Diverse patterns of ocean export productivity change across the Cretaceous-Paleogene boundary: new insights from biogenic barium

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ABSTRACT

One of the best-studied aspects of the K-Pg mass extinction is the decline and subsequent recovery of open ocean export productivity (e.g., the flux of organic matter from the surface to deep ocean). Some export proxies, including surface-to-deep water $\delta^{13}C$ gradients and carbonate sedimentation rates, indicate a global decline in export productivity triggered by the extinction. In contrast, benthic foraminiferal and other geochemical productivity proxies suggest spatially and temporally heterogeneous K-Pg boundary effects. Here we address these conflicting export productivity patterns using new and compiled measurements of biogenic barium. Unlike a previous synthesis, we find that the boundary effect on export productivity and the timing of recovery varied considerably between different oceanic sites. The northeast and southwest Atlantic, Southern Ocean and Indian Ocean records saw export production plummet and remain depressed for 350 thousand to 2 million years. Biogenic barium and other proxies in the central Pacific and some upwelling or neritic Atlantic sites indicate the opposite, with proxies recording either no change or increased export production in the early Paleocene. Our results suggest that widespread declines in surface-to-deep ocean $\delta^{13}C$ do not record a global decrease in export productivity. Rather, independent proxies –including barium and other geochemical proxies, and benthic community structure– indicate that some regions were characterized by maintained or rapidly recovered organic flux from the surface ocean to the deep sea floor, while other regions had profound reductions in export productivity that persisted long into the Paleocene.

1. INTRODUCTION

The Cretaceous-Paleogene (K-Pg) mass extinction provides a natural experiment in processes of extinction and recovery, as it is the most recent and well studied of the five major mass extinctions. The K-Pg extinction was triggered by the Chicxulub impact [e.g., *Bralower et al.*, 2010; *Miller et al.*, 2010; *Schulte et al.*, 2010] and is thought to have precipitated a sudden decrease in primary and/or export productivity in the global ocean [*Hsü et al.*, 1982b; *Zachos et al.*, 1989; *D'Hondt et al.*, 1998]. A decrease in organic matter export from the surface ocean is indicated by the collapse of surface-to-deep water $\delta^{13}C$ gradients in carbonates, a sharp decrease in biogenic sedimentation rates, and improved carbonate preservation [*Hsü et al.*, 1982a; *Stott and Kennett*, 1989; *Zachos et al.*, 1989; *D'Hondt*, 2005]. In the aftermath of the K-Pg extinction, the recovery to pre-impact levels of surface-to-deep $\delta^{13}C$ gradients coincided with the re-diversification of planktonic foraminiferal species richness [*Coxall et al.*, 2006]. This diversity-$\delta^{13}C$ correlation is striking, and has been interpreted to suggest that stable, species-rich ocean ecosystems are either necessary for and/or dependent on relatively high export production [*D'Hondt et al.*, 1998; *Coxall et al.*, 2006].

There have been two primary hypotheses to explain the productivity change associated with the mass extinction. An early model was the Strangelove Ocean Hypothesis, which postulated the near complete cessation [*Hsü et al.*, 1982b; *Hsü and McKenzie*, 1985] or reduction [*Zachos et al.*, 1989] of *primary productivity* in the surface ocean leading to reduced export of organic matter to the deep ocean. Carbon cycle modeling showed that it was not necessary for productivity to stop entirely to explain the loss of surface-to-deep $\delta^{13}C$ gradients; a 10% reduction in the efficiency of the biological pump sufficed [*Kump*, 1991]. More recently, *D'Hondt et al.* [1998] suggested that primary productivity was nearly unchanged by the

extinction, but the replacement of large grazers by microbially dominated communities in the surface ocean drastically reduced export production to the sea floor. This hypothesis of a dominant microbial food loop has been called "The Living Ocean Hypothesis" [*D'Hondt et al.*, 1998; *D'Hondt*, 2005] because it posits a shift in the way organic production is recycled rather than the reduction of oceanic primary productivity.

Both the Living Ocean hypothesis and Strangelove Ocean hypothesis assume that a prolonged (3-4 million years) global decline in export production is responsible for collapsed surface-to-deep $\delta^{13}C$ gradients [*Hsü and McKenzie*, 1985; *Zachos et al.*, 1989; *D'Hondt et al.*, 1998; *D'Hondt*, 2005]. It is therefore surprising that benthic foraminifera did not suffer a mass extinction at the K-Pg boundary [*Culver*, 2003]. Benthic communities are largely dependent on the flux of organic matter from the pelagic realm [*Gooday*, 2003], and the lack of extinction in benthic species is paradoxical in light of an apparent global decrease in food supply [*Thomas*, 2007]. Many benthic foraminiferal communities do appear to have experienced a period of altered community composition across the K-Pg boundary, suggestive of a decrease in the local food supply [*Widmark and Malmgren*, 1992; *Culver*, 2003; *Alegret and Thomas*, 2005]. Surprisingly, this is not true everywhere; at some locales (Figure 1) benthic foraminiferal community structure suggests robust or even increased organic fluxes across the K-Pg boundary [*Alegret and Thomas*, 2009], even in cases where $\delta^{13}C$ gradients or sedimentation rates suggest reduced export production. In these locations, the robust export productivity to the deep sea suggested by both the lack of species extinctions and the structure of benthic foraminiferal communities directly conflicts with the Living Ocean hypothesis for decreased export productivity from the surface ocean and the standard interpretation of collapsed $\delta^{13}C$ gradients. Thus, hypotheses for the apparent pelagic-benthic decoupling across the K-Pg boundary include

weaker bentho-pelagic coupling in warmer seas [*Thomas et al.*, 2000, although later discounted in Thomas 2007], a more rapid recovery of export productivity from the end-Cretaceous mass extinction than indicated by $\delta^{13}C$ gradients [*Thomas*, 2007], and/or the regional maintenance of pre-extinction levels of export productivity [*Alegret and Thomas*, 2009]. The last two mechanism require that the collapse and recovery of $\delta^{13}C$ gradients and other carbonate proxies primarily record processes other than a reduction in the amount of export productivity during this time interval [*Thomas*, 2007], and calls into question inferred changes in export productivity across the K-Pg boundary based on carbonate proxies alone.

Other export productivity proxies have also indicated the maintenance or rapid rebound of organic fluxes after the extinction,, providing some support for the benthic foraminiferal patterns. For example, siliceous sediments are commonly associated with productive regions of the ocean so it is notable that New Zealand sites had siliceous blooms through the first million years of the Paleocene, with an order of magnitude increase in diatom to radiolarian (primary producer : consumer) ratios and a conspicuous lack of radiolarian extinctions [*Hollis et al.*, 1995]. New Zealand sites also record an increase in "biogenic" barium (associated with sinking organic matter) accompanying the siliceous blooms [*Hollis et al.*, 2003]. In addition, geochemical export productivity proxies including reactive phosphorus and organic carbon content did not decline at the K-Pg boundary at one upwelling site in the western North Atlantic [Blake Nose, *Faul et al.*, 2003], although the $\delta^{13}C$ gradient collapsed [*Quillevere et al.*, 2008]. Finally, a very high resolution record of biomarkers (biodegradation resistant sterane and hopane ratios) and $\delta^{13}C_{organic}$ and $\delta^{15}N_{organic}$ from the Fish Clay, Denmark, detail the initial decline and rapid recovery to pre-boundary levels of algal export productivity and community composition within 100 years of the impact [*Sepulveda et al.*, 2009].

Here, we seek to resolve the paradox of conflicting effects of the K-Pg boundary on global surface ocean export productivity as recorded in carbonate productivity proxies (surface-to-deep water $\delta^{13}C$ gradients, sedimentation rates, and carbonate preservation) and non-carbonate productivity proxies (benthic foraminiferal community structure, biomarkers, and other geochemical proxies like biogenic barium and organic carbon content). We estimate the relative changes in export productivity in multiple ocean basins using biogenic barium. Biogenic barium (Ba_{bio}) is a widely used productivity proxy that correlates well with modern export production [*Dymond et al.*, 1992; *Francois et al.*, 1995; *Eagle et al.*, 2003] and has been used to trace changes in Cenozoic productivity [e.g., *Paytan et al.*, 1996; *Thompson and Schmitz*, 1997; *Bains et al.*, 2000; *Griffith et al.*, 2010]. We compare our export production records to existing carbonate and non-carbonate paleoproductivity proxy records to test the spatial extent of the Living Ocean Hypothesis.

2. METHODS

2.1 Biogenic Barium as an Export Productivity Proxy

Marine barite ($BaSO_4$) is the primary form of biogenic barium (Ba_{bio}) and has a strong, empirical relationship with the export of organic carbon to the deep sea in oxic to suboxic, open ocean sedimentary environments [*Dymond et al.*, 1992; *Francois et al.*, 1995; *Eagle et al.*, 2003; *Paytan and Griffith*, 2007]. Barite has been found to precipitate in the decaying organic remains of siliceous plankton, phytoplankton, and acantharians [as reviewed in *Paytan and Griffith*, 2007], although the dominant mechanisms by which Ba_{bio} provides a tracer of export productivity are still uncertain. We use the term Ba_{bio} to refer to all barium productivity proxies considered in this study including excess barium (Ba_{excess}) and Ba/Al, Ba/Ti, and/or Ba/Fe ratios.

Barium has both a biogenic source and a terrestrial source. Biogenic barium (Ba_{bio}) can be determined by normalizing the total barium content of sediment to the non-biogenic component ($Ba_{detrital}$) using a conserved terrestrially sourced tracer such as aluminum (Al) or titanium (Ti) [e.g., *Dymond et al.*, 1992; *Francois et al.*, 1995; *Reitz et al.*, 2004]. Alternatively, Ba_{bio} can be calculated directly by dissolution of other sedimentary components and analysis of the remaining distinctive euhedral crystals of barite formed in sinking organic matter [*Paytan*, 1996; *Paytan and Griffith*, 2007]. Ba_{bio} determined by normalization–excess Barium (Ba_{excess})– may deviate widely from those determined with direct barite extraction [e.g., *Dymond et al.*, 1992; *Eagle et al.*, 2003]. However, in practice, both methods yield comparable results in calcareous sediments without large diatom, radiolarian or biogenic mud components, with Ba_{bio} levels greater than ~100ppm, and with $Ba_{bio} >> Ba_{detrital}$ [*Eagle et al.*, 2003; *Gonneea and Paytan*, 2006]. Ba_{excess} (calculated from sedimentary barium content) and barite (extracted from sediment) must be normalized to accurate sedimentary mass accumulation rates (MARs) to interpret the data in terms of relative or absolute export productivity. The need for accurate MAR introduces a large source of potential error in productivity calculations [*Dymond et al.*, 1992; *Anderson and Winckler*, 2005; *Calvert and Pedersen*, 2007].

Ba/Al or Ba/Ti ratios provide an alternate means of inferring export productivity and are not dependent on accurate MAR [*Goldberg and Arrhenius*, 1958; *Murray et al.*, 2000; *Calvert and Pedersen*, 2007]. However, different terrestrial sources can contain varying amounts of Ba relative to Ti and Al [*Paytan and Griffith*, 2007] so long-term trends in these ratios could simply reflect changes in the terrestrial sources of barium and other lithogenic elements. For instance, changes in Ba/Al ratios do not always parallel changes in barite and/or Ba_{excess} in Pleistocene sediments [*Averyt and Paytan*, 2004], and it is unclear which proxy most accurately reflects

export productivity over this time. The discrepancy between Ba/Al and barite could be due to changes in Ba-depleted dust fluxes affecting Ba/Al ratios [*Anderson and Winckler*, 2005] or, alternatively, may reflect problems with accurately calculating MAR for barite and Ba_{excess} fluxes [*Calvert and Pedersen*, 2007]. Here we include and compare both Ba_{excess} (calculated from total sedimentary barium content) and Ba/Al (or Ba/Ti) ratios to account for the differing strengths of each approach. We also consider Ba/Fe ratios in addition to Ba/Al and Ba/Ti ratios, as Fe is better measured by XRF core scanning than Ti and Al and, in certain environments, should also primarily reflect the deposition of terrestrial material.

2.2 Measurement of Biogenic Barium: excess Barium and Barium Ratios

We examined Ba_{excess} (determined by direct measurement of barium concentrations), Ba/Al, Ba/Ti, and/or Ba/Fe at five sites (Figure 1): i) the Vigo Seamount, North Atlantic, Deep Sea Drilling Project (DSDP) Hole 398D, ii) São Paulo Plateau, South Atlantic, DSDP Site 356, iii) Maud Rise, Antarctica, Ocean Drilling Program (ODP) Hole 690C, iv) Shatsky Rise, North Pacific, DSDP Site 577B and ODP Site 1209, and v) Wombat Plateau, Indian Ocean, ODP Hole 761C. Age models were derived using shipboard bio- and magnetostratigraphy and the time scale of *Berggren et al.* [1995] (age models provided in Supplemental Tables 5), at all sites except for the Shatsky Rise sites. At Shatsky Rise we used the age model of Westerhold et al. [2008] for ODP Site 1209 and tied DSDP Hole 577B to Westerhold et al.'s age model for ODP Site 1211 using XRF Fe measurements. We shifted Westerhold et al.'s age model in both Shatsky Rise sites by 0.28 million years to match the 65 million year age of the K-Pg boundary used by *Berggren et al.* [1995].

We used X-ray fluorescence (XRF) measurements at 10 kV and 50 kV to obtain high-resolution records of barium (Ba), iron (Fe) and titanium (Ti) in total counts from DSDP Sites

356, 398D, and 577 and ODP Sites 690C and 1209 (Supplemental Tables 1-4). We also use existing Ba, Fe, and Al records from Shatsky Rise [DSDP Site 577, *Michel et al.*, 1985] and the Wombat Plateau [ODP Hole 761C, *Rocchia et al.*, 1992] to calculate Ba/Al, Ba/Fe and Ba_{excess}. Ba_{excess} was calculated according to Dymond [1992] using a detrital barium ratio of 0.0037 (determined empirically by Reitz et al. [2004] to be more accurate than the crustal average of 0.0075 used by Dymond). The Vigo Seamount and São Paulo Plateau cores were scanned on the Avaatech XRF at the Center for Marine Environmental Science, University Bremen, Germany, and the Maud and Shatsky cores on the Avaatech XRF at Scripps Institution of Oceanography Geological Collections. We collected XRF data every centimeter over the intervals shown (Figure 3), using a 1 cm^2 footprint and 30 second count time for 10kV and 50kV respectively (see Supplemental Tables 1-4 for site and core specific μA settings). XRF measurements are reported as total counts and, without empirical standardization, can only be used to calculate elemental ratios (Ba/Ti and Ba/Fe) not Ba_{excess}. Notably, Ba/Ti XRF measurements have been used in previous paleoproductivity studies and shown to correlate very well with quantitative ICPMS measurements [*Jaccard et al.*, 2009; *Jaccard et al.*, 2010]. We compared our XRF Ba and Ti measurements against quantitative Ba and Al measurements for DSDP Hole 577B, Shatsky Rise (Figure 4), and obtained qualitatively similar trends in spite of extensive core aging (recrystallization, reprecipitation, mold, and desiccation). Al was poorly detected by XRF in our carbonate rich, deep sea sediments so we use Fe and Ti counts to normalize our XRF measurements of Ba. As cores were measured on different machines and with different instrument settings, the ratio of Ba/Ti can only be considered within a given site; absolute ratio values cannot be compared across sites without quantitative measurements.

2.3 Ba_{bio} Preservation Considerations

General site characteristics at all sites suggest that biogenic barium should be well preserved: all sites are biostratigraphically complete within the boundary sections examined here, are comprised of nannofossil oozes to chalks with minor amounts of biogenic silica, and have evidence of oxic depositional environments including bioturbated K-Pg boundaries and pale tan to reddish boundary sediments [*Perch-Nielsen et al.*, 1977; *Ryan and al.*, 1979; *Moore et al.*, 1984; *Heath et al.*, 1985; *Barker et al.*, 1988; *Bralower et al.*, 2002]. We considered, but did not include, barium proxies at DSDP Site 527, Walvis Ridge, South Atlantic as this site had a relatively high proportion of detrital to biogenic barium (20-100% detrital). In cores with high detrital barium, small changes in source Ba and Al composition can dramatically affect the calculated Ba_{excess} or Ba/Al, thereby precluding the use of Ba_{excess} or Ba/Al for inferences about productivity [*Dymond et al.*, 1992; *Reitz et al.*, 2004].

2.4 Productivity Proxy Compilation

We compare our results with published accounts of early Paleocene primary productivity from studies of benthic foraminifera and non-carbonate geochemical proxies. We restrict our comparison to a small subset of the available benthic foraminiferal proxy records, choosing the taxonomic and stratigraphic stability of a single research group over the extensive coverage offered by considering studies from the entire literature. In studies of benthic foraminiferal community structure, the increased ratios of infaunal to epifaunal forms, buliminid taxa, and Benthic Foraminiferal Accumulation Rates (BFAR) can be indicative of increased influxes of export production to the seafloor [e.g., *Gooday*, 2003; *Jorissen et al.*, 2007]. Therefore, the benthic foraminiferal proxies summarized by our map (Figure 1) represent the dominant conclusions based on infaunal to epifaunal ratios and the proportion of buliminid taxa reached by

Alegret, Thomas, and others at the following 16 sites: Mexican Sites (Los Ramones, El Penon, El Tecolote, La Ceiba, El Mulato, La Lajila, El Mimbral, and Coxquihui) [*Alegret et al.*, 2001; *Alegret and Thomas*, 2001; *Alegret et al.*, 2002]; Blake Nose, east of Florida [*Alegret and Thomas*, 2005]; Agost, Spain [*Alegret et al.*, 2003]; Loya, Spain [*Alegret*, 2007]; Bidart, France [*Alegret et al.*, 2004]; Aïn Settara, Tunisia [*Peryt et al.*, 2002]; Walvis Ridge, eastern South Atlantic [*Alegret and Thomas*, 2007]; Maud Rise, Antarctica [*Thomas*, 1990]; Hess Rise, North Pacific [*Alegret and Thomas*, 2009]; and Shatsky Rise, North Pacific [*Alegret and Thomas*, 2009]. We limit our discussion of this body of work to conclusions regarding the relative amount of organic matter reaching the seafloor. It is notable, however, that these studies also discuss the temporal stability and relative quality of the export production, generally finding decreased stability and/or food quality in the earliest Danian even in sites lacking evidence of declines in total export production. We also consider the results and interpretations of three geochemical studies: Blake Nose, east of Florida, using reactive P and organic C [*Faul et al.*, 2003]; Marlborough, New Zealand, using biogenic barium, excess silica, and diatom/radiolarian ratio proxies [*Hollis et al.*, 1995; *Hollis et al.*, 2003]; and the Fish Clay, Denmark, using sterane and hopane biomarkers, and $\delta^{13}C_{organic}$ and $\delta^{15}N_{organic}$ [*Sepulveda et al.*, 2009].

3. RESULTS AND DISCUSSION

3.1 K-Pg Boundary Related Changes in Export Productivity

Proxy data suggests that the K-Pg extinction did not affect export production the same way in all ocean basins or habitats (Figure 1; heterogeneous benthic patterns previously discussed in [e.g., *Culver*, 2003; *Alegret and Thomas*, 2005; 2007; 2009] and $\delta^{13}C$ in [*Meyers and Simoneit*, 1990; *Stott and Kennett*, 1990]). These results contrast with a previous synthesis

[*D'Hondt*, 2005], which found global declines in export productivity based on carbonate proxies (e.g., surface-to-deep water $\delta^{13}C$ gradients, sedimentation rates, and carbonate preservation).

We find a decrease in export productivity coincident with the K-Pg boundary in the Atlantic (Vigo and São Paulo), Antarctic (Maud), and Indian (Wombat) Oceans (Figure 2) using barium proxies (Ba_{excess}, Ba/Al, Ba/Ti, and Ba/Fe) of organic flux to the deep sea. At Maud Rise, Ba/Ti and Ba/Al ratios recover to pre-impact levels within ~350 kyr, supporting the rapid resurgence in export productivity previously hypothesized on the basis of surface to deep $\delta^{13}C$ gradients [*Stott and Kennett*, 1989, using same age model]. In contrast, barium proxies and inferred organic fluxes fail to recover over the interval studied at São Paulo, Wombat, and Vigo—a period of more than 600 kyr at Sao Paulo and Wombat (Figure 2) and more than 2 million years at Vigo (Figure 3).

At Shatsky Rise in the Pacific, barium proxies are somewhat ambiguous due to differences between Ba/Al, Ba/Fe, and Ba_{excess} at DSDP Site 577B and Ba/Ti and Ba/Fe at ODP Site 1209 (Figure 2e-f), but provide no evidence for a distinct, prolonged K-Pg-associated decline in export productivity. At DSDP Hole 577B, Ba/Al ratios and Ba_{excess} actually increase sharply in the very earliest Danian, supporting inferences of increased export production based on benthic foraminifera proxies at Shatsky Rise (ODP Site 1210) and Hess Rise (DSDP Site 465) [*Alegret and Thomas*, 2009] and a sparse $\delta^{13}C_{organic}$ record from Shatsky Rise [*Meyers and Simoneit*, 1990]. XRF Ba/Ti measurements also increase sharply at DSDP Hole 577B and match Ba/Al results in expressing a longer duration excursion of elevated export productivity than revealed by Ba_{excess} (Figure 4). Ba/Fe ratios are unchanged or increase slightly across the K-Pg boundary at both DSDP Hole 577B and ODP Site 1209, but diverge from measurements of Ba/Ti and Ba/Al in the same site. Ba/Ti decreases slightly across the boundary at ODP Site 1209, but is

well within the range of pre-boundary oscillations and exceeds pre-boundary export productivity fluxes within ~300 kyr. We regard our measurements of Ba/Ti with some skepticism at ODP Site 1209 during this interval given XRF limitations in measuring the very low Ti concentrations in these sediments. When considered together, the best proxies at each Shatsky Rise site support either no change (Ba/Fe ratios at ODP Site 1209) or a short, ~100 kyr burst in export production in the North Pacific (Ba/Al, Ba/Ti, and Ba_{bio} at DSDP Hole 577B and benthic foraminifera proxies at ODP Site 1210).

The sites investigated to date using barium, benthic foraminifera, and other geochemical proxies indicate differences in biotic responses by geography and habitat. At the largest scale, organic fluxes at sites in the Pacific appear to be maintained or increased in the earliest Danian, while most sites in the North Atlantic show large, persistent declines in export production (Figure 1). This global heterogeneity does not appear to be a proxy artifact. Both benthic foraminifera and barium proxies in North Atlantic and Tethyan sites near Vigo Seamount (e.g., Loya, Bidart, Agost and Aïn Settara) show boundary declines, while both benthic foraminifera and barium in North Pacific sites at Shatsky and Hess Rise support maintained to increased organic fluxes in the very earliest Danian.

The pattern in the South Atlantic is more complex. At Walvis Ridge, in the eastern South Atlantic, benthic foraminifera proxies indicate no change in total export production across the boundary [*Alegret and Thomas*, 2007]. Conversely, there is a large drop in export production measured by Ba/Ti at São Paulo, in the western South Atlantic. A drop in export production is also indicated at Maud Rise, near Antarctica, by benthic foraminifer (low resolution) and barium proxies. However, the export productivity decline at Maud Rise is within the scope of pre-boundary oscillations (Figure 2c) and is reversed and surpassed about 350 kyr after the

extinction. From this limited sample size, it is unclear whether South Atlantic sites are generally less affected by boundary events than the North Atlantic, or if this pattern merely reflects the chance sampling of a few relatively unaffected sites in a region characterized by K-Pg-related declines in export production.

Most sites in the North Atlantic indicate large K-Pg related declines in export productivity, with a few notable exceptions. Export productivity was relatively unaffected by the K-Pg boundary events at Blake Nose, in the western North Atlantic, and the Fish Clay, Denmark in contrast to most North Atlantic sites [*Faul et al.*, 2003; *Alegret and Thomas*, 2005; *Sepulveda et al.*, 2009]. Benthic foraminifera proxies at Blake Nose –hypothesized to have been located in a productive, coastal upwelling region– indicate a short, ~100,000 year decline in export productivity in the early Paleocene [*Alegret and Thomas*, 2005]. This brief decline in export productivity is not captured by the relatively low-resolution geochemical proxy record of *Faul et al.*[2003] which records no affect of the K-Pg boundary on export productivity. Similarly, the Fish Clay is a neritic site and has a very brief, decadal-scale decline in productivity as indicated by biomarkers [*Sepulveda et al.*, 2009]. We represent the Fish Clay site as roughly unaffected by the K-Pg boundary in regards to export productivity (Fig. 1) as the decline and recovery in biomarkers spans a much shorter temporal scale than can be resolved in the deep sea.

Export productivity in the modern ocean varies between habitats, with the proportion of productivity exported from the surface ocean ranging from around 5-60% of total surface productivity [Laws et al., 2000; Dunne et al., 2005], and corresponding to concordant differences in temperature, primary productivity, and community structure, among others. The K/Pg collapse of surface to deep $\delta^{13}C$ gradients in sites throughout the global ocean suggested a prolonged decrease in export productivity across oceanic environments with different

background levels of export productivity and ecological structure. Our results support a more heterogeneous pattern of export changes, with different oceanic regions varying in the magnitude, direction, and duration of export productivity change.

One existing hypothesis for the spatially heterogeneous response of benthic foraminiferal export proxies is that the response of individual locales is related to differences in habitat type [e.g., *Culver*, 2003; *Alegret and Thomas*, 2005; 2007; 2009]. This could arise, for instance, if post-extinction communities in highly productive, temporally variable environments rebounded much more rapidly from the K-Pg impact due to the ecological similarity of early Danian species to some pre-extinction nearshore species [*D'Hondt et al.*, 1996]. Indeed, early Paleocene bloom taxa in planktonic foraminifera are descendants of coastal taxa in the late Maastrichtian and therefore may have been adapted to the generally high productivity and temporal variability of coastal waters [*MacLeod*, 1993; *D'Hondt et al.*, 1996].

However, the habitat-type related hypothesis appears to only partially capture the variability of the direction, magnitude, and duration of export productivity change. For instance, there is some evidence that export productivity in coastal and upwelling sites was generally unaffected or rapidly recovered (Fish Clay and Blake Nose, North Atlantic) or even increased by the K-Pg mass extinction (New Zealand sites) [e.g., *Culver*, 2003; *Alegret and Thomas*, 2005; 2007; 2009]. This pattern is countered, however, by the response of other coastal sites that do experience a period of depressed export production (e.g., Aïn Settara, Agost, Bidart). In addition, the two most open ocean, oligotrophic sites in the study –Hess Rise and Shatsky Rise, North Pacific– indicate a brief burst of export productivity, the opposite of the expected habitat effect as described above. Other environmental factors like the proportion of calcareous to siliceous primary producers also do not appear to explain the boundary change in export productivity. The

most carbonate dominated (Shatsky Rise) and siliceous dominated (New Zealand) sites both exhibited an early burst in export productivity despite dramatic differences in extinction of dominant fossilized primary producers and consumers.

We similarly do not find support for the hypothesized hemispherical effect of the K-Pg impact [*Jiang et al.*, 2010], which suggested a delayed recovery in northern hemisphere sites relative to southern hemisphere sites due to impact-related heavy metal poisoning. Some sites with an early Paleocene export productivity burst (Shatsky and Hess Rise, North Pacific) or with relatively unaffected export productivity (Fish Clay, Denmark) are in the northern hemisphere. Conversely, some southern hemisphere sites have decreased, rather than increased, export productivity (São Paulo, Wombat). The distance from the impactor (shown to be important for recovery of nearly coastal mollusks [*Jablonski*, 1998]) also appears unrelated to the change in export productivity, with relatively unaffected or rapidly recovered sites (Fish Clay, Denmark and Blake Nose, South Atlantic) equal or closer to the impact site than sites with strongly depressed export productivity (e.g., Vigo Seamount).

A change in circulation, weathering, and/or stratification [the first two as proposed in *Alegret and Thomas*, 2009] could drive a spatially heterogeneous change in export productivity. However, there is no evidence for regional changes in any of these three drivers at the K-Pg boundary, and it is unclear what could drive and maintain regional changes in circulation, weathering, or stratification for up to 2-million years. Regional variation in the extinction intensity and recovery of un- or poorly fossilized marine groups offers an equally speculative hypothesis for the spatially heterogeneous changes in export productivity. In sum, we find evidence against a number of potential drivers of the spatial and temporal heterogeneity of export productivity change –including habitat type, dominant primary producer, hemispherical impactor

effects, distance from the impactor. Other plausible scenarios currently lack positive support and include heterogeneity in the K-Pg response of circulation, weathering, stratification, or the extinction and recovery of unfossilized marine species. Insight into the mechanisms driving the spatial and temporal heterogeneity of export productivity change across the K-Pg boundary thus awaits further empirical and theoretical research.

3.2 The K-Pg Impact and the Fidelity of Carbonate Productivity Proxies

An apparent global collapse in export productivity indicated by the surface-to-deep $\delta^{13}C$ gradient contradicts benthic foraminiferal and non-carbonate geochemical proxies in the Pacific and some Atlantic sites (Fig.1, 2). In these locations, processes other than export productivity must dominate the signal in one or more of the productivity proxies. We highlight several biological and biogeochemical effects of the K-Pg impact and extinction that may affect the fidelity of carbonate productivity proxies in the early Paleocene.

The K-Pg impact lead to the extinction of nearly all species of the dominant surface ocean carbonate producers, including the calcareous nannoplankton and the planktonic foraminifera, with direct biological and ecological effects on $\delta^{13}C$ values [e.g., *Berggren and Norris*, 1997; *Minoletti et al.*, 2005; *Paytan*, 2008; *Alegret and Thomas*, 2009]. Early Paleocene nannoplankton assemblages are dominated by otherwise rare calcareous dinoflagellate cysts (*Thoracosphaera*) that have distinctly light, or more benthic-like, $\delta^{13}C$ signatures [*Minoletti et al.*, 2005]. The planktonic foraminifera that diversified in the early Paleocene also had relatively negative $\delta^{13}C$ signatures compared to late Cretaceous species, an observation consistent with a lack of photosymbionts, a deep depth habitat, and a small test size [*Berggren and Norris*, 1997; *Bornemann and Norris*, 2007]. Together, biological and ecological changes in pelagic carbonate

producers at the K-Pg may have had a large effect on planktonic $\delta^{13}C$ values, shifting the ratio towards more negative values independent of a change in export production.

Sedimentation rates of calcite and biogenic opal can provide a proxy for changes in export productivity when the relationship between fossilized and unfossilized groups is constant [*Paytan*, 2008], an assumption that does not appear to hold following the end-Cretaceous extinction. A decrease in nannoplankton (primarily coccolithophorid) sedimentation does not necessarily indicate a decrease in global primary production [*Alegret and Thomas*, 2009]. Modern coccolithophorids are poor competitors in unstable, variable environments [*Litchman*, 2007], and benthic foraminiferal assemblages suggest that such conditions characterized early Paleocene seas [*Alegret and Thomas*, 2007]. Furthermore, there is evidence that other primary producers such as diatoms in New Zealand and naked algae in Denmark may have had increased population sizes in response to K-Pg boundary environmental and ecological perturbations [*Hollis et al.*, 1995; *Hollis et al.*, 2003; *Sepulveda et al.*, 2009]. In addition, the decrease in sedimentation rates at the K-Pg boundary is predominantly driven by decreased nannoplankton sedimentation [*D'Hondt*, 2005], with an increase in coarse carbonate fractions in the early Paleocene [*Zachos and Arthur*, 1986; *Zachos et al.*, 1989; *Bralower et al.*, 2010].

4. **CONCLUSIONS**

The end-Cretaceous mass extinction temporarily changed the global geography of the export of organic matter from the surface ocean to the deep sea; some regions had profound reductions in export productivity that persisted for up to 2-million years, while others were characterized by constant or rapidly re-established organic flux from the surface ocean to the deep sea floor. A globally and temporally heterogeneous response of export productivity is in

keeping with the highly regional responses of ecosystems in other environments –terrestrial, shallow marine, and near coastal– to the K-Pg boundary events [*Hollis et al.*, 1995; *Jablonski*, 1998; *Stilwell*, 2003; *Wilf and Johnson*, 2004; *Sepulveda et al.*, 2009; *Wappler et al.*, 2009], but challenges the Living Ocean Hypothesis which posits a global response on the bases of carbonate proxies.

Our study demonstrates the utility of barium proxies for quantifying changes in export productivity during events when proxies like carbonate $\delta^{13}C$ or sedimentation rate may be affected by biological factors like extinction and ecological change. We find general concordance between non-carbonate geochemical proxies for export productivity –like barium– and the response of benthic foraminiferal community structure, suggesting that carbonate proxies may record other changes in factors other than (or in addition to) local export productivity during this interval.

More generally, our results highlight the need for multiproxy, multi-site studies to quantify the response of the global ocean to massive perturbations. At present it is not clear what mechanisms are responsible for the temporal heterogeneity in the recovery of export productivity to pre-extinction levels or for the spatial heterogeneity in the magnitude and direction of change. Additional multiproxy records from other locations are needed in order to develop a robust model that can account for the temporal and regional heterogeneity of organic flux change at the K-Pg boundary. Generalizing the response of the ocean, or even of an ocean basin, to the K-Pg mass extinction on the basis of a single or a few sites is not suggested at present given the lack of mechanistic understanding for the observed spatial heterogeneity in export productivity change.

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FIGURE CAPTIONS

Figure 1. Map of change in export production across the K-Pg boundary as inferred from multiple, independent proxies. Paleoreconstruction of continental configuration 65 Mya generated using ODSN plate reconstruction (www.odsn.de/odsn/services/paleomap/paleomap.html).

Figure 2. Barium proxies of export production in the latest Maastrichtian to early Danian by relative age. Ba/Ti and Ba/Fe ratios of total counts from XRF core scanning in dotted grey and solid black respectively at (A) the Vigo Seamount (DSDP Hole 398D), North Atlantic, (B) São Paulo (DSDP Site 356), South Atlantic, (C) Maud Rise (ODP Hole 690C), Antarctica, and (F) Shatsky Rise (ODP Site 1209), North Pacific. Ba/Al, Ba/Fe, and Ba_{excess} in solid grey, solid black and dotted black respectively and calculated from existing records of Ba (ppm), Al (ppm) and Fe (ppm) for (D) Wombat Plateau (ODP Hole 761C), Indian Ocean [*Rocchia et al.*, 1992], and (E) Shatsky Rise (DSDP Hole 577B) [*Michel et al.*, 1985]. The K-Pg boundary is placed at 0 million years in relative age.

Figure 3. Full records of barium proxies of export production in the latest Maastrichtian to early Danian by relative depth. Ba/Ti and Ba/Fe ratios of total counts from XRF core scanning in dotted grey and solid black respectively at (A) the Vigo Seamount, North Atlantic, (B) São Paulo, South Atlantic, (C) Maud Rise, Antarctica, and (F) Shatsky Rise (ODP Site 1209), North Pacific. Ba/Al, Ba/Fe, and Ba_{excess} in solid grey, solid black and dotted black respectively and calculated from existing records of Ba (ppm), Al (ppm) and Fe (ppm) for (D) Wombat Plateau,

Indian Ocean [*Rocchia et al.*, 1992], and (E) Shatsky Rise 577B [*Michel et al.*, 1985]. The K-Pg boundary is placed at 0 m relative depth. First (⊥) and last (⊤) occurrence of nannofossils (N) and foraminifera (F) and magnetostratigraphy (M) indicate relative age in panels A-D. In panel E, relative ages were obtained by tying the XFR Fe record of DSDP Hole 577B to ODP Site 1211 and *Westerhold et al.*'s [2008] age model (see Supplemental Table 5 for tie points). In panel F, relative ages were obtained from a high-resolution study of cyclostratigraphy (C), although age model uncertainties characterize the period indicated by the thick dashed line.

Figure 4. Barium proxies of export production in the latest Maastrichtian to early Danian at DSDP Site 577B, Shatsky Rise, North Pacific. Ba/Ti ratios of total counts from XRF core scanning in dotted grey against Ba/Al and Ba_{excess} measured with neutron-activation analysis [*Michel et al.,* 1985] in solid grey and dotted black respectively. The K-Pg boundary is placed at 0 million years in relative age.

Figure 1.

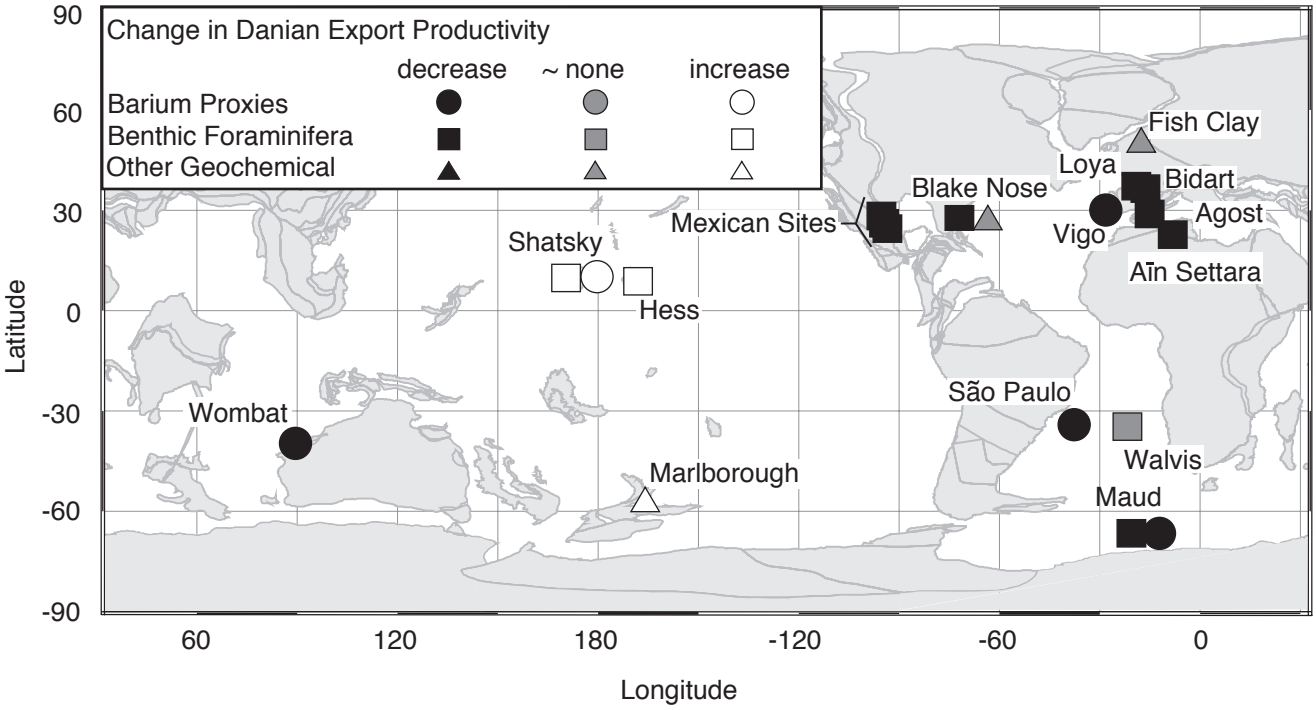

Change in Danian Export Productivity
decrease
~ none
increase
Barium Proxies
Benthic Foraminifera
Other Geochemical
Fish Clay
Loya
Bidart
Blake Nose
Agost
Mexican Sites
Vigo
Shatsky
Aīn Settara
Hess
São Paulo
Wombat
Walvis
Marlborough
Maud
90
60
30
0
-30
-60
-90
Latitude
60
120
180
-120
-60
0
Longitude

Figure 2.

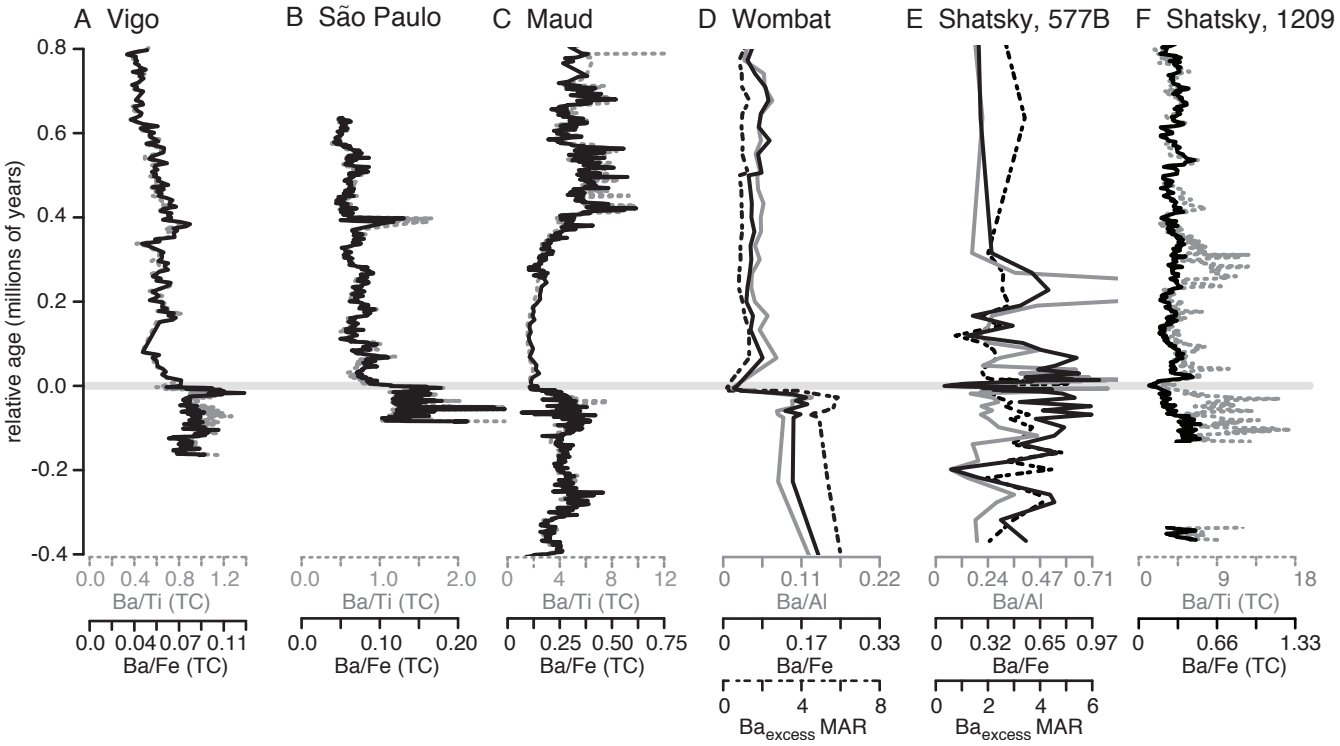

A Vigo
B São Paulo
C Maud
D Wombat
E Shatsky, 577B
F Shatsky, 1209
relative age (millions of years)
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0.0 0.4 0.8 1.2
Ba/Ti (TC)
0.0 0.04 0.07 0.11
Ba/Fe (TC)
0.0 1.0 2.0
Ba/Ti (TC)
0.0 0.10 0.20
Ba/Fe (TC)
0 4 8 12
Ba/Ti (TC)
0 0.25 0.50 0.75
Ba/Fe (TC)
0 0.11 0.22
Ba/Al
0 0.17 0.33
Ba/Fe
0 4 8
Baexcess MAR
0 0.24 0.47 0.71
Ba/Al
0 0.32 0.65 0.97
Ba/Fe
0 2 4 6
Baexcess MAR
0 9 18
Ba/Ti (TC)
0 0.66 1.33
Ba/Fe (TC)

Figure 3.

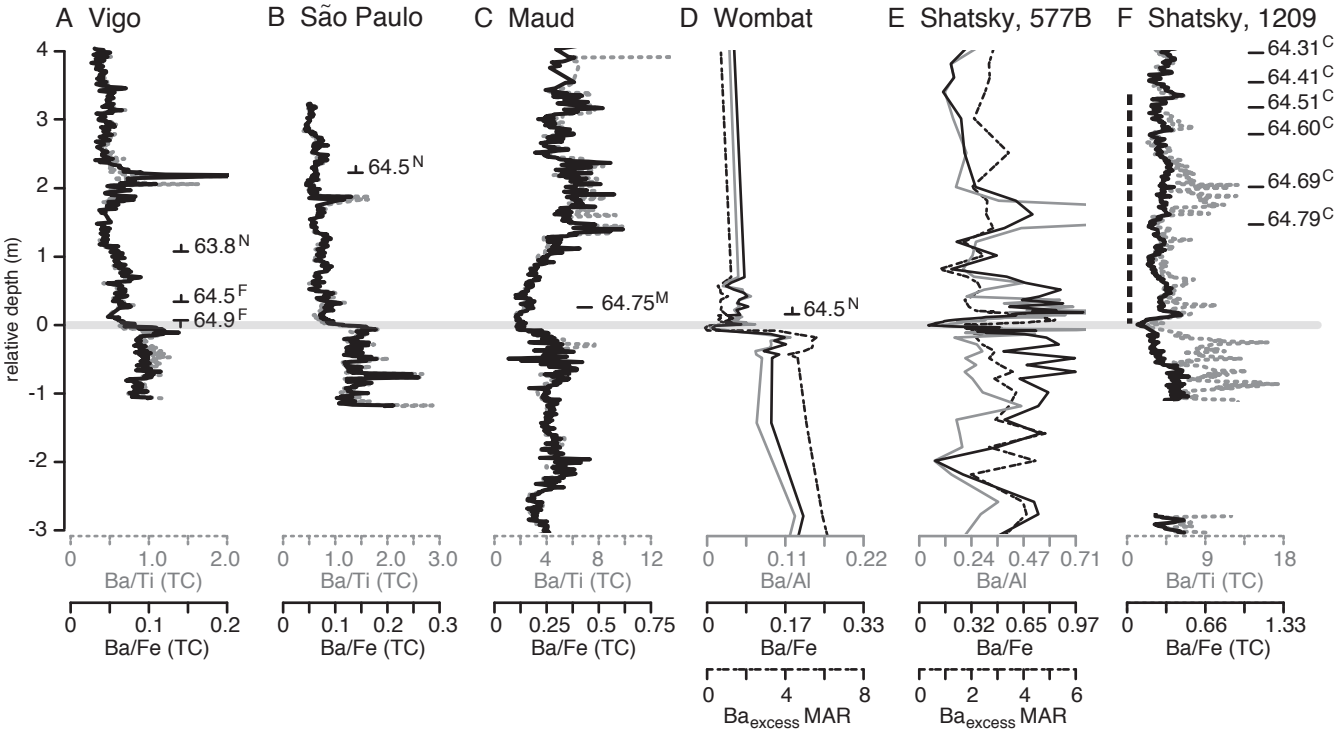
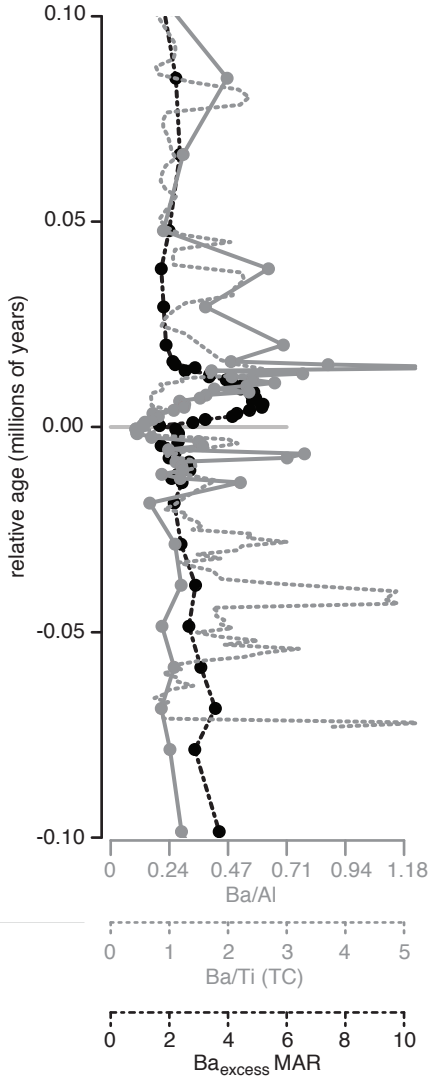

A Vigo
B São Paulo
C Maud
D Wombat
E Shatsky, 577B
F Shatsky, 1209
relative depth (m)
63.8N
64.5F
64.9F
64.5N
64.75M
64.5N
64.31C
64.41C
64.51C
64.60C
64.69C
64.79C
Ba/Ti (TC)
Ba/Fe (TC)
Ba/Al
Ba/Fe
Baexcess MAR

Figure 4.


0.10
0.05
0.00
-0.05
-0.10
relative age (millions of years)
0
0.24
0.47
0.71
0.94
1.18
Ba/Al
0
1
2
3
4
5
Ba/Ti (TC)
0
2
4
6
8
10
Ba$_{excess}$ MAR