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Elevated Post K-Pg Export Productivity in the Gulf of Mexico and Caribbean

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Abstract

The global heterogeneity in export productivity after the Cretaceous-Paleogene (K-Pg) mass extinction is well documented, with some sites showing no change on geologic timescales, some demonstrating sustained decline, and a few showing a somewhat surprising increase. However, observational data come from sites so widespread that a key outstanding question is the geographic scale of changes in export productivity, and whether similar environments (e.g., open ocean gyres) responded similarly or whether heterogeneity is unrelated to environment. To address this, we developed three new Ba/Ti export productivity records from sites in the Gulf of Mexico and Caribbean which, combined with published data from a fourth site in the Chicxulub Crater itself, allows us to reconstruct regional changes in post K-Pg export productivity for the first time. We find that, on a regional scale, export productivity change is homogenous, with all four sites showing a ~300 kyr period of elevated export production just after the boundary, followed by a longer period of decline. Interestingly, this interval of elevated export production appears to coincide with the post K-Pg global micrite layer, which is thought to at least partially have been produced by blooms of carbonate-producing cyanobacteria and other picophytoplankton. We note from a global comparison of sites that elevated export productivity appears to be most common in oligotrophic gyres, which suggests that changing plankton ecology evidenced by

the micrite layer altered the biological pump, leading to a temporary increase in export production in these settings.

Plain Language Summary

Primary producers are the base of the food chain; this group was severely damaged by the environmental effects associated with the Cretaceous-Paleogene mass extinction. Determining how primary production recovered after this calamity is an important foundation for understanding how ecosystems recovered. Most previous work on this topic has focused on a process called export production, whereby organic carbon produced by phytoplankton is transferred to the ocean interior (some of which sinks to the seafloor and is buried). This work has shown that although most parts of the ocean recorded a decline in export production after the extinction event, some regions actually showed an increase. However, it was not clear on what geographic scale these differences occurred, or what caused them. We generated three new records of export production from a single region, the Gulf of Mexico/Caribbean Sea, and found a consistent increase in export production at each site for the same period of time after the extinction event. Comparison with other sites with increased export production shows that many are from open ocean gyres and suggests that these regions were predisposed to increased export production in the earliest Paleocene because they were characterized by low productivity prior to the extinction.

1. Introduction

The end Cretaceous mass extinction is associated with a severe disruption of marine productivity (Hsü and Mackenzie, 1985; Zachos et al., 1989; D'Hondt et al., 1998; Coxall et al., 2003; Birch et al., 2016). A reduction in sunlight caused by dust, soot, and sulfate aerosols ejected by the Chicxulub impact resulted in a reduction in photosynthesis which is believed to have led to the collapse of marine food webs (Alvarez et al., 1980; D'Hondt et al 1998). Models show that the reduction in insolation lasted only a few years after the impact (Toon et al., 1997; Bardeen et al., 2016; Brugger et al., 2016; Artemieva et al.,

2016; Artemieva and Morgan, 2020), removing the proximal external stress on marine primary producers and clearing the way for the recovery of primary production. How, exactly, marine productivity recovered has been a central focus of K-Pg boundary research for decades; the K-Pg mass extinction represents a geologically unique disruption of marine ecosystems, perhaps the only major event in Earth history which happened faster than modern climate change and environmental disruption. Modern oceans are likely on the verge of a major reorganization of dominant plankton types due to warming, acidification, and changes in circulation patterns (e.g., Barton et al., 2016; Jonkers et al., 2019), and primary production is expected to decline 20% due to warming (Moore et al., 2018). The earliest Paleocene provides a window into understanding how such ecological changes may impact food webs and marine carbon burial.

Of course, we can't observe ancient primary production in the euphotic zone directly, and so most work on the collapse and recovery of productivity after the K-Pg boundary is focused on sedimentary records of export production (the transfer of particulate organic matter from the euphotic zone to the deep sea; e.g., Passow and Carlson, 2012)). The movement of particulate organic matter (POM) from the euphotic zone to the seafloor is complicated and can be divided into a series of steps, all of which are influenced by different processes. Most net primary production (NPP) occurs in the euphotic zone (dependent on sunlight penetration but typically defined as 0-100 or 200 m water depth; Passow and Carlson, 2012), and the large majority of POM is remineralized in these near surface waters. The precise amount varies by region and season, but typically ~ 90% of NPP is consumed and recycled before it can sink out of the euphotic zone. The movement of POM out of the euphotic zone is typically what biological oceanographers define as "export flux" or "export productivity" (Passow and Carlson, 2012). Paleoceanographers typically use the latter term to refer to the whole process by which POM is buried in the sediments. However, here we follow the biological oceanographers and use "export productivity" to refer to this initial sinking out of surface waters, mainly because this is the process that can be tracked in ancient sediments by biogenic barium – see below). As POM continues sinking through the mesopelagic zone (typically defined as 100-1000 m water depth; Passow and Carlson, 2012) it is subject to grazing by

mesopelagic organisms of all sizes, which gradually break down long chain organic carbon molecules back to their constituent inorganic carbon molecules, turning POM into dissolved organic carbon (DOC) and then dissolved inorganic carbon (DIC) (e.g., Boyd and Trull, 2007). The amount of remineralization that occurs in the mesopelagic zone is controlled by the rate at which the POM is sinking (i.e., how long it is exposed to mesopelagic grazers), the composition of the grazing ecosystem, and the quality of the organic carbon (i.e., is it labile and easy to degrade or refractory and more difficult to break down) (e.g., Buessler and Boyd, 2009; Henson et al., 2012). POM which sinks below the mesopelagic zone is effectively removed from the short-term carbon cycle, and so the export of organic matter below 1000 m is often referred to as "sequestration flux" (e.g., Passow and Carlson, 2012) or "transfer efficiency" (Henson et al., 2012). By this point, most remineralization has occurred, but POM sinking out of the mesopelagic zone has traveled through less than one third of the average depth of the ocean, and additional remineralization occurs all the way to (and at) the seafloor, before surviving POM is buried and removed from the carbon cycle on geologic time scales (referred to as "burial flux" by Griffith et al., 2021). The amount of net primary production that reaches the deep sea varies by region and is largely controlled by plankton ecology (Henson et al., 2012), but on the whole only 1-3% of modern net primary production reaches the deep ocean or sediments (e.g., Müller and Suess, 1979; de la Rocha and Passow, 2007; Griffith et al., 2021).

Initial reconstructions of productivity change across the K-Pg boundary focused on carbonate proxies, specifically carbonate mass accumulation rates and carbon stable isotopes (e.g., Hsü and Mackenzie, 1985; Zachos et al., 1989). A drop in carbonate mass accumulation rate in the deep sea has been observed at many boundary sites across the globe, and is interpreted to represent a reduction in the production of carbonate by pelagic calcifiers like calcareous nannoplankton and planktic foraminifera (e.g., D'Hondt et al., 1998), both of which suffered a severe (>90% species diversity) extinction at the K-Pg boundary (e.g., Thierstein, 1982; Bown, 2005; Fraass et al., 2015; Lowery et al., 2020). The most striking carbonate proxy response, though, is the collapse of the $\delta^{13}C$ gradient between the surface ocean

and the deep sea (Zachos and Arthur, 1986; Zachos et al., 1989; D'Hondt et al., 1998; Coxall et al., 2003; Alegret et al., 2012; Esmeray-Senlet, 2015; Birch et al., 2016). In the modern ocean (and likely since phytoplankton first evolved) the sinking of ^{12}C-rich organic matter depletes the surface ocean and enriches the seafloor in that light isotope, resulting in an isotopic gradient from surface to seafloor. This gradient collapsed at the Cretaceous-Paleogene (K-Pg) boundary (e.g., Kump, 1991), reflecting a reduction in export production and a weakening of the biological pump for 1.8 myr (Birch et al., 2016, 2021). Taking into account observed changes in planktic foraminifer ecology and physiology (which account for a portion of the change in the $\delta^{13}C$ gradient – Birch et al., 2016, 2021), modelling suggests that a ~50% decrease in the amount of organic carbon exported from the euphotic zone, from 10% of net primary production to 5%, would account for the observed collapse of the $\delta^{13}C$ gradient (D'Hondt et al., 1998; Henehan et al., 2019).

The continued flux of some organic matter to the deep ocean is confirmed by fossil data which indicate a lack of extinction in some groups of pelagic fishes (Doyle, 1979; Siebert and Norris, 2015) and deep sea benthic foraminifera (e.g., Culver, 2003; Alegret and Thomas, 2005, 2007, 2009; Alegret et al., 2012, 2021). Meanwhile, geochemical data indicate a rapid recovery of primary producers (Sepúlveda et al., 2009, 2019). One of the most striking features of the benthic foraminiferal record at the K-Pg boundary is how it varies globally. Although no major extinction occurred, assemblage compositions shifted at many sites (e.g., Culver et al., 2003; Alegret et al., 2012, 2021). At some localities, benthic foraminifer assemblages indicate a reduction in the flux of organic matter to the seafloor, but others show no change across the boundary, and some actually indicate an *increase* in organic matter flux (e.g., Alegret and Thomas 2005, 2007, 2009; Alegret et al., 2012, 2021).

In practice, it is difficult to use carbon isotope gradients to reconstruct post K-Pg export production in any sort of geographic detail. Isotopic analysis of planktic and benthic foraminifera requires well-preserved carbonate material, otherwise diagenetic overprinting will obscure the signal. Localities with well-preserved 66-myr-old foraminifera are not particularly common, and for that reason carbon

isotope gradients have only been produced from a handful of well-studied sites like Walvis Ridge (Hsu and Mackenzie, 1985; D'Hondt, 1998a; Coxall et al., 2006; Birch et al., 2016, 2021), Shatsky Rise (Zachos and Arthur, 1986; Zachos et al., 1989; Coxall et al., 2006), J-Anomaly Ridge (Zachos and Arthur, 1986), and São Paulo Plateau (Zachos and Arthur, 1986). While these sites have all yielded high quality data that have fundamentally changed our understanding of K-Pg recovery, they only cover a small part of the ocean.

For this reason, additional proxies not dependent on pristine microfossil preservation are necessary. Benthic foraminifera, which track burial flux of POM, are one such proxy, and another is based on barium. Biogenic barium abundance in marine sediments (where it is commonly preserved as barite – $BaSO_4$) has been shown to correlate with export production in the modern and ancient ocean (Dymond et al., 1992; Francois et al., 1995; Eagle et al., 2003; Paytan and Griffith, 2007) and is not subject to the same diagenetic effects as carbon isotopes. Like so many other proxies, though, studies have shown that the relationship between the measurement (biogenic barium) and the thing for which it is a proxy (export production) is not quite as straight forward as it seemed at first. A good recent review of the various processes which can affect the formation, burial, and preservation of marine barite can be found in Carter et al. (2020). Here we summarize the most important processes that impact the reconstruction of changes in export production across the K/Pg boundary.

Although marine barite is linked to export production, Ba can also be sourced from detrital settings, and the Ba content can vary from source area to source area (e.g., Carter et al., 2020), so elemental Ba data need to be normalized against a terrigenous element like titanium or aluminum to control for any possible detrital barium component (e.g., Dymond et al., 1992; Payton et al., 1996; Bains et al., 2000; Paytan and Griffith, 2007; Griffith and Paytan, 2012). Most marine barite formation occurs between 200-600 m water depth, where most organic matter remineralization occurs (Martinez Ruiz et al., 2020; Carter et al., 2020), and so biogenic Ba production tracks "export flux" or the amount of POM which sinks below the euphotic zone (see above). However, Ba formation is probably mediated by

147 bacteria which consume oxygen during remineralization of POM, which means that increased bacteria
148 production could lead to increased barite formation (e.g., Dehairs et al., 2008; Jacquet et al., 2011;
149 Planchon et al., 2013) without a change in export production. This microbial activity can be influenced by
150 organic matter quality, temperature (as warmer temperatures result in increased bacterial activity), and the
151 composition of the microbial ecosystem itself (Carter et al., 2020). Ba *production* is thus (mostly)
152 correlated directly to the export flux of POM, but the ocean is undersaturated in barite, which means that
153 70% of particulate barite (and more in anoxic regions) dissolves in the water column and the upper few
154 cm of the sediments before it is buried (Carter et al., 2020). This means that the replacement of one
155 watermass with another of a different Ba^{2+} saturation state could lead to a change in barite accumulation
156 which could be misinterpreted as a change in export flux (e.g., Carter et al., 2020).

157 These caveats make it difficult to directly extrapolate from Ba flux to absolute values of export
158 flux in mass of organic carbon per unit time, particularly all the way back in the Paleocene, but if major
159 variables (terrigenous flux, water mass changes) are controlled for then marine barite can provide
160 important insights to changes in export flux. Hull and Norris (2011) used XRF-derived Ba/Ti and Ba/Fe
161 ratios from five K-Pg boundary sites to bolster the export productivity record of benthic foraminifera, and
162 demonstrated that changes in export production across the boundary were indeed geographically
163 heterogeneous, with some sites showing an increase in export production after the boundary.

164 Understanding geographic heterogeneity in export production is necessary to understand the
165 overall recovery of marine primary producers after the K-Pg boundary. In particular, the calcareous
166 nannoplankton, which have the best fossil record among primary producers in the early Paleocene, exhibit
167 geographic heterogeneity in their post K-Pg recovery (Jiang et al., 2010; Schueth et al. 2015; Jones et al.,
168 2019). Post-extinction calcareous nannoplankton assemblages are characterized by a dominance of
169 "disaster taxa," chiefly *Braarudosphaera* and *Cervisiella*, which eventually give way to a succession of
170 acme events as new Paleocene genera appear and briefly dominate the assemblage (Bown, 2005; Jones et
171 al., 2019; Gibbs et al., 2020). Gibbs et al. (2020) found that some of the survivors and earliest new genera

have adaptations which indicate a mixotrophic lifestyle (i.e., they supplemented photosynthesis by ingesting small prey like bacteria); later incoming taxa lack these adaptations, indicating changing trophic conditions (specifically the under exploitation of small prey species following the extinction of many heterotrophic plankton) may have played a role in nannoplankton recovery (Gibbs et al., 2020). The timing of these acme events is geographically variable, and at sites with elevated export productivity after the K-Pg (Shatsky Rise and Chicxulub Crater), it is coincident with an observed decline in export production (Jones et al., 2019). In the ocean today, eutrophic waters tend to be dominated by a few taxa best suited to take advantage of widely available food, while oligotrophic waters tend to have much higher diversity with greater degrees of specialization (e.g., Hallock, 1987). Jones et al. (2019) hypothesized that the recovery of primary producer assemblages (and by extension the ecosystems which they supported) after the K-Pg is similarly linked to nutrient state controlled by the recovery of the biological pump, but the linkages are not well understood and a better picture of export productivity trends is a necessary first step.

Unfortunately, the geographic trends in early Paleocene export productivity are still poorly known. Modelling work by Henehan et al. (2019) indicated that typically oligotrophic gyre environments in the North and South Pacific Oceans, the Arctic Ocean, and northern Indian Ocean, would have experienced increased export productivity in a scenario in which global average export productivity declined 50% (in line with estimates of post-K-Pg declines in export production; D'Hondt et al., 1998; Henehan et al., 2019). However, these modelling results are currently unconstrained by data, and sites with observed increases in post-extinction export production (e.g., Shatsky Rise Site 1209; Hull and Norris, 2011) are close to but fall outside of modelled areas of increased post-extinction export production. Although the work of Hull and Norris (2011) represents a significant improvement in observations of export productivity trends, they are still limited to the ocean basin scale: Shatsky Rise in the North Pacific compared to São Paulo Plateau in the South Atlantic compared to Maud Rise in the Southern Ocean. This is a good starting place but leaves open the question of the scale of heterogeneity.

Do regions exhibit similar trends (implying an oceanographic driver of variability) or do sites vary even within a region (implying that variability is driven by local effects or is just stochastic)? To address this question, we developed three new Ba/Ti datasets from the Gulf of Mexico and Caribbean at Deep Sea Drilling Project (DSDP) Site 95 and Ocean Drilling Program (ODP) Sites 999 and 1001, which we combined with published data from International Ocean Discovery Program (IODP) Site M0077 in the Chicxulub Crater (Lowery et al., 2021) to produce the first regional-scale study (~1700 km) of export productivity after the K-Pg. This region was modelled to have been characterized by low export production in the latest Cretaceous (Henehan et al., 2019) and thus may be predicted to exhibit increased export production after the boundary. We found that earliest Danian export productivity is elevated at all Gulf of Mexico and Caribbean sites and that an initial reduction in export production occurs ~ 300 kyr

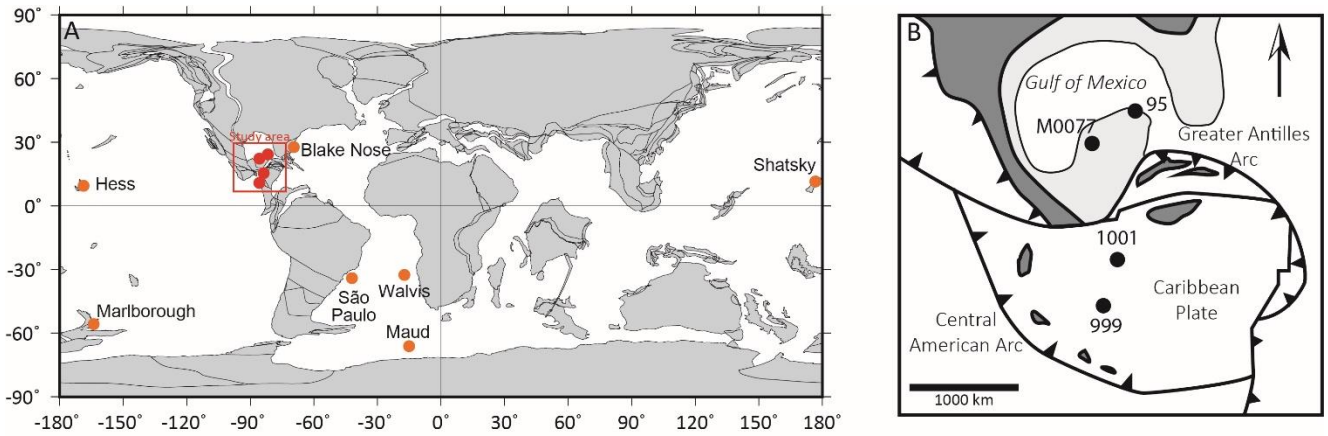

Figure 1. *A) Global plate tectonic reconstruction from 66 Ma showing location of our study area (in red) and other notable sites discussed in this paper (in orange). Grey areas are continental blocks, terranes, and plateaus; map from ODSN generated at https://www.odsn.de/odsn/services/paleomap/paleomap.html. B) Regional map showing position of our study sites around the time of the K-Pg Boundary. Map modified after Pindell and Barrett (1990) and Snedden et al. (2021). Black indicates land and grey indicates continental platforms.*

after the boundary at all sites, indicating that export productivity trends are homogeneous at a regional scale.

1.1 Study Sites

We looked at three scientific ocean drilling sites in the greater Caribbean region with an identified and well-preserved K-Pg boundary interval and compared them to published XRF data from IODP Site M0077 in the Chicxulub Crater (Figure 1). An additional site, DSDP Site 536, below the

Campeche Escarpment in the southeastern Gulf of Mexico (Buffler et al., 1984), was considered but rejected because a preliminary examination of planktic foraminifera in the nominally lowermost Paleocene cores found a mix of biozones ranging from the Cretaceous to the late Paleocene, indicating significant reworking and/or drilling disturbance, suggesting that XRF data would be untrustworthy. All four of these sites appear to have been at roughly bathyal water depths in the earliest Danian (Worzel et al., 1983; Buffler et al., 1984; Sigurdsson et al., 1997; Lowery et al., 2018). These tropical/subtropical sites are characterized by pelagic carbonate deposition throughout the study interval.

DSDP Site 95, drilled in 1970 on the northeasterly margin of the Yucatan Platform on the Campeche Escarpment (Worzel et al., 1973), contains the correct order of planktic foraminifer biozones and decent preservation in a mostly-complete section overlying the K-Pg impact layer. The Chicxulub impact (and associated earthquakes, tsunami, and seiche waves) caused widespread mass-wasting across the Gulf of Mexico, resulting in K-Pg boundary deposits 10s to 100s of m thick (e.g., Bralower et al., 1998; Denne et al., 2013; Sanford et al., 2016). Site 95, due to its perched position on the edge of the Yucatan Platform, only has ~ 3 m of reworked Cretaceous material and impact debris (Figure 2A). The top of the K-Pg boundary layer occurs at the top of Core 13. This is not the K-Pg boundary per se, because the base of the Paleocene is defined at its Global Stratotype Section and Point at El Kef, Tunisia, as the lowest occurrence of impact material which means that the Cretaceous ended at “the moment of the meteorite impact” (Molina et al., 2009). The impact layer in the Gulf of Mexico is thus technically earliest Danian in age.

Site 1001 was drilled in 1995-6 during ODP Leg 165, and is located on a feature called the Hess Escarpment on the Nicaragua Rise (Figure 1). Shipboard biostratigraphy placed the K-Pg boundary between Core 1001A-38R-CC and 1001A-39R-1 (Figure 2B). Unlike the thick K-Pg boundary deposits found in the Gulf of Mexico, here the whole interval is just a few cm thick. Maastrichtian limestone is overlain by a 1 cm thick dark greenish gray clay, which is in turn overlain by a 3.5 cm bluish gray claystone containing 1 mm scale dark green spheroids interpreted to be tektites (Sigurdsson et al., 1997).

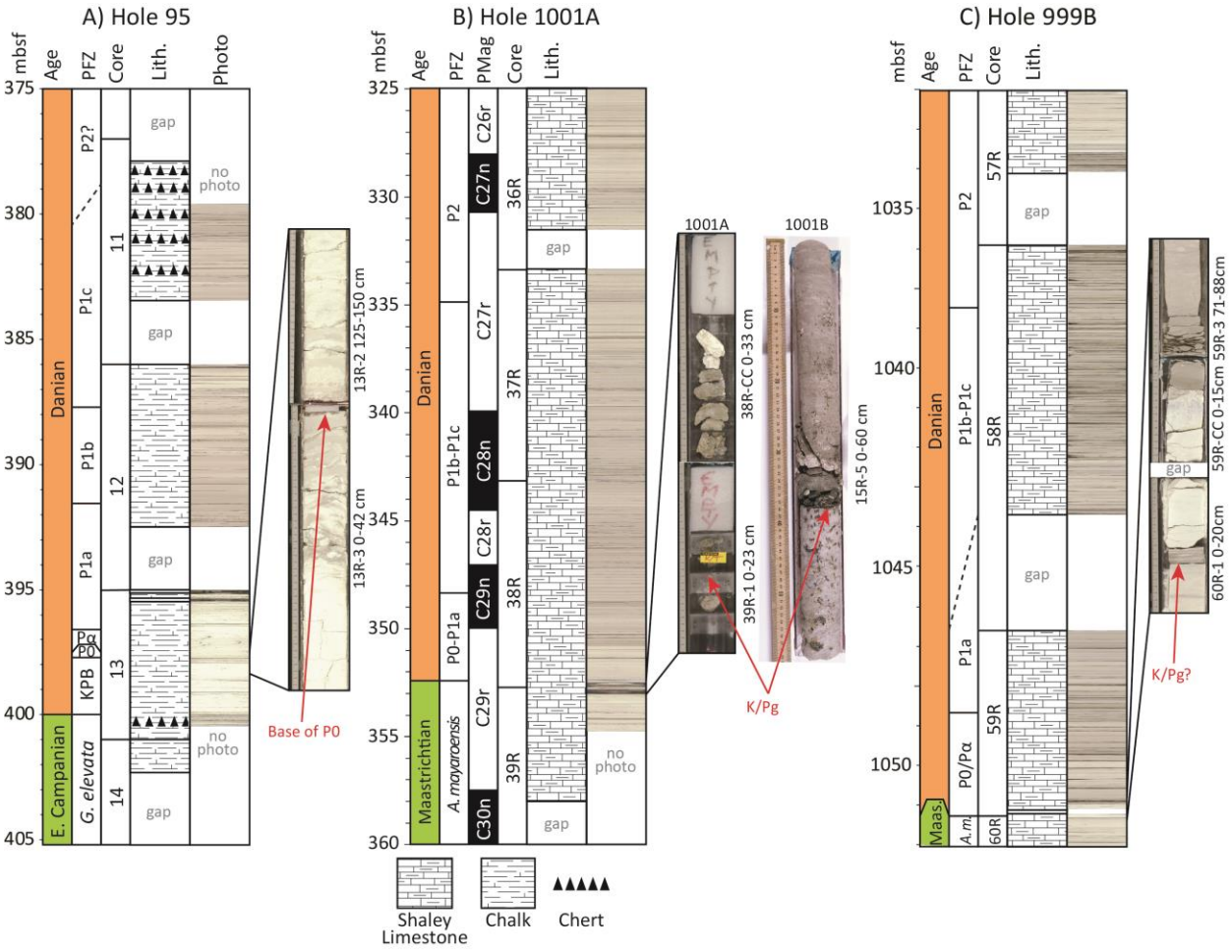

Figure 2. *Stratigraphic sections showing lithostratigraphy, core scan photographs, and images of the K-Pg boundary of the studied intervals from DSDP Hole 95, ODP Hole 1001A, and ODP Hole 999B. Lithostratigraphy follows shipboard descriptions Worzel, Bryant et al. (1973) for Site 95 and Sigurdsson et al., 1997 for Sites 999 and 1001). Core scan photographs were collected at the GCR at the same time XRF data were collected (except for the photograph of the K-Pg boundary in Hole 1001B, which is from the ODP photo archives). Mbsf = meters below sea floor, PFZ = Planktic Foraminifer Zone, Lith. = lithology, PMag = Paleomagnetic polarity, E. Campanian = Early Campanian, Maas. = Maastrichtian, G. elevata = Globotruncanita elevata, A.m. and A. mayaroensis = Abathomphalus mayaroensis.*

This tektite layer is turn overlain by a 3.5 cm medium gray to greenish gray claystone which contains shocked quartz (Sigurdsson et al., 1997). The boundary sequence is overlain by a 4 cm thick light grey limestone assigned to planktic foraminifer Biozones P0/Pα undifferentiated based on thin section analysis (the zones are undifferentiated because the biostratigraphers were not confident in their ability to identify the taxon differentiating the zones, *Parvularugoglobigerina eugubina*, in thin section; Sigurdsson et al., 1997). Shipboard biostratigraphy in the Paleocene is of poor quality due to the extremely poor preservation of fossil material in the indurated limestone. Fortunately, a magnetic polarity timescale was published for Site 1001 by Louvel and Galbrun (2001) based on whole core scans and single samples, as well as a downhole wireline tool called the Geological High-sensitivity Magnetic Tool (GHMT), and the resulting magnetic reversal timescale means that Site 1001 has the best age model of the sites examined here. Although Hole 1001B recovered a more complete boundary section than Hole 1001A (Figure 2B), Hole 1001B has a number of coring gaps in both the uppermost Cretaceous and the early Paleocene, so XRF scans were conducted on Hole 1001A.

Site 999 was also drilled in 1995-6 during Leg 165 and is located on a small feature called Kogi Rise in the Colombian Basin (Figure 1). Shipboard biostratigraphy placed the K-Pg boundary near the boundary between Cores 999B-59R and 999B-60R (Figure 2C). The highest occurrence of common Maastrichtian calcareous nannoplankton was observed in Sample 999B-60R-1 10 cm, and that of Maastrichtian planktic foraminifera in a thin section in Sample 999B-60R-1 1-21 cm (Sigurdsson et al., 1997). The few foraminifera observed in thin section between Samples 999B-59R-CC 15cm (the base of the core catcher) and 999B-60R-1 1 cm were composed primarily of survivor species *Guembelitria cretacea* (Sigurdsson et al., 1997). The shipboard biostratigraphers were not confident that tiny trochospiral specimens observed in the same sample were or were not *P. eugubina* and thus conservatively assigned this interval to Zones P0/Pα undifferentiated (Sigurdsson et al., 1997). The bases of Zones P1a (top of *P. eugubina*), P1b (base of *Subbotina triloculinoides*), and P2 (base of *Praemurica uncinata*) were identified shipboard (Sigurdsson et al., 1997) and form the basis for the age model used

here, although the latter two are of lower confidence. We washed and examined samples from Site 999 to see if we could refine the shipboard age model but poor microfossil preservation in the indurated limestone material prevented us from adding anything new. A white indurated limestone overlies the highest Cretaceous nannoplankton observed in Core 60, and the base of Section 59R-CC contains a 1 mm thick claystone. Comparison of the recovered core and borehole images collected by the formation microscanner tool reveals that this claystone is ~ 9 cm thick in the borehole, and thus ~ 8 cm of this unit were not recovered (Sigurdsson et al., 1997). It seems reasonable to assume that this missing interval is equivalent to the 8 cm of ejecta-bearing claystones described at Site 1001. The claystone is overlain by 10 cm thick mottled blue limestone described by shipboard scientists as having the appearance of "Roquefort Blue Cheese" and assigned to planktic foraminifer Zones P0/Pα (Sigurdsson et al., 1997). This white limestone is a common feature of K-Pg boundary sections in the deep sea, and is comprised of micrite (i.e., microcrystalline calcite; Bralower et al., 2020). Although the white limestone only extends 10 cm above the boundary, Bralower et al. (2020) observed micrite at Site 999 over a total thickness of 2.42 m. A 2 m coring gap occurs at the base of Core 999B-58R in planktic foraminifer Zone P1a. Micrite was also identified at Site 1001 but it was limited to the core catcher of core 1001A-38R, which contains a few discontinuous bits of rubble and a large void space (Figure 2B), so Bralower et al. (2020) considered the observed 17 cm interval to be a minimum.

2. Methods

We scanned the cores at the XRF Core Scanning Lab at the IODP Gulf Coast Repository at Texas A&M University in College Station, TX. The archive halves of selected cores were scraped to ensure a fresh face of the core for scanning, and, in the case of the softer sediments of Site 95, to ensure a flat surface for the XRF core scanner (the split surface was generally smooth in the unlithified cores from Site 95 but decades in shrink wrap and added a bit of texture in some places). Lithified sections from Sites 999 and 1001 were likewise scraped and leveled within the core liner to ensure a flat horizontal surface. Cores were then covered with 4 μm thick Ultralene film to prevent sediment from sticking to the scanner.

Cores were scanned on an Avaatech XRF Core Scanner at two excitation conditions focused on different element groups. The first scan was at 10kVp with no filter to analyze major and minor elements (Al, Si, K, Ca, Ti, Mn, Fe, Cr, P, S, and Mg) and the second was at 50kVp with a Cu filter to analyze heavier trace elements (Sr, Rb, Zr, and Ba). Scan resolution was set depending on relative distance above the K-Pg boundary, based on low resolution shipboard biostratigraphy. Core sections within Zone Pα or the lower part of Zone P1a (very roughly, within ~ 500 kyr after the boundary) were scanned at 1 or 2 cm steps, and sections below the boundary and >500 kyr after the boundary were scanned at 5 cm steps. Some steps were skipped or moved based on visual examination of the core before scanning (e.g., to avoid cracks or uneven surfaces). Laboratory standards were run at the beginning and end of each day to monitor instrumental performance.

Raw spectral data were processed into peak areas in the lab using the software program bAxil. Quality control of processed data was carried out using the following parameters: 1) throughput (samples with values <150,000 cps, which indicates a gap between the sensor and the core, were removed); 2) Argon peak (samples with positive Ar values, indicating that the sensor was measuring ambient air, were removed); and 3) standard deviation (samples with elemental peaks of Ba or Ti within 2 standard deviations of zero were removed).

To improve the age model for this study we analyzed planktic foraminifera from Site 95 at a resolution of up to 5 cm. Lightly lithified samples were gently broken into cm-sized pieces using a mortar and pestle. All samples were soaked in a solution of hydrogen peroxide and borax for at least 48 hours and then washed over a 45 μm sieve to ensure capture of typically very small early Paleocene taxa; the sieve was soaked in methylene blue dye between samples to mark contaminants. Finally, samples were dried overnight in an oven. Samples were examined for presence/absence of key marker species on a Zeiss Discovery.V8 light microscope. Species concepts follow those of Olsson et al., (1999); biozones are the Wade et al. (2011) update of the Paleocene biozonation scheme published by Berggren and Pearson (2005) and calibrated to the timescale of Gradstein et al. (2012).

3. Results

3.1 Biostratigraphy

Site 95 is comprised of firm but unlithified calcareous ooze that yielded fairly well preserved material. We examined 25 samples from Cores 11 to 13 to identify and then refine the boundaries between planktic foraminifer biozones. An obvious lithologic change occurs in Section 95-13R-3 at 24 cm (397.92 mbsf). Samples below this level are composed of mixed Cretaceous species remobilized by impact-induced seismic disturbance and tsunami, termed the K-Pg Boundary Cocktail (Bralower et al., 1998). From Sample 95-13R-2, 139 cm to Sample 95-13R-3, 24 cm (397.76 to 397.92 mbsf), the core is mottled and contains some signs of drilling disturbance (biscuiting, soft sediment deformation). Samples taken within what we interpret to be the biscuits, however, contain mostly Cretaceous species until 95-13R-3, 0-2 cm (397.70 mbsf), where the survivor species *Guembelitria cretacea* starts to become more common; this level is assigned to the base of Zone P0. The lowest occurrence of *P. eugubina*, which defines the base of Zone Pα, is found just above this level, in Sample 95-13R-2 130-132 cm (397.5 mbsf). The highest occurrence of *P. eugubina*, which marks the base of Zone P1a, occurs in sample 95-13R-1 130 cm (396.60 mbsf). Most of Zone P1a is erased by a coring gap, but Zone Pα and the portion of Zone P1a preserved here contain abundant calcispheres, the resting cyst of calcareous dinoflagellates. Above the coring gap between Cores 95-12R and 13R, the bases of Zone P1b (lowest occurrence of *S. triloculinoides*) and Zone P1c (lowest occurrence of *Globanomalina compressa*) are both present. The base of Zone P2 (*P. uncinata*) is missing in another coring gap between Cores 11R and 12R, and the age model from the base of Zone P1c to the coring gap is based on extrapolating the sedimentation rate from Zone P1b; this method suggests that most of Zone P1c is present.

3.2 Ba/Ti

A key underlying assumption in the use of XRF scan data to reconstruct changes in biogenic Ba is that there is no change in the Ba/Ti ratio of terrigenous material delivered to the site. The extensive

volcanism documented in the Caribbean region throughout the early Cenozoic (Sigurdsson et al., 1997) could be a source of discrete or diffuse tephra deposition to the study sites which may vary through time and alter that ratio. Thus, we have plotted Ba from Site 999 and 1001 against Rb and Zr, which are enriched in volcanogenic minerals. Both Zr and Rb show weak positive correlation with Ba at Site 999 (Figure 3A-B) and a slightly less-weak positive correlation with Ba at Site 1001 (Figure 3C-D). This is to be expected, as any volcanic ash would have introduced more detrital Ba in the record. However, when we normalize Ba against Ti and compare this to Rb and Zr at both sites, the positive correlation goes away (Figure 3E-H). To demonstrate how overall changes in lithology affect Ba abundance, we plotted Ba against Ca (any decrease in Ca in a pelagic setting above the lysocline is likely due to dilution by terrigenous material). At both sites, there is a weak negative correlation between Ca and Ba (Figure 3I-J). This is what we'd expect, as dilution of pelagic Ca by terrigenous material would introduce detrital Ba; this is also precisely why we normalize Ba to a terrigenous element like Ti, to eliminate any signal from terrigenous Ba. Overall, the relationship between Ca and Ba is not very strong, likely because overall terrigenous content in these pelagic clays is very low. We conclude that the Ba/Ti ratios at these sites do not reflect changes in terrigenous flux from either volcanism or other sources, and are thus primarily driven by changes in export productivity.

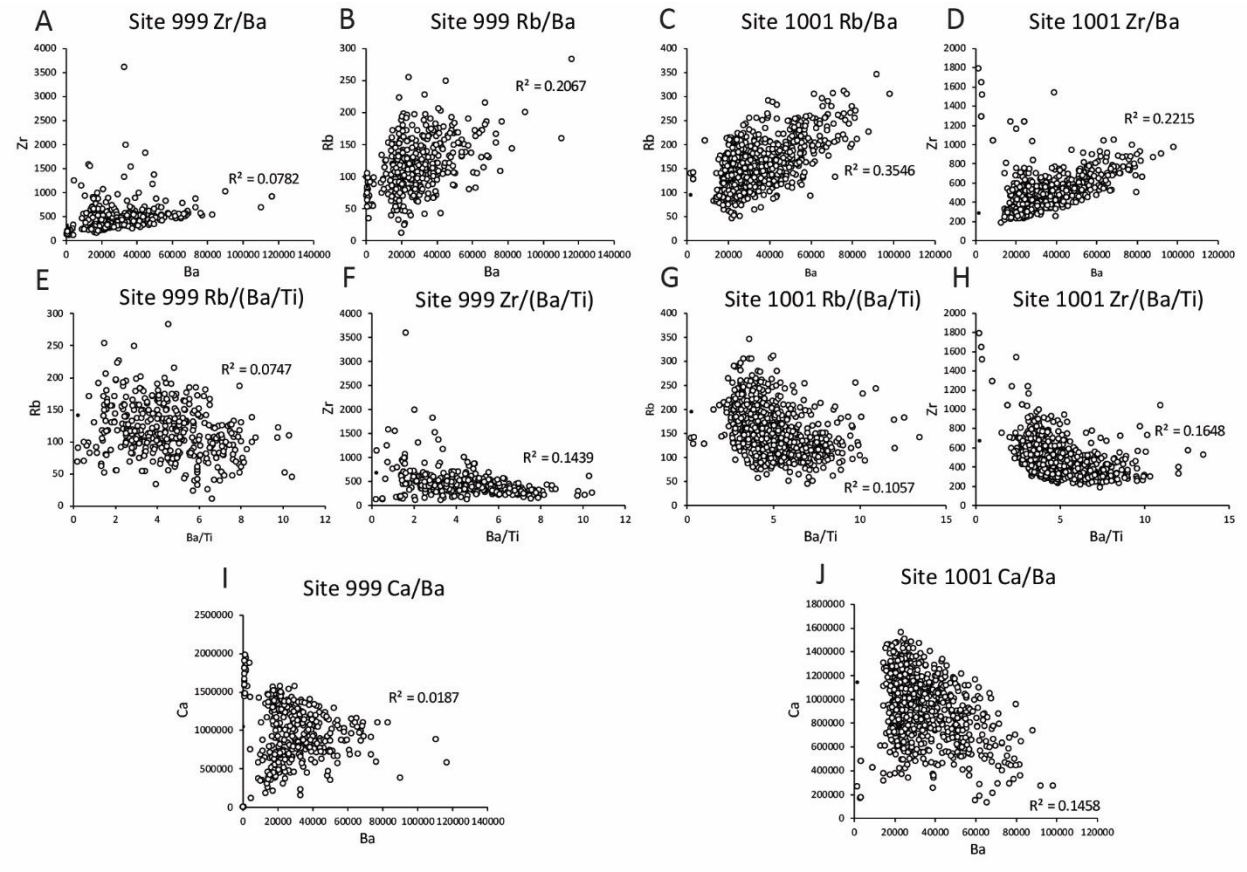

Figure 3. *Crossplots of Rb, Zr, and Ca with Ba and Ba/Ti ratios from Sites 999 and 1001. R^2 values showing correlation (or lack thereof) for each parameter are included on the plots.*

3.2.1 Site M0077

Data from the Chicxulub Crater have been published previously (Lowery et al., 2018, 2021) but contain several interesting trends that should be summarized here. The highest Ba/Ti ratios in the study interval are found in the earliest Paleocene, representing the first ~320 kyr after the impact (Figure 3A). At that point, there is a sharp drop in Ba/Ti values, followed by a steady decline from moderate values to a minimum about 1.2 myr after the K-Pg boundary, at which point values stabilize and remain low with some small-scale variability. Interestingly, this transition around 1.2 myr post-impact coincides with turnover in the calcareous nannoplankton ecosystem, as disaster taxa began to give way to acmes of new Paleocene taxa (Jones et al., 2019; Lowery et al., 2021).

3.2.2 Site 95

Ba/Ti ratios at Site 95 are also highest in the earliest Paleocene, with a peak around the Pα/P1a zonal boundary and a sharp drop off ~340 kyr after the impact. A difference of 20 kyr between two sites whose age models are entirely based on biostratigraphy is basically within error and we feel comfortable assuming that this drop was contemporaneous with the one observed at Chicxulub Crater Site M0077. Approximately 300 kyr of the record in the middle of Zone P1a is erased by a coring gap, but above this level Ba/Ti values trend lower until about 1.1 myr after the K-Pg boundary. Values then remain low until about 1.6 myr post-impact and finally increase somewhat, varying through the rest of the record.

3.2.3 Site 1001

Site 1001 is the first of our sites in which there are data for the uppermost Cretaceous, and we can see that (above a gap where the boundary layer is mostly missing) Ba/Ti values increase in the Danian relative to the Maastrichtian. Although there is no obvious large peak like in the two Gulf of Mexico sites, there is still an interval of overall higher values lasting to ~ 280 kyr after the impact. Above this level, values are much more variable than in the Gulf of Mexico but there is still a clear downward trend to a nadir around 1.4 myr after the K-Pg boundary, above which point values increase slightly and vary a little bit for the rest of the record.

3.2.4 Site 999

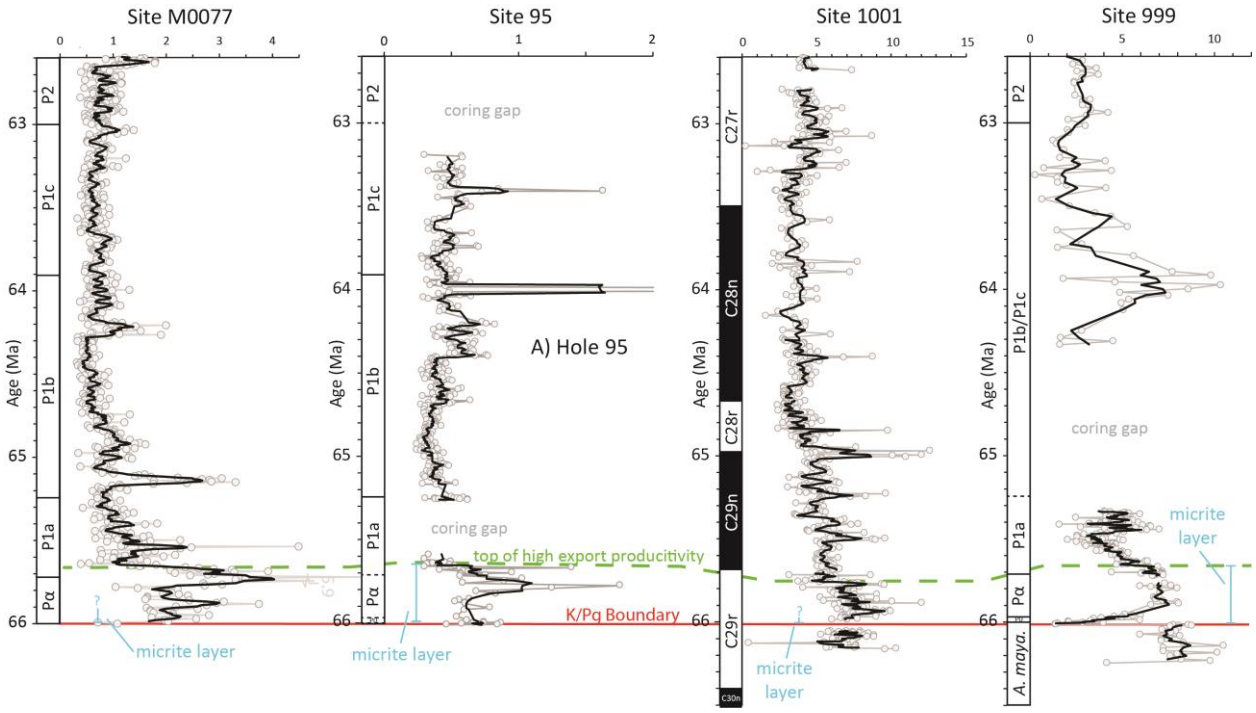

Figure 4. *Barium-Titanium export productivity proxy data for IODP Site M0077, DSDP Site 95, and ODP Sites 1001 and 999. Individual datapoints are grey circles, thick black lines is a 5-point moving average. Red line indicates the K-Pg boundary (or the top of the boundary interval in the case of Sites M0077 and 95), blue line indicates the thickness of the micrite layer identified at each site by Bralower et al. (2020), and the green dashed line indicates the top of the interval of highest export productivity at each site. PFZ: Planktic Foraminifer Zone (after Wade et al., 2011); A. maya.: Abathomphalus mayaroensis.*

Site 999 is the southernmost site, and the most distal from the Chicxulub impact crater. Ba/Ti values are very low directly above the boundary layer, quickly increasing through the lower part of Zone Pα. Higher values after this brief recovery interval do no exceed the Ba/Ti values observed in the uppermost Cretaceous, but they are much higher than subsequent Paleocene values (with the exception of a brief peak around 2 myr after the K-Pg boundary). Once again, there is a sharp decrease in values approximately 320 kyr post-impact followed by gradually declining values. The very poor quality of the biostratigraphy in this core (the Pα/P1a zonal boundary marker is really the only reliable datum) makes it difficult to determine the timing of this decline and whether the increase observed below the coring gap really occurs just 600 kyr after the boundary or much later. While we do not place much confidence in the ages above this level, we are confident in age control in the key interval above the boundary, specifically the highest occurrence of *P. eugubina* (Pα/P1a zonal boundary).

4. Discussion

4.1 Regional Homogeneity of Post K-Pg Export Production

The most striking feature of the four export productivity records presented here, and the key result of this investigation, is the consistent occurrence of relatively elevated Ba/Ti values in the earliest Paleocene. Interestingly, this is in line with trends from other sites in oligotrophic regions like the North Pacific Gyre. Three other open ocean sites have evidence of increased export productivity in the earliest Danian: the North Pacific Shatsky Rise and Hess Rise (Alegret and Thomas, 2005, 2009; Hull and Norris, 2011), and the mid-latitude South Pacific sections around Marlborough, South Island, New Zealand (Hollis et al., 1995, 2003). The high export productivity at Marlborough appears to be the result of increased upwelling along the continental margin (Hollis et al., 2003). Shatsky Rise and Hess Rise, though, are open ocean sites on roughly the same paleolatitude as our study area and were generally oligotrophic during this time interval (e.g., Deprez et al., 2017; Henehan et al., 2019). It is tempting to interpret the Ba/Ti data as elevated export production in the earliest Paleocene at all of these sites, in contrast with the overall global trend of reduced export production. But first we need to rule out other possible explanations.

As discussed above, there is no evidence that changes in terrigenous Ba/Ti ratios influence the record at our Caribbean sites, and in any case this is too regional an explanation to explain how the same trend could be extended to the Gulf of Mexico and North Pacific sites. Likewise, we do not think transient (100-kyr-scale) changes in intermediate or deep water masses affecting barite dissolution rates make sense across such widely dispersed sites. The most likely explanations must be related to the oligotrophic gyres themselves, either oceanographic changes in the gyres themselves or, more likely, ecological changes in the populations of phytoplankton and/or grazers that lived in these gyres.

There are several possible mechanisms which could drive an increase in marine barite production while export production is kept steady. Different groups of plankton incorporate different amounts of Ba

into their biomass. For example, coccolithophores have less Ba in their cells than diatoms, which in turn have less Ba in their cells than chrysophytes (gold algae), which have less Ba than chlorophytes (green algae) (e.g., Paytan and Griffith, 2007). Calcareous nannoplankton suffered a severe extinction at the K-Pg, and if they were briefly replaced in oligotrophic gyres by any of these other groups, then biogenic Ba flux to the seafloor would increase even if export production held steady. Alternatively (or additionally), an increase in temperature or a shift in bacterial ecology at mesopelagic depths could have increased bacterial remineralization and thus barite production. A reduction in the abundance of grazers which break apart sinking POM or an increase in ballasting or the formation of aggregates (which have the effect of making POM sink more quickly) may have increased the amount of POM which sank below the mesopelagic zone and to the seafloor. However, such a change wouldn't necessarily be expressed by increased biogenic barium, since marine barite formation is a byproduct of the remineralization of organic matter (Dehairs et al., 2008; Jacquet et al., 2011; Planchon et al., 2013) and quickly sinking POM has less time to remineralize. On the other hand, a more robust grazer community at mesopelagic depths may have broken apart more POM, slowed sinking and increased the time it was exposed to remineralization, although it is difficult to imagine a more robust grazer community after a major mass extinction. Many of these change (mesopelagic temperature increase, shifts in the grazer community or toward phytoplankton with higher Ba abundance in their cells) are impossible to test for with existing paleoceanographic tools. What we can do, though, is look to other parts of the biological pump and see if they indicate whether the observed increase in Ba/Ti is indeed related to export productivity.

Benthic foraminiferal accumulation rate and assemblages provide additional export productivity information at these sites. Benthic foraminifera, which are responsive to the amount and quality of organic matter that reaches the seafloor, record a different part of the biological pump than biogenic barium, which is formed during the remineralization of organic matter at mesopelagic depths. Indeed, these two proxies can sometimes show opposite trends (e.g., Griffith et al., 2021), which can help us determine if our observations are the result of increased export production or some other process. At Site

M0077 in the Chicxulub Crater, elevated Ba/Ti ratios are associated with an interval of higher benthic foraminiferal abundance, indicating increased export production was associated with increased food supply to the seafloor (this was no doubt helped by the fact that the seafloor was at mesopelagic depth; Lowery et al., 2018) (Lowery et al., 2021). Unfortunately, we don't have benthic foraminifera data from Site 95 because it is difficult to tell reworked benthics from *in situ* ones there, and we don't have benthic foraminifera from Sites 999 and 1001 because of overall poor preservation of microfossils. On Shatsky Rise in the North Pacific gyre benthic foraminifera from Site 1210 (from Alegret and Thomas, 2009) and barium proxy data from the adjacent Site 577 (from Hull and Norris, 2011) are elevated for roughly the first 100 kyr after the extinction. On Hess Rise, also in the North Pacific gyre, no barium data exist but benthic foraminifera at Site 465 indicate a peak in post K-Pg burial flux within 100 kyr of the boundary (within planktic foraminifer Zone Pα) (Alegret and Thomas, 2005). At the three sites with both Ba and benthic foraminifer data exist, they indicate increased transport of POM out of the euphotic zone and to the seafloor; we therefore interpret the Ba/Ti data at all our sites as primarily recording an increase in export productivity.

In the Gulf of Mexico and Caribbean, the interval of highest export production ends right around the Pα/P1a zonal boundary at each site, roughly 300 kyr after the K-Pg boundary, followed by a general decline over the next million years or so. The precise features of this record vary from site to site; notably, the prominent early peak observed in the Gulf of Mexico (Sites M0077 and 95) is absent in the Caribbean cores (Sites 999 and 1001). Likewise, Site 999 records very low values immediately above the K-Pg boundary followed by a rapid recovery of values that is not evident at any of the other sites. Finally, the timing of the sharp decline of these high productivity intervals varies by a few tens of kyrs between sites. Because the age models are based on biostratigraphy *or* paleomagnetic reversals, with no higher resolution techniques like orbital chronology, it is impossible to say whether these differences are real or merely artifacts of the limits of the age models. These are superficial differences, though, and a clear

overall trend exists that export productivity was elevated across Gulf of Mexico and Caribbean (a distance of ~1700 km) for ~300 kyr after the K-Pg mass extinction, and began to decline thereafter.

The observed homogeneity in regional export productivity in the earliest Paleocene provides important context for previous observations of global-scale heterogeneity determined with the Ba proxy. Previous work had shown major differences in the amount of organic matter remineralized in the mesopelagic zone between ocean basins, with an increase in export production observed in the middle of the North Pacific, a decline in the western North Atlantic, western South Atlantic, and Southern Ocean, and no change in the eastern South Atlantic (Hull and Norris, 2011). Those sites are widely separated and represent different oceanographic environments (oligotrophic gyres, western boundary currents, eastern boundary currents). With only one site in each region, it is hard to know whether these observations are indicative of regional trends or more limited, local change. With the discovery that sites within the Gulf of Mexico/Caribbean all exhibit the same trends, we can be more confident that previously observed regional differences are real, and therefore conclude that oligotrophic open ocean sites were prone to increased export production immediately after the K-Pg boundary, as suggested by Henehan et al. (2019). But what was the driver for this increased export production?

4.2 Drivers of Post-Extinction Export Productivity

In the modern ocean, oligotrophic gyres are typically dominated (in terms of biomass) by picophytoplankton (0.2-2.0 μm in size) like cyanobacteria and algae, but larger nano and micro phytoplankton (2-20 μm and >20 μm, respectively), though less numerous, account for the majority of productivity measured in incubation experiments (e.g., Marañón et al., 2003). Because picophytoplankton have no fossil record, we cannot say for sure whether this was the case at the end of the Cretaceous, but this seems like a safe assumption.

A switch from calcareous nannoplankton, the dominant phytoplankton of the Cretaceous (Bown, 2005) to smaller phytoplankton like cyanobacteria and chlorophyte algae would serve to reduce export

flux globally and retain more nutrients in the euphotic zone, because smaller cell sizes sink more slowly and are less likely to be consumed by zooplankton and packaged in fecal pellets, or bunch together in aggregates (Legrendre and Michaud, 1998; de la Rocha and Passow, 2007, although it should be noted that some modelling studies dispute the role of plankton size on export, e.g., Fakhraee et al., 2020). Henehan et al. (2019) pointed out that in oligotrophic regions, this post-extinction increase in nutrients could actually lead to an increase in primary and/or export productivity.

But how would NPP dominated by picophytoplankton lead to increased export production? After all, if export increased then there would be a mechanism to remove nutrients from the euphotic zone and NPP would necessarily decrease. Yet our work and that of others has found that high export production was maintained in typically oligotrophic regions for 100-300 kyr (Alegret and Thomas, 2005, 2009; Hull and Norris, 2011). To explain this dichotomy, we suggest that POM exported from the euphotic zone became more refractory. The continuous remineralization of very small POM in the euphotic zone is termed the "microbial loop", and the only POM that manages to sink out of the euphotic zone is more refractory and difficult to metabolize (Legrendre and Michaud, 1998; de la Rocha and Passow, 2007). This refractory organic matter is less likely to be completely remineralized by grazers as it sinks through intermediate depths, which would result in less marine barite formation and lower Ba contents. However, if NPP increased after the K-Pg boundary at these sites as a result of the loss of larger phytoplankton, then the export of refractory POM would also have increased, as would the amount of barite formation from that POM. Thus, even if only a small fraction of the refractory POM was remineralized, the overall increase in POM sinking below the euphotic zone would have elevated total remineralization and barite production. This also would explain why food supply increased to the seafloor, as evidenced by increases in benthic foraminifera.

An alternate explanation could be the occurrence of blooms of specific groups of phytoplankton with barium-rich cells or which favor barite formation. For example, in the modern ocean *Phaetocystis* is a common haptophyte which secretes extracellular polymers which form aggregates that speed sinking

and enhance export production (e.g., Verity et al., 2007). These polymers may also play a key role in marine barite formation as nucleation sites (Martinez-Ruiz et al., 2020). Acantharians have barium-rich skeletons and are known to form blooms in oligotrophic regions (e.g., Decelle et al., 2012) but, like the other groups, do not typically fossilize. Blooms of plankton like this may serve to increase export to the seafloor and also increase marine barite production without necessarily relying on a stronger microbial loop in the euphotic zone. While we currently lack direct evidence of blooms of non-fossilizing phytoplankton like these groups, more work is required to provide a clear answer to this question. But we can see some evidence for ecosystem changes associated with increased export productivity after the K-Pg.

4.3 Evidence of Ecosystem Changes

The second-most striking feature of our data is that at two of the sites studied (Sites 95 and 999) the interval of high export productivity ~300 kyr after the boundary coincides almost exactly with well-defined intervals of microcrystalline calcite ("micrite"). The widespread deposition of micrite in marine settings after the K-Pg boundary was documented by Bralower et al. (2020), and proposed to be primarily formed by microbial blooms. The structure of individual micrite crystals is similar to that produced by various cyanobacteria (Bralower et al., 2020) and the micrite layer itself at several sites is associated with elevated biomarkers for photosynthetic bacteria and eukaryotic algae (Sepúlveda et al., 2009; Schaefer et al., 2020; Bralower et al., 2020). Some portion of the global micrite layer was also likely formed by the backreaction of CaO or CaOH vaporized by the Chicxulub impact, but this process would have been limited to the years after the impact as ejecta fell out of the atmosphere (Bralower et al., 2020) and wouldn't explain micrite deposition over ~300 kyr.

Extensive recrystallization of carbonate material at Site M0077 obscures the micrite record at that location. At Site M0077, abundant micrite is limited to a zone of good preservation which includes the "Transitional Unit" at the top of the K-Pg boundary layer (Morgan et al., 2017) and an overlying layer of green marlstone dated to the base of planktic foraminifer Zone Pα (Bralower et al., 2020). Above this in

539 the overlying white limestone layer, poor preservation prevents the consistent identification of micrite,
540 and so the top of the micrite layer is not identified. At Site 1001, coring gaps in the boundary interval in
541 Hole 1001B limit the identification of the micrite layer to a minimum thickness (17 cm, Bralower et al.,
542 2020). Thus, we have two sites showing a clear deposition of micrite ending at the same stratigraphic
543 position (Sites 95 and 999), and two other sites with insufficient data to determine the relative timing
544 (Sites M0077 and 1001).

545 Unfortunately, none of the previously published Pacific sites which show an increase in post-K-
546 Pg export production have both Ba/Ti data and micrite data (although we can compare nearby sites 1210
547 and 577 – see below). Micrite is enriched at Shatsky Rise Site 1209 over a 6 cm interval above the
548 boundary, and at 1210 over a 7 cm interval above the boundary (Bralower et al., 2020), associated with
549 the ~ 100 kyr peak in benthic foraminifer proxies for burial flux (Alegret and Thomas, 2009) and the ~
550 100 kyr interval of elevated Ba/Ti at nearby Site 577 (Hull and Norris, 2011). At Hess Rise Site 465,
551 micrite is enriched over a 24 cm interval above the boundary (Bralower et al., 2020), and benthic
552 foraminifera likewise show a peak in burial flux in this interval (Alegret and Thomas, 2005). It is
553 important to point out that foraminifer samples at both Sites 465 and 1210 were taken at a 10 cm
554 resolution (Alegret and Thomas, 2005, 2009) so a precise tie between the decline in export productivity
555 and the end of micrite deposition is impossible to make with existing data.

556 Although various types of "ballast," including calcite plankton shells, have been thought to
557 influence export production in the modern ocean (Amrstrong et al., 2001; Francois et al., 2002), it does
558 not seem likely that micrite itself, or more specifically the cyanobacteria that produced it, is the cause of
559 increased export production in the earliest Paleocene. Micrite is abundant at many sites which did not
560 experience elevated export production after the K-Pg. For example, Blake Nose Site 1049, which
561 experienced either a decline or no change in export production after the boundary (Alegret and Thomas,
562 2007), has a 30 cm thick micrite layer. Walvis Ridge Site 1267, which similarly experienced no change in
563 post-extinction export production based on benthic foraminifera (Alegret and Thomas, 2005), has a 1.82

m thick micrite layer. All told, Bralower et al. (2020) identified micrite layers at 31 sites globally; of these, only 5 record elevated export production in the early Danian based on available proxies. All of these sites are in open ocean settings which are predisposed to oligotrophy.

The general association of the micrite layer (indicating dominance of microbial primary producers) with the elevated post-impact export production observed across Pacific and Caribbean/Gulf of Mexico sites described here suggests that a post-extinction dominance of picophytoplankton is the primary mechanism driving elevated export productivity at previously oligotrophic parts of the open ocean in the earliest Paleocene.

While it appears that the dominance of picophytoplankton is the proximal cause of elevated post K-Pg export production in tropical open ocean waters, it is important to note that the timing is different between the Caribbean and the central Pacific. The period of highest export production drops off ~ 300 kyr after the K-Pg in the Gulf of Mexico and Caribbean but ends much earlier at Shatsky and Hess Rises, after ~ 100 kyr (Alegret and Thomas, 2005, 2009; Hull and Norris, 2011). This is in line with previous results which indicate a global diachroneity in the turnover of calcareous nannoplankton assemblages in the earliest Paleocene (Jones et al., 2019), driven by transition from surface waters characterized by efficient recycling of nutrients due to the prevalence of picophytoplankton feeding the microbial loop, to surface waters characterized by less efficient recycling of nutrients caused by greater export of larger plankton out of the euphotic zone (Jones et al., 2019; Lowery et al., 2021). At Shatsky Rise, disaster assemblages of calcareous nannoplankton gave way to acmes of Paleocene taxa soon after the K-Pg (Alvarez et al., 2019; Jones et al., 2019). On the other hand, disaster taxa in the Chicxulub Crater continue until the final decline in export productivity about a million years after the K-Pg (Jones et al., 2019), and at Site 999, disaster taxa continue at least into Zone P1a >300 kyr after the K-Pg (Sigurdsson et al., 1997). Whether the recovery in calcareous nannoplankton caused the observed change in export production or if a reduction in export production spurred the local diversification of calcareous nannoplankton remains an open question.

Conclusions

Our new XRF-derived Ba/Ti export productivity proxy data from the Gulf of Mexico and Caribbean show a post K-Pg peak in export productivity across the region, with an interval of high values lasting for ~ 300 kyr after the boundary and then declining values for another ~ 700 kyr. This is a major improvement on previous compilations of earliest Paleocene export productivity, which showed that post-extinction changes in export production were globally heterogeneous but only on an ocean basin scale. Our results show that broad regions followed similar trends. In particular, we find that most elevated export production in the earliest Danian is found at tropical open ocean sites (Shatsky Rise, Hess Rise, and our Caribbean/Gulf of Mexico sites) which were oligotrophic at the end of the Cretaceous (Henehan et al., 2019).

Our other major observation is that at sites with elevated export production and at which preservation makes such observations possible, the post K-Pg global micrite layer corresponds with the interval of elevated export production. We interpret this as evidence that the dominance of picophytoplankton like cyanobacteria and chlorophyte algae, which appear to be associated with the micrite deposition (Bralower et al., 2020), altered the dynamics of the biological pump to increase recycling of organic matter in the euphotic zone. Enhanced recycling of organic matter left only refractory material, which is more difficult to recycle, to be exported from the euphotic zone. Because it is refractory this organic matter would have been more likely to sink through the water column than more labile material exported under normal conditions. In typically oligotrophic environments, this slight increase in efficiency of the biologic pump could have resulted in overall higher export production; as larger phytoplankton recovered and more labile organic matter was exported and grazed, enhanced export production would have subsided.

More datasets from a wider range of latitudes and ocean basins are needed to build a more complete picture of post K-Pg export production to more fully understand how the marine biosphere recovered from the most recent major mass extinction.

Data Availability Statement

XRF core scan data and age models are archived at the NCEI Paleoclimate Database here: https://www.ncei.noaa.gov/access/paleo-search/study/35081

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Figure 1. A) Global plate tectonic reconstruction from 66 Ma showing location of our study area (in red) and other notable sites discussed in this paper (in orange). Grey areas are continental blocks, terranes, and plateaus; map from ODSN generated at https://www.odsn.de/odsn/services/paleomap/paleomap.html. B) Regional map showing position of our study sites around the time of the K-Pg Boundary. Map modified after Pindell and Barrett (1990) and Snedden et al. (2021). Black indicates land and grey indicates shelves.

Figure 2. Stratigraphic sections showing lithostratigraphy, core scan photographs, and images of the K-Pg boundary of the studied intervals from DSDP Hole 95, ODP Hole 1001A, and ODP Hole 999B. Lithostratigraphy follows shipboard descriptions Worzel, Bryant et al. (1973) for Site 95 and Sigurdsson et al., 1997 for Sites 999 and 1001). Core scan photographs were collected at the GCR at the same time XRF data were collected (except for the photograph of the K-Pg boundary in Hole 1001B, which is from the ODP photo archives). Mbsf = meters below sea floor, PFZ = Planktic Foraminifer Zone, Lith. =

lithology, PMag = Paleomagnetic polarity, E. Campanian = Early Campanian, Maas. = Maastrichtian, *G. elevata* = *Globotruncanita elevata*, *A.m.* and *A. mayaroensis* = *Abathomphalus mayaroensis*.

Figure 3. Crossplots of Rb, Zr, and Ca with Ba and Ba/Ti ratios from Sites 999 and 1001. R^2 values showing correlation (or lack thereof) for each parameter are included on the plots.

Figure 4. Barium/Titanium export productivity proxy data for IODP Site M0077, DSDP Site 95, and ODP Sites 1001 and 999. Individual datapoints are grey circles, thick black lines are a 5-point moving average. Red line indicates the K-Pg boundary (or the top of the boundary interval in the case of Sites M0077 and 95), blue line indicates the thickness of the micrite layer identified at each site by Bralower et al. (2020), and the green dashed line indicates the top of the interval of highest export productivity at each site. PFZ = Planktic Foraminifer Zone, *A. maya.* = *Abathomphalus mayaroensis*.

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