, 1996; Thomas et al., 1999, 2002; Zachos et al., 2001, 2005; Colosimo et al., 2006; McCarren et al., 2008; Kelly et al., 2010; Uchikawa and Zeebe, 2010). Together, these lines of evidence indicate that massive quantities (4500–6800 Pg) of 13C-depleted carbon were rapidly (~5–10 kyr) injected into the ocean–atmosphere system during the PETM (Panchuk et al., 2008; Zeebe et al., 2009).

The source(s) of carbon input is a subject of ongoing debate (see Pagani et al., 2006). Some of the more plausible scenarios thus far proposed involve oxidation of terrestrial and marine stores of organic matter (Kurtz et al., 2003; Higgins and Schrag, 2006), formation/release of thermogenic methane by the emplacement of igneous intrusions into organic-rich marine sediments coupled with mantle out-gassing (Svensen et al., 2004; Storey et al., 2007), and/or rapid sublimation of methane hydrate within seafloor sediments (Dickens et al., 1995; Katz et al., 1999). Irrespective of source, it is clear that massive carbon input caused the lysocline and attendant calcite compensation depth (CCD) to shoal throughout the global ocean as evidenced by a decline in sedimentary calcite at the base of deep-sea PETM records (e.g., Dickens et al., 1997; Zachos et al., 2005). This pulse of intense dissolution reflects severe carbonate undersaturation driven by pH-buffering reactions that acted to neutralize ocean acidification fueled by the carbon input, a scenario broadly similar to that unfolding today due to oceanic uptake of anthropogenic carbon (Feely et al., 2004).

Constraints on such salient aspects of the PETM as the source/size of carbon input, carbon exchange pathways within the ocean and...
biogeochemical processes that helped arrest PETM conditions can be refined by delineating spatiotemporal patterns of deep-sea dissolution (e.g., Zachos et al., 2005; Zeebe and Zachos, 2007; Zeebe et al., 2009). Mapping such spatiotemporal variation in carbonate dissolution on a global scale will require PETM records from a broad spectrum of geographic and bathymetric settings. Unfortunately, much of our present knowledge about lysocline shoaling in the Southern Ocean is based on a single PETM record from the Weddell Sea. Thus, a clear need exists for additional PETM records from the circum-Antarctic region.

Added incentive for studying PETM records from the Southern Ocean is that such high-latitude locations are a bellwether for biotic and environmental change driven by rising global temperatures, and it is well established that marine ecosystems were profoundly affected by PETM warming. In the deep-sea, a benthic foraminiferal extinction event (BEE) eliminated up to 50% of species (Thomas, 1990a, 2003, 2007; Kaiho et al., 1996; Thomas and Shackleton, 1996; Thomas et al., 2000), while ostracodes experienced a brief faunal perturbation during the PETM (Steineck and Thomas, 1996). The complexion of pelagic ecosystems was altered as well with the calcareous plankton, radiolarians, dinoflagellates, and larger benthic foraminifera inhabiting the euphotic zone responding through increased taxonomic turnover and transient restructurings of their paleobiogeographic distributions (Lu and Keller, 1993; Kelly et al., 1996; Schmitz et al., 1996; Speijer et al., 1996; Pardo et al., 1997; Crouch et al., 2001; Bralower, 2002; Tremolada and Bralower, 2004; Schebelner et al., 2005; Gibbs et al., 2006; Hollis, 2006).

In this study, we report the first records delineating secular change in carbonate dissolution/sedimentation within a PETM section recovered at Ocean Drilling Program (ODP) Site 689 (Fig. 1), and use these records to gain added insight into the carbonate saturation dynamics that unfolded in the Weddell Sea. Biochemostratigraphic correlation of the Site 689 record to that published for the nearby Site 690 PETM reference section provides a depth transect spanning the uppermost reaches of lysocline shoaling in the Weddell Sea. The objectives of this study are as follows: (1) delimit the stratigraphic position of the PETM interval at Site 689, (2) gauge the stratigraphic completeness of the Site 689 PETM section through direct comparison to the Site 690 reference section, (3) provide added constraints on the scale of lysocline shoaling in the Weddell Sea region, and (4) document the response of deep-sea carbonate sedimentation to massive carbon input.

2. Study site and stratigraphic context

ODP Site 689 (64°31.009’S, 03°05.996’E) is located atop Maud Rise in the Weddell Sea at a water depth of 2,080 m (Fig. 1), placing it ~160 km southwest of ODP Site 690 (65°9.629’S, 1°12.296’E; 2,941 m water depth) at a water depth that is ~860 m shallower (Barker and Kennett, 1988). Late Paleocene benthic foraminiferal assemblages indicate a mid-bathyal paleodepth (~1,100 m) for Site 689 and a lower bathyal paleodepth (~1,900 m) for Site 690 (Thomas, 1990b; Steineck and Thomas, 1996; Thomas and Shackleton, 1996). The study section (204.50–209.60 m below seafloor, mbsf) consists of homogeneous foramin-nannofossil ooze/chalk, and extends from the upper part of Core 23X across a core gap into the base of overlying Core 22X: Core 689B-23X-2-90 cm to Core 689B-22X-5-100 cm (Barker and Kennett, 1988). Previous studies have shown that the entire study section is confined to calcareous nannofossil Zone NP9 (Pospelov and Wise, 1990), which straddles the Paleocene–Eocene boundary (Zones AP4-AE1) as defined by the Antarctic Paleogene Biozonation for planktic foraminifera (Stott and Kennett, 1990; Huber and Quillévéré, 2005) (Fig. 2).

The first indication that a partial record of the PETM was recovered within the uppermost part of Core 23X of Hole 689B was provided by a low-resolution foraminiferal stable isotope record (Stott et al., 1990). This preliminary investigation reported decreases in the δ18O and δ13C values of deep-dwelling planktic foraminifera (Subbotina spp.) of ~1.2‰ and ~2.0‰, respectively. This finding was corroborated by a complementary study that constrained the BEE to the same (689B-23X-1, 41–116 cm) stratigraphic interval (Thomas, 1990b). Subsequent studies provided further stable isotopic and biostratigraphic evidence for assigning the BEE to 208.00 mbsf (Steineck and Thomas, 1996; Thomas and Shackleton, 1996; Zachos et al., 2005). These studies also showed that the Site 689 PETM section is interrupted by a substantial stratigraphic gap due to incomplete core recovery. Initial estimates suggest that ~1.8 m of section may have been lost within this coring gap (Barker and Kennett, 1988). Thus, the Site 689 PETM record has received scant attention due to incomplete core recovery and a perceived hiatus (Stott et al., 1990).

![Fig. 1](image-url) (A) Generalized bathymetric map delineating the 2,000-m isopleth throughout the South Atlantic region showing the locations of the Maud Rise study area and the Walvis Ridge. (B) Inset showing bathymetric settings (1,000-m contours) and locations of Site 689 (star) and Site 690 (open circle) atop Maud Rise in the Weddell Sea.
3. Materials and methods

3.1. Sampling and bulk-carbonate δ¹³C measurements

The biochemostratigraphic constraints provided by earlier studies (e.g., Stott et al., 1990; Steineck and Thomas, 1996; Thomas and Shackleton, 1996) served as a guide for sampling the Site 689 PETM section. A stratigraphic series of 58 samples, taken at ~5 cm increments over the intervals immediately below (207.23–209.60 mbsf) and above (204.50–205.39 mbsf) the core gap, were used to generate a bulk-carbonate ("bulk") δ¹³C record for the Site 689 section. The stable isotope analyses were performed on ~0.5 mg splits of freeze-dried and powdered bulk sediment at the University of California–Santa Cruz Stable Isotope Laboratory using a PRISM or Optima dual-inlet isotope ratio mass spectrometer coupled to a common acid bath carbonate preparation system. Analytical precision was better than 0.07‰ (±1σ) for δ¹⁸O and 0.06‰ (±1σ) for δ¹³C based on replicate analyses of NBS-19 and in-house Carrara Marble standards (n = 80). All stable isotope values are reported relative to VPDB using the standard δ notation and are electronically archived (Appendix A) with the PANGAEA data repository (http://www.pangaea.de).

3.2. Character of the sedimentological data

A contiguous, U-channeled interval (207.20–208.62 mbsf) measuring 1.42 m was extracted from the uppermost section of Core 23X to delineate changes in carbonate sedimentation and preservation. Bulk-sediment samples (n = 121) were taken at ~1 cm increments from this contiguous U-channel beginning ~62 cm below the level of the BEE (208.00 mbsf) and extending up to the base of the core gap. This high-resolution record was extended down core by taking an additional 12 bulk-sediment samples (~4 cm spacing) over the 52 cm interval (208.63–209.15 mbsf) directly below the U-channeled interval. An additional 21 samples (~5 cm spacing) were taken from the interval immediately above the core gap (204.50–205.39 mbsf). Each bulk-sediment sample (n = 154) was oven dried at 30 °C and weighed prior to being soaked in a mild 3% solution consisting of sodium hexametaphosphate, hydrogen peroxide and pH-buffered distilled water. The disaggregated samples were rinsed with tap water over a 63-μm sieve, oven dried, and the mass of the coarse fraction (>63 μm) recorded. Weight-percent coarse fraction (wt.% CF) of each sample was calculated by dividing the mass of the coarse fraction by the total dry bulk weight. Foraminiferal shells are the dominant component of the coarse fraction in such deep-sea carbonates, making wt.% CF a useful proxy for changes in carbonate production and dissolution (e.g., Thunell, 1976; Peterson and Prell, 1985; Bassinot et al., 1994; Howard and Prell, 1994).

Fifty of the bulk-sediment samples (i.e., 35 below the core gap: 207.23–209.10 mbsf and 15 above the core gap: 204.50–205.39 mbsf) were sub-sampled to generate a (~5 cm spacing) record of sedimentary carbonate content (%CaCO₃). The %CaCO₃ analyses were performed on ~20–50 mg splits of freeze-dried and powdered bulk sediment using standard methods on a UIC Carbon Coulometer Analyzer at the University of California–Santa Cruz (UCSC) Marine Analytical Laboratory. Analytical precision was better than ±1.2% (one RSD)
based on replicate analyses of a pure CaCO₃ reagent standard (n = 16). Sample reproducibility was better than ± 1.6% (one RSD) based on replicate analyses (n = 18) of three samples. All %CaCO₃ and wt.% CF values are electronically archived (Appendix A) with the PANGAEA data repository (http://www.pangaea.de).

3.3. Carbonate preservation data

Records of carbonate preservation were generated for a subset of samples (n = 22) from the Site 689 section (≈ 10 cm resolution). The coarse fraction (> 63 μm) of each sample was dry sieved over a 150-μm screen, and the percentage of planktic foraminiferal fragments (%PF) was calculated by dividing the number of planktic fragments by the sum of all planktic “grains” (whole tests + fragments) counted in a given sample (e.g., Thunell, 1976). Specimens with more than half a test were treated as being whole, and a minimum of 240 grains was counted in each sample. In addition, percentages of benthic foraminifera (%BF) were tallied for each sample by dividing the number of benthic tests observed by the total number of tests (planktic and benthic) counted. A minimum of 247 tests (benthics + planktics) was counted for each sample. The tests of deep-sea benthic foraminifera tend to be more resistant to dissolution so their relative abundances typically increase in strongly dissolved assemblages (Thunell, 1976). All carbonate preservation (%PF, %BF) data are electronically archived (Appendix B) with the PANGAEA repository (http://www.pangaea.de).

3.4. Planktic foraminiferal biostratigraphy

A minimum of 250 planktic foraminiferal tests was counted in each of the 22 samples used to delineate changes in carbonate preservation at Site 689. The sieve-size cutoff (≥ 150 μm) is slightly less than that (≥ 180 μm) previously used to tabulate planktic foraminiferal diversity in the Site 690 PETM record (Kelly, 2002); hence, only the salient features of faunal change were used to correlate the two PETM records. The taxonomic groups used for biostratigraphic correlation are: Subbotina spp., Morozovella spp. (= M. aequa/M. subbotiniae), Globanomalina altaiformis, and Acarinina subsphaerica. Previous study of the Site 690 planktic foraminiferal assemblages has also shown that calcification within the species Acarinina soldadoensis (sensu lato) and A. coalingensis (sensu lato) varies over the course of the PETM, and that these changes in biocalcification coincide with critical stages in the CIE (Kelly, 2002). As a result, heavily calcified variants of these two species are collectively assigned to a fifth group informally referred to as “robust acarininids.” Planktic foraminifera not assigned to the aforementioned taxa are ascribed to a miscellaneous group. All planktic foraminiferal assemblage data are electronically archived (Appendix B) with the PANGAEA repository (http://www.pangaea.de).

3.5. Chemo- and chronostratigraphic frameworks

Intensive study of the Site 690 PETM record has produced a high-resolution (~10³ years) bulk δ¹³C stratigraphy that captures the fine-scale structure of the CIE profile. This fine-scale structure provides a series of tie points that are used to partition the CIE profile into a succession of chronostratigraphic subdivisions that have been shown to be correlative throughout the Atlantic Ocean basin (Bains et al., 1999; Norris and Röhl, 1999; Röhl et al., 2000; Farley and Eltgroth, 2003; Zachos et al., 2005; Nunes and Norris, 2006; Röhl et al., 2007). These same isotopic tie points and chronostratigraphic subdivisions are used to correlate the Site 689 and 690 PETM records (Table 1). The chronostratigraphic subdivisions and tie points used in this study are [1] the “pre-CIE interval” representing background conditions that predate carbon input and includes a subtle δ¹³C decrease denoted “A-” (Zachos et al., 2005; Röhl et al., 2007), [2] a “CIE interval” that begins with the CIE onset (tie-point “c” of Bains et al., 1999), extends up-section through two more δ¹³C decreases (tie points “e” and “g” of Bains et al., 1999) as well as the CIE minimum, and ends at the inflexion (tie-point “D”) of Zachos et al., 2005) marking the base of a gradual δ¹³C increase in the CIE curve, [3] a CIE recovery interval over which bulk δ¹³C values gradually increase and terminates at a minor δ¹³C shift towards slightly higher values (tie-point “G” of Zachos et al., 2005; Röhl et al., 2007), and [4] a post-CIE interval where δ¹³C values stabilize on an Eocene baseline that includes tie-point “H” (Zachos et al., 2005; Röhl et al., 2007).

The biochemostratigraphic data are also plotted within a relative-depth domain in which the CIE onset (tie-point “c”) is prescribed to 0.00 m. Once correlated, the sedimentological data from both records are recast within a relative-time domain that prescribes an age of 0.00 ka to the CIE onset (tie-point “c”). The age model upon which the relative-time domain is based was originally developed for the Site 690 PETM section using cyclostratigraphic analysis of high-resolution, X-ray fluorescence core scanner records of barium, iron and calcium contents (Röhl et al., 2007). This “floating” PETM age model was used to assign ages to various tie points embedded within the Site 690 CIE profile that were, in turn, applied to the Site 689 PETM record (Table 1). Ages for intervening samples and datums were estimated using linear interpolation between successive tie points of the CIE profile. The resultant chronostratigraphies also serve as a template for calculating and comparing linear sedimentation rates at the two study sites.

4. Results

4.1. Chemostratigraphic correlation

Below the Site 689 core gap, the bulk δ¹³C records of the two sites appear broadly congruent when plotted within the relative-depth domain (Fig. 2). As in the Site 690 record, values within the Site 689 pre-CIE interval (~1.45 to 0.00 m) vary about a mean of ~2.0‰, decreasing slightly at about ~0.59 m (tie-point “A-” of Zachos et al., 2005) before increasing just prior to the CIE onset. In addition, the Site 689 record captures the three isotopic decreases embedded within the Site 690 CIE profile. The first decrease represents tie-point “c” of Bains et al. (1999) and is the CIE onset (0.00 m), but the magnitude

\[
\text{Table 1} \\
\begin{array}{c|c|c|c|c|c|c|c}
\text{Tie} & \text{Site 690} & \text{Site 689} & \text{Age (ka)} \\
\text{points} & \text{Depth} & \text{Depth} & \text{Röhl et al., 2007} \\
& (mbsf) & (mbsf) & \\
\hline
H & 166.13 & 4.51 & 196.87 \\
PAR & 166.14 & 4.50 & 196.43 \\
C & 167.12 & 3.52 & 205.05 & 3.10 & 153.50 \\
F & 169.05 & 1.59 & NR & NR & 94.23 \\
E & 169.39 & 1.25 & NR & NR & 81.17 \\
D & 169.56 & 1.08 & NR & NR & 71.25 \\
C & 170.02 & 0.62 & NR & NR & 42.38 \\
MA & 170.11 & 0.53 & 207.20 & 0.95 & 36.43 \\
“g” & 170.16 & 0.48 & 207.35 & 0.80 & 33.13 \\
B & 170.33 & 0.31 & 21.90 \\
“e” & 170.46 & 0.18 & 207.95 & 0.20 & 12.71 \\
“c” & 170.63 & 0.01 & 208.15 & 0.00 & 0.75, 0.01 \\
Peb & 170.64 & 0.00 & 208.15 & 0.00 & 0.00 \\
A & 171.24 & –0.60 & 208.74 & –0.59 & –30.80 \\
\end{array}
\]
of tie-point “c” at Site 689 is less than that (~1.0‰) at Site 690. Site 689 values temporarily level off at ~1.30‰ before decreasing a second time at ~0.20 m. This second isotopic decrease represents tie-point “e” of Bains et al. (1999), but as with the previous isotopic decrease the magnitude (~0.6‰) of tie-point “e” is less than that (~1.0‰) at Site 690. Following this second decrease, values temporarily stabilize at ~0.8‰ before decreasing just below the core gap at 0.80 m. This third isotopic decrease represents tie-point “g” of Bains et al. (1999). Bulk δ¹³C values (~1.4‰) immediately above the core gap at Site 690 (2.76 m) are similar to those associated with the stratigraphic level (~3.52 m) where the CIE recovery interval ends at Site 690 (Fig. 2). This correlation is also suggested by the step-like manner in which values in both records increase and then stabilize at ~1.7‰. This relatively minor increase toward slightly higher isotopic values represents tie-point “G” of Zachos et al. (2005), and indicates that the very tail end of the CIE recovery interval was recovered immediately above the core gap at Site 689. A corollary of this correlation is it suggests that the upper half of the CIE interval, and virtually all of the CIE recovery, are lost within the core gap at Site 689. Finally, tie-point “H” located ~4.50 m above the CIE onset at Site 690 (Zachos et al., 2005) is not evident at Site 689 (Fig. 2).

4.2. Biostratigraphic correlation

An important element of the planktic foraminiferal response to PETM conditions is the first appearance of species belonging to the *Morozovella aequa–M. subbotinae* clade in the circumpolar region. This biostratigraphic datum is correlative with the Paleocene–Eocene boundary and the CIE onset (tie-point “c”) (Stott and Kennett, 1990; Huber, 1991; Lu and Keller, 1993; Kelly, 2002; Huber and Quillévéré, 2005). *Morozovellids* first appear ~9 cm below tie-point “c” at Site 690 (Fig. 3A and B), while they are first encountered ~5 cm above the tie-point “c” at Site 689 (Fig. 3G and H). Further, the *Morozovellids* attain an abundance acme (~6%) just above tie-point “c” at Site 689. A corollary of this correlation is it suggests that the upper half of the CIE interval, and virtually all of the CIE recovery, are lost within the core gap at Site 689. Finally, tie-point “H” located ~4.50 m above the CIE onset at Site 690 (Zachos et al., 2005) is not evident at Site 689 (Fig. 2).

![Fig. 3. Biostratigraphic correlation of Weddell Sea PETM sections from Site 690 (upper panel, A–F) and 689 (lower panel, G–L). (A and G) Complementary bulk δ¹³C records with chemostratigraphic subdivisions and tie points shown at far left; gray bands delimit intervals bound by isotopic tie points. Stratigraphic variation in the relative abundances of select planktic foraminiferal taxa: (B and H) the genus *Morozovella*, (C and I) robust acarininids, (D and J) *Globanomalina australiformis*, (E and K) *Acarinina subsphaerica*, (F and L) the genus *Subbotina*. All records plotted in relative-depth domain with CIE onset (tie-point “c”) set to 0.00 m.](image-url)
“g” in both PETM records (Fig. 3A, B, G and H). The full extent of the morozovellid acme may not be captured by the Site 689 record so the placement of this datum at ~0.95 m is somewhat provisional. By comparison, the morozovellid acme occurs at ~0.53 m in the Site 690 section. Morozovellids are absent within the overlying CIE recovery and post-CIE intervals at Site 690 (Fig. 3B). A similar stratigraphic distribution is suggested for the Site 689 section by the absence of morozovellids within the series of samples immediately above the core gap (Fig. 3H). Accordingly, the last occurrence of morozovellids within the Site 689 PETM section is loosely constrained to somewhere within the core gap.

The first appearance of morozovellids at Site 689 coincides with a marked change in the proportions of various species belonging to the genus Acarinina. The relative abundances of A. soldadoensis and A. coalingensis increase sharply just above tie-point “c” in both PETM records. This aspect of the faunal response is enhanced by the rapid increase of “robust” forms belonging to these two species. At Site 690, the relative abundance of these robust variants increases from pre-CIE levels of only ~2% to as high as ~52% at 0.06 m within the CIE interval (Fig. 3C). A similar increase in abundance is seen at Site 689 where robust acarinids increase from pre-CIE levels of <10% to ~50% at 0.05 m within the CIE interval (Fig. 3I).

Another biostratigraphic datum associated with the early stages of the CIE is the first appearance of the marker species, Globanomalina australiformis. This datum has been used to approximate the Paleocene–Eocene boundary (base of Zone AE1) in various circum-Antarctic planktic foraminiferal biozonations (Stott and Kennett, 1990; Huber, 1991; Lu and Keller, 1993; Kelly, 2002; Huber and Quillévéré, 2005). Rare specimens of G. australiformis (~1%) first appear at ~0.18 m within the CIE interval at Site 690, which is roughly correlative with tie-point “e” (Fig. 3D). A somewhat similar stratigraphic range is preserved at Site 689 where rare specimens first appear at ~0.30 m and attain a local abundance peak (~4%) within the portion of the CIE interval bound by tie points “e” and “g” (Fig. 3I).

Several lines of biostratigraphic evidence support the view that the upper half of the CIE interval and nearly all the CIE recovery interval were not recovered at Site 689. At Site 690, the stratigraphically expanded CIE recovery interval contains an unusual planktic foraminiferal assemblage typified by an absence of morozovellids, a temporary disappearance of A. soldadoensis and A. coalingensis, and concomitant increases in the abundances of subbotinids and high-trophic fossil assemblages to Archaef Дальнейшая часть текста:}

The stratigraphies of these two records are plotted within a bivariate space delimited by the relative-depth and relative-time domains to assess spatiotemporal variation in sedimentation rates (Fig. 4). Owing to stratigraphic ambiguities related to the core gap in the Site 689 record, the resulting age-depth plot is restricted to the lower part of the two records straddling the critical transition between the pre-CIE and CIE intervals. Thus, the interval (~30.8 to 36.4 ka) shown begins at tie-point “A–” and extends just above tie-point “g” to the level of the morozovellid acme.

Comparison of the two age-depth curves shows that sedimentation rates (~2.0 cm kyr⁻¹) were similar during the pre-CIE interval and decrease slightly across the base of the CIE interval at both sites (Fig. 4). Linear sedimentation rates over the earliest part of the CIE interval (0.00–12.7 ka) bound by tie points “c” and “e” drop to ~1.6 cm kyr⁻¹ and ~1.4 cm kyr⁻¹ at sites 689 and 690, respectively. However, sedimentation rates at Site 689 start to outpace those at Site 690 just prior to tie-point “e” (12.7 ka). The two curves continue to diverge over the succeeding interval bound by tie points “e” and “g” (12.7–33.1 ka) where linear sedimentation rates at Site 689 (~3 cm kyr⁻¹) are twice those (~1.4 cm kyr⁻¹) at Site 690. Moreover, linear sedimentation rates continue to increase at Site 689 peaking at ~4.5 cm kyr⁻¹ over the brief interval (33.1–36.4 ka) delimited by tie-point “g” and the morozovellid acme, whereas they remain relatively constant (~1.5 cm kyr⁻¹) over this same interval at Site 690 (Fig. 4). The Site 689 age-depth curve also reveals that linear sedimentation rates during the latter part of the CIE interval (12.7–36.4 ka) are notably higher than those in the pre-CIE interval (~30.8 to 0.00 ka).

4.4. Patterns of carbonate sedimentation and preservation

Plotting the carbonate sedimentation (%CaCO₃, wt.% CF) and preservation (%PFF, %BF) data within the relative-age domain shows that the CIE onset (tie-point “c”) is accompanied by marked sedimentological change (Fig. 5). Sedimentary carbonate content decreases at both sites, but the magnitude of this decrease at Site 689 (i.e., ~90% to ~82%) is only about half that at deeper Site 690 (i.e., ~83% to ~60%) (see Fig. 5B and G). At Site 689, %CaCO₃ values remain relatively low (83–87%) over the interval bound by tie points “c” and “e,” then rebound to higher values (~90%) just above tie-point “g” at
~34.7 ka (Fig. 5G). A similar increase in %CaCO₃ is not seen at Site 690 until much later (~100 ka) during the CIE recovery interval (Fig. 5B). Unfortunately, it appears that virtually all the carbonate-rich (>90%) CIE recovery interval preserved in the Site 690 record was lost to the core gap at Site 689. Above the core gap at Site 689, %CaCO₃ is relatively high (~90%) over the part (~153.50–196.43 ka) of the section spanning the very end of the CIE recovery (tie-point "G") and the post-CIE interval (Fig. 5C), while carbonate content (~84%) within the correlative part of the Site 690 record is slightly lower (Fig. 5B).

The wt% CF records are initially similar at the two sites with values varying between 5 and 10% over the lower part of the pre-CIE interval (Fig. 5C and H); however, the records begin to diverge over the uppermost half of the pre-CIE interval due to a steady increase at Site 689. This divergence is evident across tie-point "c" where wt% CF drops to ~3% at Site 690 (Fig. 5C) and increases to ~14% at Site 689 (Fig. 5H). The most striking difference between the wt% CF records is the increase in variance over the portion of the CIE interval (0.00–36.43 ka) bound by tie points “c” and “g” at Site 689. This part of the Site 689 wt% CF record exhibits high frequency,
large amplitude oscillations delimited by a series distinct minima (6–8%) and maxima (20–25%). In contrast, a similar increase in variance is not expressed in the Site 690 wt.% CF record (Fig. 5C). The significance of this inter-site discrepancy is hard to grasp since Site 690 record may be aliased by inadequate sampling. Omission of the CIE recovery interval at Site 689 precludes direct comparison of this part of the PETM record to that at Site 690; still, it is evident that wt.% CF values in the post-CIE interval (153.50 ka to −205 ka) are lower (<3%) than pre-CIE values at both sites.

Increased carbonate dissolution during the transition between the pre-CIE and CIE intervals is signaled by an increase in planktic foraminiferal fragmentation (%PFF) at both sites. At Site 690, pre-CIE values centered on −11% rapidly spike to a maximum of −40% at −5.6 ka before dropping off to −25% for the remainder of the CIE interval (Fig. 5D). The %PFF increase seen at Site 689 is more subtle in nature for just dropping off to ~25% for the remainder of the CIE interval (153.50 ka to −205 ka) are lower (<3%) than pre-CIE values at both sites.

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Application of the Site 690 PETM age model (Röhl et al., 2007) indicates that the initial 36.43 ka of the CIE interval is present within the part of the Site 689 section below the core gap. Several lines of biostratigraphic evidence corroborate this interpretation. For instance, tie-point “c” coincides with a marked increase in the abundances of robust variants belonging to the species Acarinina soldaodosensis and A. coalingensis as well as the first appearances of such marker taxa as the morozovellids and Globanomalina australiformis at both sites (Fig. 3A–D and G–J). The incursion of morozovellids into the Weddell Sea area attests to the extra-tropical migration of warm-water species into the circumpolar Antartic region during the earliest stages of the PETM (Lu and Keller, 1993; Kelly, 2002; Huber and Quillévéré, 2005). Furthermore, the morozovellid acme occurs just above tie-point “g” in both records (Fig. 3A, B, G, and H). An important corollary of this correlation is that sedimentation rates at the two sites begin to diverge ~13 ka after the CIE onset at tie-point “e” (Fig. 4). This divergence is due to an increase at shallower Site 689 where sedimentation rates higher than pre-CIE rates are recorded over the interval boundary. The %CaCO3 values at Site 690 are higher than those at Site 690 (Fig. 2). We attribute these dissimilarities to the time-averaging effects of sediment-mixing processes (bioturbation), which tend to smooth chemostratigraphies by dampening the amplitudes of isotopic excursions (e.g., Schiffelbein, 1984). Hence, the stratigraphy at shallower Site 689 has been more intensely smoothed by sediment mixing relative to that at Site 690. It therefore follows that, despite its higher carbonate content, the stratigraphy of the Site 689 section spanning the CIE onset is not expanded relative to that at Site 690. This supposition is supported by the similar sediment accumulation rates (~1.5 cm kyr⁻¹) recorded for the first 13 ka of the CIE interval at the two sites (Fig. 4), and by the lack of intermediate values in δ¹³C records compiled from individual foraminiferal shells across the base of the CIE interval at both sites (Thomas et al., 2002; Zachos et al., 2007).

5. Discussion

Previous studies have established that the early stages of the PETM were recovered at Site 689 (Stott et al., 1990; Zachos et al., 2007), and that PETM conditions profoundly perturbed the benthic ecosystem at this bathymetric setting (Steinbeck and Thomas, 1996; Thomas and Shackleton, 1996). The smoothed, gradual appearance of the CIE onset (tie-point “c”) and relatively high carbonate content (≥82%) suggest that the Site 689 stratigraphy spanning the transition into the PETM is more complete than at Site 690 (Fig. 4A, B, F, and G). Conversely, there is the issue of how much of the PETM record was lost within the core gap at Site 689. We address these, and related questions by comparing the Site 689 biochemosтратigraphy to that of the Site 690 PETM section. Geographic proximity of the two sites enhances inter-site correlation by minimizing spatial variation in such factors as surface-ocean carbonate production and planktic foraminifer biogeographic ranges.

5.1. How complete is the site 689 PETM record?

Comparison of the bulk δ¹³C records reveals that the portion of the Site 689 record below the core gap (~1.45 to 0.95 m) captures the step-wise series of three isotopic decreases (tie points “c,” “e,” “g”) embedded within the CIE at Site 690 (Fig. 2). However, the isotopic decreases in the Site 689 record are not as sharp as at Site 690, and the amplitudes of tie points “c” and “e” appear attenuated relative to those at Site 690 (Fig. 2). We attribute these dissimilarities to the time-averaging effects of sediment-mixing processes (bioturbation), which tend to smooth chemostratigraphies by dampening the amplitudes of isotopic excursions (e.g., Schiffelbein, 1984). Hence, the stratigraphy at shallower Site 689 has been more intensely smoothed by sediment mixing relative to that at Site 690. It therefore follows that, despite its higher carbonate content, the stratigraphy of the Site 689 section spanning the CIE onset is not expanded relative to that at Site 690. This supposition is supported by the similar sediment accumulation rates (~1.5 cm kyr⁻¹) recorded for the first 13 ka of the CIE interval at the two sites (Fig. 4), and by the lack of intermediate values in δ¹³C records compiled from individual foraminiferal shells across the base of the CIE interval at both sites (Thomas et al., 2002; Zachos et al., 2007).
sites (Thomas, 1990b; Steineck and Thomas, 1996; Thomas and Shackleton, 1996); nevertheless, the %BF increase at Site 689 is slightly greater than at Site 690. This apparent paradox is reconciled by the observation that benthic foraminiferal populations inhabiting shallower water depths were less severely affected by the BEE (Thomas, 1998). In short, the records indicate that carbonate dissolution intensified over the entirety of the bathyal depth transect.

Differences in the intensity of carbonate dissolution between the two sites are primarily a function of water depth, yet sediment mixing likely played a role as well. Numerical modeling of the sedimentary response to lysocline shoaling suggests that chemical erosion (“burndown”) of seafloor carbonates is inhibited by the upward mixing of previously deposited sedimentary calcite to the sediment-water interface (Ridgwell, 2007; Panchuk et al., 2008). Thus, sediment mixing probably helped minimize carbonate dissolution and smoothed the CIE profile at Site 689.

Although the Site 690 wt.% CF record is not as finely resolved as that of Site 689, antithetic trends emerge between these records across the pre-CIE to CIE transition. At Site 690, wt.% CF initially drops across the transition then rebounds to ~9% at ~25 ka before steadily declining over the remainder of the CIE interval (Fig. 5C). In contrast, wt.% CF at Site 689 increases across the transition then oscillates between prominent minima and maxima over the interval in which carbonate content is relatively low (82–90%) (Fig. 5G and H). The volatility seen in the Site 689 wt.% CF record is suggestive of winnowing by bottom currents. Alternatively, the high-frequency oscillations in the wt.% CF record may reflect small-scale fluctuations in the relative depths of the planktic foraminiferal and coccolithophore lysoclines once the carbonate saturation horizon had shoaled (e.g., Kelly et al., 2010). In general, these records of carbonate sedimentation indicate that carbon input caused the lysocline to shoal above Site 689 (~1100 m) while the attendant CCD remained below Site 690 (~1900 m) in the Weddell Sea.

5.2.1. Meridional gradient in carbonate undersaturation in the South Atlantic

Comparison of the Weddell Sea PETM records to those recovered from a depth transect drilled along the northern flank of the Walvis Ridge has shown that carbonate undersaturation was more severe in the subtropical southeastern Atlantic (Zachos et al., 2005; Zeebe and Zachos, 2007). The relatively high carbonate content (~60%) within the basal portion of the Site 690 PETM record indicates that the CCD remained below ~1900 m in the Weddell Sea, while the series of PETM records recovered from the Walvis Ridge depth transect reveals that the CCD shoaled to depths <1500 m in this subtropical area (e.g., Zachos et al., 2005). This latitudinal gradient in the degree of undersaturation has been attributed to a deep-sea [CO3^2-] gradient that was reversed relative to that in the modern ocean (Zeebe and Zachos, 2007). However, other factors such as the buffering effects of sediment mixing on the chemical erosion of sedimentary calcite (Ridgwell, 2007; Panchuk et al., 2008) as well as spatial variation in surface-ocean carbonate production/export may have contributed to the development of this meridional gradient (Thomas and Shackleton, 1996).

Another possibility is that downwelling and advection of intermediate water may have played a role in minimizing carbonate dissolution in the Weddell Sea. This means of reducing undersaturation warrants consideration for two reasons. First, the meridional gradient in PETM dissolution delineated by the Walvis Ridge/Weddell Sea latitudinal transect resembles one currently developing in the South Atlantic in response to undersaturation driven by fossil fuel emissions. Today, the amount of anthropogenic carbon stored within the Southern Ocean is appreciably lower than projected inventories based carbon uptake levels by surface waters in the region (Sabine et al., 2004). This modern imbalance has been attributed to the advection of aqueous CO2 initially absorbed from the atmosphere by cold, surface waters in the Southern Ocean toward the Subtropical Convergence along isopycnals that descend to mid-bathyal depths in a northerly direction (Caldeira and Duffy, 2000). Secondly, such a mechanism for moderating carbonate undersaturation in the Weddell Sea seems viable since fish-tooth neodymium isotope records indicate that this region was an active area of deep-water formation during the PETM (Thomas et al., 2003).

5.2.2. Spatiotemporal variation in lysocline deepening in the Weddell Sea

Subsequent to shoaling, lysocline deepening in the Weddell Sea is signaled by increases in both sedimentation rates and %CaCO3 at both sites. Beginning ~13 ka after carbon input (tie-point “e”), linear sedimentation rates at Site 689 increase to values (~3 cm kyr^-1) higher than the average pre-CIE rate (~2 cm kyr^-1) and nearly double that registered over the same interval (12.7–33.13 ka) at deeper Site 690 (Fig. 4). However, %CaCO3 remains relatively low over this same interval (Fig. 5G). These two attributes of sedimentation become more congruent over the interval (33.13–36.43 ka) running from tie-point “g” up to the base of the core gap where sedimentation rates undergo a secondary increase to ~4.5 cm kyr^-1 and %CaCO3 values (>90%) become more comparable to pre-CIE levels (Figs. 4 and 5G). A puzzling aspect of this jump in sediment accumulation rates is that the corresponding %PFF record (12.7–36.43 ka) indicates that planktic foraminiferal preservation generally declined over this interval (Fig. 5I); still, sedimentation rates are substantially higher than those associated with the pre-CIE interval (Fig. 4). By comparison, %CaCO3 values do not approach 90% until much later (~100 ka) at deeper Site 690 (Fig. 5B). The temporal offset between the two %CaCO3 records conforms to a depth-dependent pattern whereby the lysocline deepened below shallower Site 689 first then continued its gradual descent to depths below Site 690. A similar spatiotemporal pattern in lysocline subsidence occurred along the depth transect drilled at Walvis Ridge (Zachos et al., 2005; Röhl et al., 2007; Kelly et al., 2010).

It is at this point (~100 ka) that deep-sea carbonate sedimentation becomes remarkably uniform over a wide range of bathymetric settings throughout the South Atlantic (Zachos et al., 2005; Röhl et al., 2007; Kelly et al., 2010). This striking increase in deep-sea carbonate sedimentation is particularly evident at Site 690 where %CaCO3 (>90%) and wt.% CF (<3%) are higher and lower than pre-CIE levels, respectively (Fig. 5A–C). Another hallmark of this “oversaturation event” is its unique planktic foraminiferal assemblage distinguished by the temporary disappearance of robust acarininids (Acarinina soldadoensis and A. coalingensis), and concomitant increases in subbotinids and high-spired forms tentatively ascribed to A. subspphaerica (Fig. 3C, E, and F). Overall, planktic foraminifera are scarce within this carbonate-rich interval as indicated by the local high (~16%) in %BF values over this interval at Site 690 (Fig. 5E). Collectively, these lines of evidence reflect an extremely deep lysocline suppressed by elevated fluxes of fine fraction (~63 μm), coccolithophorid carbonate (Kelly, 2002; Kelly et al., 2005).

Although most of this distinctive CIE recovery interval was lost within a core gap at Site 689, it is possible to estimate the amount of section missing by extrapolating the linear sedimentation rate (~4.5 cm kyr^-1) obtained from just below the core gap up through the unrecovered interval. Assuming that sedimentation (~4.5 cm kyr^-1) remained uninterrupted and that the missing section represents ~117.07 ka, it appears that ~5.27 m of section was omitted from the Site 689 section. We therefore provisionally report that the CIE recovery interval (75–153.50 ka) at Site 689 is likely to be highly expanded (~3.5 m) relative to that at Site 690 (~2.5 m). This tentative estimate is consistent with the view that the lysocline gradually subsided below its pre-CIE depth, and generally consonant with the hypothesis that enhanced continental weathering/pedogenesis helped reduce atmospheric greenhouse gas concentrations and neutralize ocean acidification at the close of the PETM (e.g., Dickens et al., 1997).
5.2.3. Post-CIE sedimentation in the Weddell Sea

At Site 690, the CIE recovery is delimited by an asymptotic increase in bulk δ13C values over a relatively expanded stratigraphic interval that terminates with a step-like increase (tie-point “G”) toward slightly higher isotopic values (e.g., Bains et al., 1999; Röhl et al., 2000, 2007; Zachos et al., 2005). Here we note that tie-point “G” coincides with sharp increases in both %PFF and %BF (Fig. 5A, D, and E). These lines of evidence signal a stratigraphic break. The amount of time omitted by this hiatus is difficult to ascertain, but it is likely less than one precession cycle (~21 ka) given the resolution of the Site 690 age model (Röhl et al., 2007). By comparison, the Site 689 post-CIE interval is typified by high %BF values and a stratigraphy (~34 cm thick) that is condensed relative to that (~98 cm thick) of Site 690 (Fig. 5J). Unfortunately, the post-CIE portion of the Site 689 chronostratigraphy is too poorly resolved to precisely constrain the amount of time missing within this condensed interval. This shortcoming necessitated the use of a linear sedimentation rate (0.8 cm kyr−1) for estimating the ages of post-CIE samples bound by tie-point “G” (153.50 ka) and the PAR (196.43 ka). That said, these two datums loosely constrain the amount of time missing from the Site 689 post-CIE interval to no more than ~43 ka. The collective evidence indicates that the Site 689 post-CIE interval has been truncated by hiatuses most likely related to vigorous advection of intermediate waters in the Weddell Sea.

6. Conclusions

The Paleocene–Eocene thermal maximum (PETM) was an ancient (~55.5 Ma) global warming event closely coupled to rapid carbon input and ocean acidification, yet much of what is known about the response of marine carbon cycling in the sensitive circum-Antarctic region to this hyperthermal climate state is based almost exclusively on one deep-sea record (Site 690) from the Weddell Sea. We address this shortcoming by delineating patterns of carbonate sedimentation/preservation within the PETM record recovered from the shallower sister site of Site 690, nearby Site 689. Biochemosтратigraphic correlation to the Site 690 reference section reveals that the Site 689 section captures the initial 36.4 ka of the CIE interval, and that this stratigraphic record is nearly twice (~95 cm) as thick as the correlative part of the CIE interval at Site 690 (~53 cm). The relatively expanded stratigraphy and higher carbonate content (>82%) of the portion of the CIE interval recovered at Site 689 indicates that dissolution was less severe than at deeper Site 690. A relatively shallow bathymetric setting and elevated levels of sediment mixing were the primary factors for minimizing dissolution at Site 689. Moreover, we speculate that the advection of intermediate water may have helped reduce dissolution in the study area by transferring aqueous CO2 absorbed at the sea surface out of the Weddell Sea area. The depth transect delimited by these two PETM records indicates that the lysocline initially shoaled above mid-bathyal Site 689 (~1,100 m) while the attendant CCD remained below lower bathyal Site 690 (~1,900 m) during the early stages of the PETM.

Sedimentological evidence also indicates that it took somewhere between ~13 and ~33 ka after carbon input for the lysocline to deepen below Site 689. By comparison, a similar sedimentological signal (~90% CaCO3) is not registered at deeper Site 690 until ~100 ka after carbon input. The temporal offset in the initiation of this carbonate enrichment at the two sites conforms to a bathymetric trend reflecting the gradual deepening of the lysocline, with it subsiding below shallower Site 689 first then continuing its descent to depths below Site 690.

Although the latter half of the CIE interval and practically all the CIE recovery interval were not recovered at Site 689, coarse fraction (>63 μm) content within the post-CIE interval is lower than pre-CIE levels. This distinctive shift in sediment grain-size distribution is also recorded at Site 690 and along the Walvis Ridge, and has been attributed to an increased flux of fine-fraction coccolithophore carbonate to the seafloor due to exceptionally high [CO2] within the overlying water column (Kelly et al., 2010). The persistence of this sedimentological signature well beyond the CIE recovery phase at various locations throughout the South Atlantic testifies to the long-lasting effects of transient PETM conditions, and indicates that the lysocline was repositioned to a depth deeper than it occupied prior to carbon input. This particular aspect of spatiotemporal variation in carbonate sedimentation is consistent with carbon cycle models that invoke enhanced continental weathering as a long-term mechanism for neutralizing ocean acidification and curbing greenhouse gas-induced climatic warmth (e.g., Walker et al., 1981; Berner et al., 1983; Archer et al., 1997; Dickens et al., 1997; Ravizza et al., 2001; Zachos et al., 2005).

Finally, the records of carbonate sedimentation indicate that the uppermost part of the CIE recovery interval (tie-point “G”) at both Site 689 and 690 has been truncated by a minor hiatus, and that the stratigraphy of the overlying post-CIE interval at Site 689 is condensed and/or incomplete. We attribute the incompleteness of the post-CIE stratigraphy at Site 689 to non-deposition and/or removal of sediment by vigorous advection of intermediate waters at mid-bathyal depths in the Weddell Sea.

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