Partial collapse of the marine carbon pump after the Cretaceous-Paleogene boundary

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ABSTRACT
The impact of an asteroid at the end of the Cretaceous caused mass extinctions in the oceans. A rapid collapse in surface to deep-ocean carbon isotope gradients suggests that transfer of organic matter to the deep sea via the biological pump was severely perturbed. However, this view has been challenged by the survival of deep-sea benthic organisms dependent on surface-derived food and uncertainties regarding isotopic fractionation in planktic foraminifera used as tracers. Here we present new stable carbon (δ13C) and oxygen (δ18O) isotope data measured on carefully selected planktic and benthic foraminifera from an orbitally dated deep-sea sequence in the southeast Atlantic. Our approach uniquely combines δ18O evidence for habitat depth of foraminiferal tracer species with species-specific δ13C eco-adjustments, and compares isotopic patterns with corresponding benthic assemblage data. Our results show that changes in ocean circulation and foraminiferal vital effects contribute to but cannot explain all of the observed collapse in surface to deep-ocean foraminiferal δ13C gradient. We conclude that the biological pump was weakened as a consequence of marine extinctions, but less severely and for a shorter duration (maximum of 1.77 m.y.) than has previously been suggested.

INTRODUCTION
The Cretaceous-Paleogene (K-Pg, 66.02 Ma) boundary is defined by a major mass extinction of terrestrial and marine life (Schulte et al., 2010). One indication of the impact on marine life is the reduction, or reversal in some locations, of vertical marine carbon isotope gradients (Δδ13C) between planktic and benthic species δ13C, for as long as 3 m.y. (D’Hondt et al., 1998). This has been interpreted as a global reduction in the export of organic matter sinking to deep water in the post-extinction ocean, i.e., weakening of the marine biological carbon pump (Zachos et al., 1989; D’Hondt et al., 1998; Coxall et al., 2006; Esmeray-Senlet et al., 2015). However, the lack of significant extinction of benthic foraminifera that depend on delivery of organic matter to the deep sea, and only relatively brief periods of change in their community structure (Alegret and Thomas, 2007, 2009; Thomas, 2007), has led some to challenge the idea of a large-scale prolonged (~3 m.y.) period of reduced carbon export (Culver, 2003; Alegret and Thomas, 2009). Analyzing isotopic patterns across this extinction event using depth-stratified foraminifera has special challenges: (1) the planktic foraminifera used as dissolved inorganic carbon (DIC) tracers are mostly lost to extinction (>90% taxonomic loss of Smit, 1982), such that no continuous single-species planktic δ13C record crossing the K-Pg boundary has been generated; (2) the new species that evolved in the aftermath are typically small and have strong δ13C vital effects resulting in test calcite that deviates from the DIC δ13C (Alegret and Thomas, 2009); and (3) there may have been changes in ocean circulation patterns across the K-Pg boundary (Alegret and Thomas, 2009; Hull and Norris, 2011; MacLeod et al., 2011), which could have affected the foraminiferal δ13C signal.

To overcome these issues we have generated an open ocean record with robust dating, based on a firm understanding of paleoecology of the rapidly evolving post-extinction planktic taxa. The subsequent multispecies isotopic record improves estimates of vertical δ13C changes and provide more robust constrains on the magnitude and duration of the K-Pg ocean carbon system perturbation. A comparison of our data with benthic assemblage records for the first time reveals commonalities between proxy observations that help harmonize perspectives on the pelagic ecosystem response.

MATERIALS AND METHODS
The K-Pg boundary event is captured in Ocean Drilling Program Site 1262 (Walvis Ridge; 27°11.15′S, 1°34.62′E; Fig. DR1 in the GSA Data Repository1). The K-Pg boundary occurs at ~216.6 m composite depth, calibrated to 66.02 Ma on an astronomically tuned time scale (Dinarès-Turell et al., 2014). We measured δ13C and δ18O on 10 species of planktic and 1 benthic foraminifera using a Thermo Finnigan MAT252 mass spectrometer equipped with an automated KIEL III carbonate preparation unit at Cardiff University, UK. Stable isotope results were calibrated to the Vienna PeeDee belemnite (VPDB) scale by international standard NBS19 and analytical precision was better than ±0.05‰ for δ13C and ±0.03‰ for δ18O.

The selection of species was guided by previous work on early Paleocene planktic foraminifera isotopic depth ecologies (Birch et al., 2012) (Fig. 1): thermocline dwellers—Subbotinina trivalis to S. triloculinoidea; mixed-layer dwellers—Praemurica taurica to Pr. Inconstans; and surface symbiotic—Morozovella praemangula to M. angula for downhole isotopic comparison. To establish a pre-extinction baseline of water column Δδ13C for the Cretaceous, Globotruncana falsostuarti and Racemiguembelia fructicosa were chosen as mixed-layer dwellers and surface symbiotic, respectively (Houston and Huber, 1998). The benthic species Nuttallides truempyi was picked to record δ13C of bottom water DIC because the species is considered to be in isotopic equilibrium with bottom waters (Shackleton et al., 1984). Guembelia truempyi and Hedbergella hollindeensis were picked as the only mixed-layer dwelling species to range above the K-Pg boundary. Taxonomy follows Olsson et al. (1999) for the Paleocene and Bolli et al. (1985) for the Cretaceous.

Planktic Foraminifera δ13C Adjustment Factors
Special challenges to reconstructing K-Pg upper ocean δ13C arise due to the initial dominance of small (<150 μm) post-extinction opportunists

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1GSA Data Repository item 2016088, location figure, further details of δ13C adjustment values with figure, and raw isotope data, is available online at www.geosociety.org/pubs/fl2016.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
The final stage (stage 3) of recovery, ~2.5 m.y. after the event, marks pre-extinction surface to deep Dd to pre-extinction levels and bulk accumulation rates. In stage 2, planktic-benthic 13C began to return 13C and carbonate Dd due to a reduction in the planktic Dd 13C values converge, largely showing offsets between ~1‰ and ~2.1‰ (for asymbiotic and symbiotic, in offsets from inferred DIC respired (metabolic) 12C being incorporated into the test calcite, resulting in 13C of 0.3‰–2‰. Conversely, high Dd 13C (as much as 1.5%e greater than other inferred surface taxa) and positive Dd 13C (unadjusted) can be divided thermocline, warming or change in the source and/or chemistry of bottom Dd, and deep ocean despite transitioning from Cretaceous to Paleocene taxa. The pattern of post K-Pg boundary Δδ13C (unadjusted) can be divided into three stages (Figs. 2A, 2C). An initial stage (stage 1), from the K-Pg boundary to ~300 k.y., is characterized by planktic to benthic Δδ13C values that are close to zero or negative and very low bulk Δδ13C and carbonate accumulation rates. In stage 2, planktic-benthic Δδ13C began to return to pre-extinction levels and bulk Δδ13C and carbonate accumulation rates also increased. Δδ13C increased gradually from ~0.4%e, approaching the pre-extinction surface to deep Δδ13C of ~1.0%e ~1.77 m.y. after the event. The final stage (stage 3) of recovery, ~2.5 m.y. after the event, marks the return of differences between mixed-layer and thermocline planktic foraminifera. The application of ecoadjustment factors (Fig. 2E), which take into account the effect of 12C enrichment in small species, shows no obvious reversal in the Δδ13C gradient.

Oxygen Isotope Record

δ18O data provide critical evidence for habitat depth of planktic foraminiferal species, a constraint that was not taken into account by previous studies of the δ13C gradient (D’Hondt et al., 1998). The species-specific δ18O (Fig. 2) data indicate a thermally stratified water column during the late Maastrichtian. A brief (~10 k.y.) warming is indicated by an ~0.24‰ decrease in δ18O of H. holmdelensis and N. truempyi at the K-Pg boundary. Benthic mixed-layer Δδ18O decreased but, importantly, benthic thermocline δ18O values converge for ~300 k.y. after the K-Pg boundary. Bulk carbonate δ18O shows an increase from ca. 66.2 Ma, with highest values at the boundary, but this trend is not echoed by the foraminifera, although the resolution difference between bulk and foraminifera records may account for this. Bulk δ18O values subsequently decrease and generally follow the surface mixed-layer planktic foraminifera.

DISCUSSION

The new records presented here reveal the importance of understanding and controlling the paleoecological effects of the analyzed species when interpreting the Δδ13C signal. Our records suggest that carbon export started to recover ~300 k.y. after the K-Pg boundary, with pre-extinction values restored by ca. 64.25 Ma, i.e., ~1.77 m.y. after the event, rather than 3 m.y., as suggested previously (D’Hondt et al., 1998). This recovery process was also not staggered; rather, Δδ13C values continued to steadily increase. The last stage of recovery, thought to mark the full recovery in Δδ13C in older records (D’Hondt et al., 1998; Cottrell et al., 2006), coincides with the reacquisition of photosymbiosis (Norris, 1996; Birch et al., 2012) and likely reflects an artifact of paleoecological evolution, as the change occurs in the surface rather than the thermocline or benthic foraminifera.

Paleoceanographic changes could have affected Δδ18O and our interpretations. A change in water mass would affect Δδ13C and Δδ18O. To ensure that our record is driven by export productivity changes, supported by a decrease in carbonate accumulation (Fig. 2) and net temperature and/or local water mass changes, we interrogate our Δδ18O record. Only the benthic and thermocline δ18O values converge at the boundary, suggesting a deepening of the thermocline, warming or change in the source and/or chemistry of bottom waters, and not surface waters. The timing of circulation changes, however, do not match Δδ13C decreases, as water mass changes are suggested to have started before the K-Pg boundary (Frank and Arthur, 1999; MacLeod et al., 2011). In addition, thermal stratification persisted between the surface and deep ocean despite transitioning from Cretaceous to Paleocene taxa. Therefore, potential water mass changes could only partially explain the Δδ13C reduction, and a partial reduction in organic carbon export flux is still required. Geochemical models also support this interpretation, suggesting that a reduction of between 30% and 40% (depending on ocean basin; Ridgwell et al., 2010) in organic export or 10% in burial (Kump, 1991) is needed to achieve the surface to deep Δδ18O seen at the K-Pg boundary.

Spatial heterogeneity between the major ocean basins and shelf recovery patterns has been demonstrated (Hull and Norris, 2011; Sibert et al., 2014; Esmeray-Senlet et al., 2015), with Pacific Ocean sites (e.g., Shatsky Rise) often showing increases in export production after the boundary, while Atlantic and Indian Ocean sites (e.g., São Paulo, Walvis Ridge, and Wombat Plateau) show either no change or a decrease. Evidence suggests that a thermohaline circulation system similar to today was established in the Late Cretaceous (Frank and Arthur, 1999), which could result in regional differences, as suggested by Hull and Norris (2011).While this hypothesis would have been insufficient to explain a reduction for several million years, our newly constrained and significantly shorter timing makes this hypothesis more viable.
Figure 2. Benthic and planktic foraminiferal stable isotopes from Ocean Drilling Program (ODP) Site 1262, calibrated against Vienna Peedee belemnite (VPDB) and against the time scale of Dinares-Turell et al. (2014). A: Carbon ($\delta^{13}$C) isotope. B: Oxygen ($\delta^{18}$O) isotope C: Carbon ($\delta^{13}$C) isotope differences ($\Delta$) between individual planktic and benthic foraminifera species. D: Carbon ($\delta^{18}$O) isotope differences ($\Delta$) between individual planktic and benthic foraminifera species. E: Adjustment option 2 (see the Data Repository [see footnote 1]). Bottom: Close-ups of the Cretaceous-Paleogene (K-Pg) boundary for A–D. Bulk isotope and carbonate accumulations (Carb. accum.) rate data are from Kroon et al. (2007) and benthic diversity data are from Alegret and Thomas (2007). K-Pg transition zone marks the lithologic change observed in the core. Genera abbreviations: M.—Morozovella, Pr.—Praemurica, S.—Subbotina, N.—Nuttallides, R.—Racemiguembelina, Gl.—Globotruncana, G.—Guembelitria, H.—Hedbergella.
The global survival of benthic foraminifera is compelling evidence that the food supply to the deep ocean never ended (Alegret and Thomas, 2009; Culver, 2003). Benthic foraminifera, which are associated with high food abundance (e.g., buliminids), declined and numbers remained low (Alegret and Thomas, 2007) after the K-Pg boundary. Diversity decreased and the community structure changed to smaller, agglutinated, opportunistic forms of benthic foraminifera (Alegret and Thomas, 2007, 2009). These major changes in benthic assemblages lasted for ~300 k.y., which closely matches our stage 1 (Fig. 2) of the carbon recovery, based on our independent δ13C record. The high variability in benthic community structure decreased and began to stabilize at the same time as interspecies δ13C differences between planktic and benthic foraminifera recovered.

CONCLUSIONS

The δ13C collapse at the boundary is likely a combination of vital effects and a real reduction of the biological pump. Water mass changes may have had some influence, but the timing and dominance of deep rather than surface water changes make this unlikely. Initial larger scale changes to export production to ~300 k.y. after the K-Pg boundary are indicated by both the benthic foraminiferal assemblages and our δ13C data (stage 1). A gradient between surface and deep δ13C reappeared concomitantly with stabilization of the benthic assemblages. δ13C continued to increase until pre-extinction values were reached at 1.77 m.y. after the event, significantly earlier than has previously been suggested. The final stage of the δ13C recovery likely represents a vital effect and not a change in export production, as it is coincident with the first geochemical evidence of photosymbiosis in Paleocene taxa.

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