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1	Elevated Post K-Pg Export Productivity in the Gulf of Mexico and
2	Caribbean
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8	Key Points
9	Main point #1: Post K-Pg export productivity was elevated across the Caribbean-Gulf of Mexico region
10	for $\sim 300 \text{ kyr}$
11	Main point #2: At sites with a clearly defined micrite layer, the end of micrite deposition coincides with
12	the top of the highest productivity interval
13	Main point #3: Elevated post K-Pg export productivity appears to be a feature of oligotrophic low
14	latitude open ocean sites
15	
16	Abstract
17	The global heterogeneity in export productivity after the Cretaceous-Paleogene (K-Pg) mass
18	extinction is well documented, with some sites showing no change on geologic timescales, some
19	demonstrating sustained decline, and a few showing a somewhat surprising increase. However,
20	observational data come from sites so widespread that a key outstanding question is the geographic scale
21	of changes in export productivity, and whether similar environments (e.g., open ocean gyres) responded
22	similarly or whether heterogeneity is unrelated to environment. To address this, we developed three new
23	Ba/Ti export productivity records from sites in the Gulf of Mexico and Caribbean which, combined with

24 published data from a fourth site in the Chicxulub Crater itself, allow us to reconstruct regional changes in post K-Pg export productivity for the first time. We find that, on a regional scale, export productivity 25 26 change was 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 27 28 production appears to coincide with the post K-Pg global micrite layer, which is thought to at least 29 partially have been produced by blooms of carbonate-producing cyanobacteria and other 30 picophytoplankton. Global comparison of sites shows that elevated export productivity appears to have been most common in oligotrophic gyres, which suggests that changing plankton ecology evidenced by 31 32 the micrite layer altered the biological pump, leading to a temporary increase in export production in these settings. 33

34 Plain Language Summary

35 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 36 37 primary production recovered after this calamity is an important foundation for understanding how 38 ecosystems recovered. Most previous work has focused on a process called export production, whereby 39 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 40 41 export production after the extinction event, some regions actually showed an increase. However, it was 42 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 43 44 consistent increase in export production at each site for the same period of time after the extinction event. 45 Comparison with other sites with increased export production shows that many are from open ocean gyres, suggesting that these regions were predisposed to increased export production in the earliest 46 Paleocene because they were characterized by low productivity prior to the extinction. 47

48 1. Introduction

49 The end Cretaceous mass extinction was associated with a severe disruption of marine 50 productivity (Hsü and Mackenzie, 1985; Zachos et al., 1989; D'Hondt et al., 1998; Coxall et al., 2006; 51 Birch et al., 2016). A reduction in sunlight received at Earth's surface caused by dust, soot, and sulfate aerosols ejected by the Chicxulub impact resulted in a reduction in photosynthesis which is thought to 52 53 have led to the collapse of marine food webs (Alvarez et al., 1980; D'Hondt et al 1998). Models show that 54 the reduction in insolation lasted only a few years after the impact (Toon et al., 1997; Brugger et al., 55 2017; Artemieva et al., 2017; Bardeen et al., 2017; Artemieva and Morgan, 2020; Alegret et al., 2022), 56 removing the proximal external stress on marine primary producers and clearing the way for the recovery 57 of primary production. How, exactly, marine productivity recovered has been a focus of K-Pg boundary research for decades; the K-Pg mass extinction represents a geologically unique disruption of marine 58 59 ecosystems, perhaps the only major event in Earth history which happened faster than modern climate 60 change and environmental disruption. Modern oceans are likely on the verge of a major reorganization of 61 dominant plankton types due to warming, acidification, and changes in circulation and ventilation patterns 62 (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 63 64 ecological changes may impact food webs and marine carbon burial.

65 Of course, we can't observe ancient primary production in the euphotic zone directly, so most 66 work on the collapse and recovery of productivity after the K-Pg boundary has focused on sedimentary 67 records of export production (the transfer of particulate organic matter from the euphotic zone to the deep 68 sea; e.g., Passow and Carlson, 2012)). The movement of particulate organic matter (POM) from the 69 euphotic zone to the seafloor is complicated and can be divided into a series of steps, all of which are 70 influenced by different processes. Most net primary production (NPP) occurs in the euphotic zone 71 (dependent on sunlight penetration but typically defined as 0-100 or 200 m water depth; Passow and Carlson, 2012), and most POM is remineralized in these near surface waters. The precise amount varies 72 by region and season, but typically ~ 90% of NPP is consumed and recycled before it can sink out of the 73

74 euphotic zone. The movement of POM out of the euphotic zone is what biological oceanographers define 75 as "export flux" or "export productivity" (Passow and Carlson, 2012). Paleoceanographers typically use 76 the latter term to refer to the whole process by which POM is buried in the sediments. However, here we 77 follow the biological oceanographers and use "export productivity" to refer to this initial sinking out of 78 surface waters, mainly because this is the process that can be tracked in ancient sediments by biogenic 79 barium concentration – see below). As POM continues sinking through the mesopelagic zone (typically 80 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 to their 81 82 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 in the 83 84 mesopelagic zone is controlled by the rate at which the POM is sinking (i.e., how long it is exposed to 85 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 86 87 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 88 89 "sequestration flux" (e.g., Passow and Carlson, 2012) or "transfer efficiency" (Henson et al., 2012). By 90 this point, most remineralization has occurred, but POM sinking out of the mesopelagic zone has traveled 91 through less than one third of the average depth of the ocean, and additional remineralization occurs all 92 the way to (and at) the seafloor, before surviving POM is buried and removed from the carbon cycle on 93 geologic time scales (referred to as "burial flux" by Griffith et al., 2021). The amount of net primary 94 production that reaches the deep sea varies by region and is largely controlled by plankton ecology 95 (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). 96 97 Initial reconstructions of productivity change across the K-Pg boundary focused on carbonate

98 proxies, specifically carbonate mass accumulation rates and carbon stable isotopes (e.g., Hsü and

99 Mackenzie, 1985; Zachos et al., 1989). A drop in carbonate mass accumulation rate in the deep sea has 100 been observed at many boundary sites across the globe, and is interpreted to represent a reduction in the 101 production of carbonate by pelagic calcifiers like calcareous nannoplankton and planktic foraminifera 102 (e.g., D'Hondt et al., 1998), both of which suffered severe (>90% species diversity) extinction at the K-Pg 103 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 δ^{13} C gradient between the surface ocean and the 104 105 deep sea (Zachos and Arthur, 1986; Zachos et al., 1989; D'Hondt et al., 1998; Coxall et al., 2006; Alegret 106 et al., 2012; Esmeray-Senlet, 2015; Birch et al., 2016). In the modern ocean (and likely since 107 phytoplankton first evolved) the sinking of ¹²C-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 108 109 gradient collapsed at the Cretaceous-Paleogene (K-Pg) boundary (e.g., Hsü et al., 1982; Kump, 1991), 110 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 111 (which account for a portion of the change in the δ^{13} C gradient – Birch et al., 2016, 2021), modelling 112 suggests that a \sim 50% decrease in the amount of organic carbon exported from the euphotic zone, from 113 114 10% of net primary production to 5%, would account for the observed collapse of the δ^{13} C gradient 115 (D'Hondt et al., 1998; Henehan et al., 2019).

116 The continued flux of some organic matter to the deep ocean is confirmed by fossil data which 117 indicate a lack of extinction in some groups of pelagic fishes (Doyle, 1979; Siebert and Norris, 2015) and deep sea benthic foraminifera (e.g., Thomas, 1990; Culver, 2003; Alegret and Thomas, 2005, 2007, 2009; 118 119 Alegret et al., 2012, 2021). Meanwhile, geochemical data indicate a rapid recovery of primary producers 120 (Sepúlveda et al., 2009, 2019). One of the most striking features of the benthic foraminiferal record at the 121 K-Pg boundary is its global variability. 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 122 foraminifer assemblages indicate a reduction in the flux of organic matter to the seafloor, but others show 123

no significant 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).

126 In practice, it is difficult to use carbon isotope gradients to reconstruct post K-Pg export production in geographic detail. Isotopic analysis of planktic and benthic foraminifera requires well-127 128 preserved carbonate material, otherwise diagenetic overprinting will obscure the signal. Localities with 129 well-preserved 66-myr-old foraminifera are not particularly common, and thus carbon isotope gradients 130 have only been produced from a handful of well-studied sites like Walvis Ridge (Hsü et al., 1982; Hsü 131 and Mackenzie, 1985; D'Hondt, 1998a; Coxall et al., 2006; Alegret et al., 2012; Birch et al., 2016, 2021), 132 Shatsky Rise (Zachos and Arthur, 1986; Zachos et al., 1989; Coxall et al., 2006), J-Anomaly Ridge 133 (Zachos and Arthur, 1986), and São Paulo Plateau (Zachos and Arthur, 1986). While these sites have all 134 yielded high quality data that have fundamentally changed our understanding of K-Pg recovery, they only 135 cover a small part of the ocean.

136 For this reason, additional proxies not dependent on pristine microfossil preservation are 137 necessary. Benthic foraminifera, which track burial flux of POM, are one such proxy, and another is 138 based on barium. Biogenic barium concentration in marine sediments (where it is commonly preserved as 139 barite – BaSO₄) 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 140 subject to the same diagenetic effects as carbon isotopes. Like so many other proxies, though, studies 141 142 have shown that the relationship between the measurement (biogenic barium) and the thing for which it is a proxy (export production) is not quite straight forward. Carter et al. (2020) provide a good review of the 143 144 processes which can affect the formation, burial, and preservation of marine barite. Here we summarize 145 the most important processes that impact the reconstruction of changes in export production across the 146 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

149 elemental Ba data need to be normalized against a terrigenous element like titanium or aluminum to 150 control for any possible detrital barium component (e.g., Dymond et al., 1992; Payton et al., 1996; Bains 151 et al., 2000; Paytan and Griffith, 2007; Griffith and Paytan, 2012). Most marine barite formation occurs 152 between 200-600 m water depth, where most organic matter remineralization occurs (Martinez Ruiz et al., 153 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 154 155 bacteria which consume oxygen during remineralization of POM, which means that increased bacterial 156 production could lead to increased barite formation (e.g., Dehairs et al., 2008; Jacquet et al., 2011; 157 Planchon et al., 2013) without a change in export production. This microbial activity can be influenced by 158 organic matter quality, temperature (as warmer temperatures result in increased bacterial metabolic rates), 159 and the composition of the microbial ecosystem itself (Carter et al., 2020). Ba production is thus (mostly) 160 correlated directly to the export flux of POM, but the ocean is undersaturated in barite, which means that 70% of particulate barite (and more in anoxic regions) dissolves in the water column and the upper few 161 162 cm of the sediments before it is buried (Carter et al., 2020). This means that the replacement of one watermass with another of a different Ba²⁺ saturation state could lead to a change in barite accumulation 163 164 which could be misinterpreted as a change in export flux (e.g., Paytan et al., 2007; Carter et al., 2020). 165 These caveats make it difficult to directly extrapolate from Ba flux to absolute values of export

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

Understanding geographic heterogeneity in export production is necessary to understand theoverall recovery of marine primary producers after the K-Pg boundary. In particular, the calcareous

174 nannoplankton, which have the best fossil record among primary producers in the early Paleocene, exhibit geographic heterogeneity in their post K-Pg recovery (Jiang et al., 2010; Schueth et al. 2015; Jones et al., 175 176 2019). Post-extinction calcareous nannoplankton assemblages are characterized by a dominance of 177 "disaster taxa," chiefly Braarudosphaera and Cervisiella, which eventually give way to a succession of 178 acme events as new Paleocene genera appear and briefly dominate the assemblage (Bown, 2005; Jones et 179 al., 2019; Gibbs et al., 2020). Gibbs et al. (2020) found that some of the survivors and earliest new genera 180 have adaptations which indicate a mixotrophic lifestyle (i.e., they supplemented photosynthesis by 181 ingesting small prev like bacteria); later incoming taxa lack these adaptations, indicating changing trophic 182 conditions (specifically the under exploitation of small prey species following the extinction of many 183 heterotrophic plankton) may have played a role in nannoplankton recovery (Gibbs et al., 2020). The 184 timing of these acme events is geographically variable, and at sites with elevated export productivity after 185 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 186 187 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) 188 189 hypothesized that the recovery of primary producer assemblages (and by extension the ecosystems which 190 they supported) after the K-Pg is similarly linked to nutrient state controlled by the recovery of the 191 biological pump, but the linkages are not well understood and a better picture of export productivity trends is a necessary first step. 192

Unfortunately, geographic trends in early Paleocene export productivity are still poorly known.
Modelling 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

199 increases in post-extinction export production (e.g., Shatsky Rise Site 1209; Hull and Norris, 2011) are 200 close to, but fall outside of, modelled areas of increased post-extinction export production. Hull and 201 Norris (2011) represents a significant improvement in observations of export productivity trends, but are 202 limited to the ocean basin scale: e.g., Shatsky Rise in the North Pacific compared to São Paulo Plateau in 203 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 204 205 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 Ba/Ti datasets 206 from the Gulf of Mexico and Caribbean at Deep Sea Drilling Project (DSDP) Site 95 and Ocean Drilling 207 208 Program (ODP) Sites 999 and 1001, which we combined with published data from International Ocean 209 Discovery Program (IODP) Site M0077 in the Chicxulub Crater (Lowery et al., 2021) to produce the first 210 regional-scale study (~1700 km) of export productivity after the K-Pg. This region was modelled to have 211 been characterized by low export production in the latest Cretaceous (Henehan et al., 2019) and thus may be predicted to have exhibited increased export production after the boundary. We found that earliest 212 213 Danian export productivity is elevated at all Gulf of Mexico and Caribbean sites and that an initial 214 reduction in export production occurs ~ 300 kyr after the boundary at all sites, indicating that export 215 productivity trends were homogeneous at a regional scale.

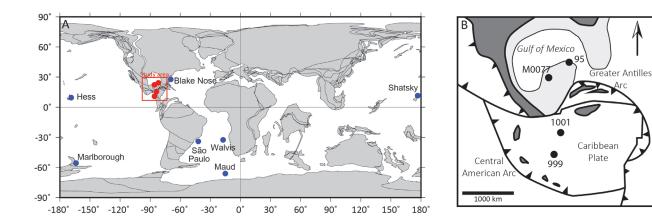


Figure 1. A) Global plate tectonic reconstruction from 66 Ma showing location of our study area (in red) and other notable sites discussed in this paper (in orange). Grey areas are continental blocks, terranes, and plateaus; map from ODSN generated at <u>https://www.odsn.de/odsn/services/paleomap/paleomap.html</u>. 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.

216 1.1 Study Sites

217 We looked at three scientific ocean drilling sites in the greater Caribbean region with a well-218 preserved K-Pg boundary interval and compared them to published XRF data from IODP Site M0077 in 219 the Chicxulub Crater (Figure 1). An additional site, DSDP Site 536, below the Campeche Escarpment in 220 the southeastern Gulf of Mexico (Buffler et al., 1984), was considered but rejected because a preliminary 221 examination of planktic foraminifera in the nominally lowermost Paleocene cores found a mix of 222 biozones ranging from the Cretaceous to the late Paleocene, indicating significant reworking and/or 223 drilling disturbance, suggesting that XRF data would be untrustworthy. All four sites appear to have been 224 at roughly bathyal water depths in the earliest Danian (Worzel et al., 1983; Buffler et al., 1984; 225 Sigurdsson et al., 1997; Lowery et al., 2018). These tropical/subtropical sites are characterized by pelagic 226 carbonate deposition throughout the study interval. DSDP Site 95, drilled in 1970 on the northeasterly margin of the Yucatan Platform on the 227 228 Campeche Escarpment (Worzel et al., 1973), contains the correct order of planktic foraminifer biozones 229 and decent preservation in a mostly-complete section overlying the K-Pg impact layer. The Chicxulub 230 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., 231 232 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 \sim 3 m of reworked Cretaceous material and impact debris (Figure 2A). The 233 234 top of the K-Pg boundary layer occurs at the top of Core 13. This is not the K-Pg boundary per se, 235 because the base of the Paleocene is defined at its Global Stratotype Section and Point at El Kef, Tunisia, 236 as the lowest occurrence of impact material which means that the Cretaceous ended at "the moment of the 237 meteorite impact" (Molina et al., 2006). The impact layer in the Gulf of Mexico is thus technically earliest 238 Danian in age.

Site 1001 was drilled in 1995-6 during ODP Leg 165, and is located on 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 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). This tektite layer is turn

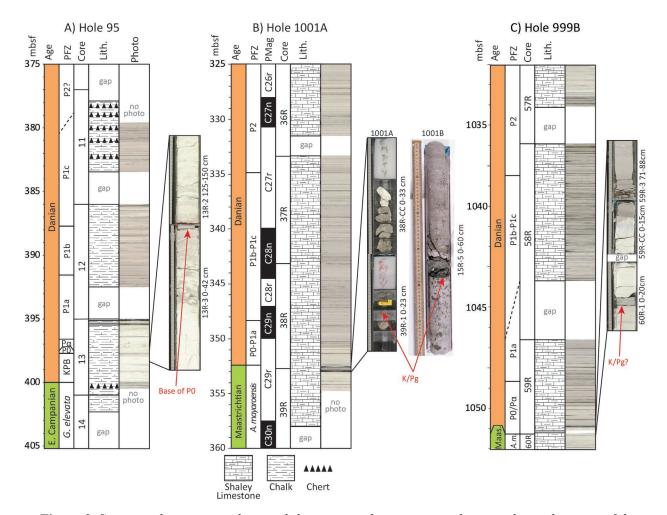


Figure 2. Stratigraphic sections showing lithostratigraphy, core scan photographs, and images of the K-Pg boundary of the studied intervals from DSDP Hole 95, ODP Hole 1001A, and ODP Hole 999B. Lithostratigraphy follows shipboard descriptions Worzel, Bryant et al. (1973) for Site 95 and Sigurdsson et 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.

245 overlain by a 3.5 cm medium gray to greenish gray claystone which contains shocked quartz (Sigurdsson 246 et al., 1997). The boundary sequence, identified on the basis of biostratigraphy and impact debris, is 247 overlain by a 4 cm thick light grey limestone assigned to planktic foraminifer Biozones P0/Pa 248 undifferentiated based on thin section analysis (the zones are undifferentiated because the 249 biostratigraphers were not confident in their ability to identify the taxon differentiating the zones, 250 Parvularugoglobigerina eugubina, in thin section; Sigurdsson et al., 1997). Shipboard biostratigraphy in 251 the Paleocene is of poor quality due to the extremely poor preservation of fossil material in the indurated 252 limestone. A magnetic polarity timescale was published for Site 1001 by Louvel and Galbrun (2000) 253 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 254 255 1001 has the best age model of the sites examined here. Although Hole 1001B recovered a more complete 256 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. 257 258 Site 999 was also drilled in 1995-6 during Leg 165 and is located on Kogi Rise in the Colombian 259 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 260 261 nannoplankton was observed in Sample 999B-60R-1 10 cm, and that of Maastrichtian planktic 262 foraminifera in a thin section in Sample 999B-60R-1 1-21 cm (Sigurdsson et al., 1997). The few 263 for a for a miniferal observed in thin section between Samples 999B-59R-CC 15cm (the base of the core catcher) 264 and 999B-60R-1 1 cm were composed primarily of survivor species Guembelitria cretacea (Sigurdsson et 265 al., 1997). The shipboard biostratigraphers were not confident that tiny trochospiral specimens observed 266 in the same sample were or were not *P. eugubina* and thus conservatively assigned this interval to Zones 267 P0/Pa 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 268

269 (Sigurdsson et al., 1997) and form the basis for the age model used here, although the latter two are of

270 lower confidence. We washed and examined samples from Site 999 to see if we could refine the 271 shipboard age model but poor microfossil preservation in the indurated limestone material prevented us 272 from adding anything new. A white indurated limestone overlies the highest Cretaceous nannoplankton 273 observed in Core 60, and the base of Section 59R-CC contains a 1 mm thick claystone. Comparison of the 274 recovered core and borehole images collected by the formation microscanner tool reveals that this 275 claystone is ~ 9 cm thick in the borehole, and thus ~ 8 cm of this unit were not recovered (Sigurdsson et 276 al., 1997). It seems reasonable to assume that this missing interval is equivalent to the 8 cm of ejecta-277 bearing claystones described at Site 1001. The claystone is overlain by 10 cm thick mottled blue 278 limestone described by shipboard scientists as having the appearance of "Roquefort Blue Cheese" and 279 assigned to planktic foraminifer Zones P0/Pa (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 280 281 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 282 283 occurs at the base of Core 999B-58R in planktic foraminifer Zone Pla. 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 284 285 rubble and a large void space (Figure 2B), so Bralower et al. (2020) considered the observed 17 cm interval to be a minimum. 286

287 **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 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.

295 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 296 297 (Al, Si, K, Ca, Ti, Mn, Fe, Cr, P, S, and Mg) and the second was at 50kVp with a Cu filter to analyze 298 heavier trace elements (Sr, Rb, Zr, and Ba). Scan resolution was set depending on relative distance above 299 the K-Pg boundary, based on low resolution shipboard biostratigraphy. Core sections within Zone $P\alpha$ or 300 the lower part of Zone P1a (very roughly, within ~ 500 kyr after the boundary) were scanned at 1 or 2 cm 301 steps, and sections below the boundary and >500 kyr after the boundary were scanned at 5 cm steps. 302 Some steps were skipped or moved based on visual examination of the core before scanning (e.g., to 303 avoid cracks or uneven surfaces). Laboratory standards were run at the beginning and end of each day to monitor instrumental performance. 304

Raw spectral data were processed into peak areas in the lab and exported as count data 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 311 resolution of up to 5 cm. Lightly lithified samples were gently broken into cm-sized pieces using a mortar 312 313 and pestle. All samples were soaked in a solution of hydrogen peroxide and borax for at least 48 hours 314 and then washed over a 45 µm sieve to ensure capture of typically very small early Paleocene taxa; the 315 sieve was soaked in methylene blue dye between samples to mark contaminants. Finally, samples were 316 dried overnight in an oven. Samples were examined for presence/absence of key marker species on a 317 Zeiss Discovery.V8 light microscope. Species concepts follow those of Olsson et al., (1999); biozones are 318 the Wade et al. (2011) update of the Paleocene biozonation scheme published by Berggren and Pearson 319 (2005) and calibrated to the timescale of Gradstein et al. (2012).

320 **3. Results**

321 **3.1 Biostratigraphy**

322 Sediment at Site 95 is comprised of firm but unlithified calcareous ooze that yielded fairly well 323 preserved material. We examined 25 samples from Cores 11 to 13 to identify and refine the boundaries 324 between planktic foraminifer biozones. An obvious lithologic change occurs in Section 95-13R-3 at 24 325 cm (397.92 mbsf). Samples below this level are composed of mixed Cretaceous species remobilized by 326 impact-induced seismic disturbance and tsunami, termed the K-Pg Boundary Cocktail (Bralower et al., 327 1998). From Sample 95-13R-2, 139 cm to Sample 95-13R-3, 24 cm (397.76 to 397.92 mbsf), the core is 328 mottled and contains some signs of drilling disturbance (biscuiting, soft sediment deformation). Samples 329 taken within what we interpret to be the biscuits, however, contain mostly Cretaceous species until 95-330 13R-3, 0-2 cm (397.70 mbsf), where the survivor species Guembelitria cretacea starts to become more 331 common; this level is assigned to the base of Zone P0. The lowest occurrence of *P. eugubina*, which 332 defines the base of Zone Pa, is found just above this level, in Sample 95-13R-2 130-132 cm (397.5 mbsf). 333 The highest occurrence of P. eugubina, which marks the base of Zone P1a, occurs in sample 95-13R-1 334 130 cm (396.60 mbsf). Most of Zone P1a falls within a coring gap, but Zone P α and the portion of Zone 335 Pla 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. 336 triloculinoides) and Zone P1c (lowest occurrence of Globanomalina compressa) are both present. The 337 338 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 339 340 Zone P1b; this method suggests that most of Zone P1c is present.

341 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 value of terrigenous material delivered to the site. The extensive

344 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 345 and alter that ratio. Thus, we have plotted Ba from Site 999 and 1001 against Rb and Zr, which are 346 347 enriched in volcanogenic minerals of the regional type of volcanism. Both Zr and Rb show weak positive 348 correlation with Ba at Site 999 (Figure 3A-B) and a slightly less-weak positive correlation with Ba at Site 349 1001 (Figure 3C-D). This is to be expected, as any volcanic ash would have introduced more detrital Ba 350 in the record. However, when we normalize Ba against Ti and compare this to Rb and Zr at both sites, the 351 positive correlation goes away (Figure 3E-H). To demonstrate how overall changes in lithology affect Ba 352 counts, we plotted Ba against Ca (any decrease in Ca in a pelagic setting above the lysocline is likely due 353 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 354 355 detrital Ba; this is why we normalize Ba to a terrigenous element like Ti. Overall, the relationship between Ca and Ba is not very strong, likely because overall terrigenous content in these pelagic clays is 356 357 very low. We conclude that the Ba/Ti values 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. 358

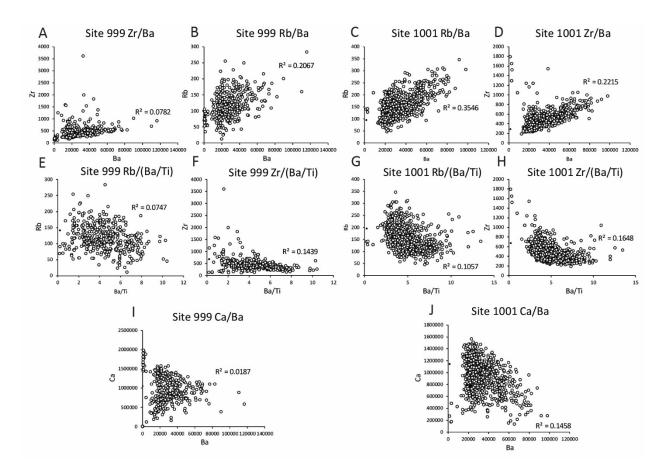


Figure 3. Crossplots of Rb, Zr, and Ca with Ba and Ba/Ti from Sites 999 and 1001. R^2 values showing correlation (or lack thereof) for each parameter are included on the plots.

361 3.2.1 Site M0077

360

Data from the Chicxulub Crater have been published (Lowery et al., 2018, 2021) but contain 362 several interesting trends that should be summarized here. The highest Ba/Ti values in the study interval 363 are found in the lowermost Paleocene, representing the first ~320 kyr after the impact (Figure 3A). At that 364 365 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 366 some small-scale variability. Interestingly, this transition around 1.2 myr post-impact coincides with 367 368 turnover in the calcareous nannoplankton ecosystem, as disaster taxa began to give way to acmes of new 369 Paleocene taxa (Jones et al., 2019; Lowery et al., 2021).

370 3.2.2 Site 95

Ba/Ti values at Site 95 are also highest in the lowermost Paleocene, with a peak around the 371 372 $P\alpha/P1a$ 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 373 374 comfortable assuming that this drop was contemporaneous with the one observed at Chicxulub Crater Site 375 M0077. Approximately 300 kyr of the record in the middle of Zone P1a is erased by a coring gap, but 376 above this level Ba/Ti values trend lower until about 1.1 myr after the K-Pg boundary. Values then 377 remain low until about 1.6 myr post-impact and finally increase somewhat, varying through the rest of the 378 record.

379 **3.2.3** Site 1001

Site 1001 is the first of our sites in which there are data for the uppermost Cretaceous, and (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 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.

387 3.2.4 Site 999

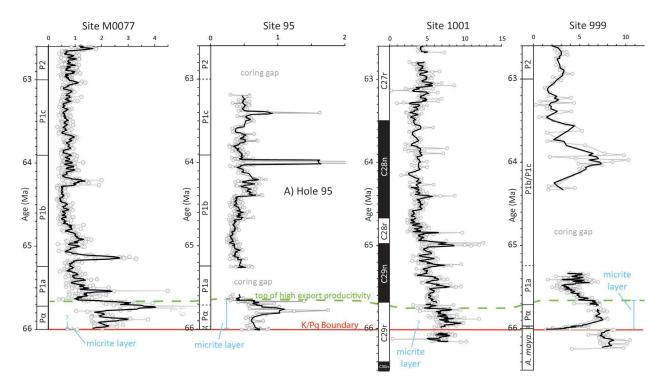


Figure 4. Barium-Titanium export productivity proxy data for IODP Site M0077, DSDP Site 95, and ODP Sites 1001 and 999. Individual datapoints are grey circles, thick black lines is a 5-point moving average. Red line indicates the K-Pg boundary (or the top of the boundary interval in the case of Sites 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.

388 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 389 Pa. Higher values after this brief recovery interval do no exceed the Ba/Ti values observed in the 390 391 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, values decreased sharply approximately 392 393 320 kyr post-impact followed by gradually declining values. The very poor quality of the biostratigraphy in this core (the $P\alpha/P1a$ zonal boundary marker is the only reliable datum) makes it difficult to determine 394 395 the timing of this decline and whether the increase observed below the coring gap occurred just 600 kyr 396 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 397 398 *P. eugubina* (Pα/P1a zonal boundary).

399 4. Discussion

400

0 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 401 402 result of this investigation, is the consistent occurrence of relatively elevated Ba/Ti values in the earliest 403 Paleocene. Interestingly, this is in line with trends from other sites in oligotrophic regions like the North 404 Pacific Gyre. Three other open ocean sites have evidence of increased export productivity in the earliest 405 Danian: the North Pacific Shatsky Rise and Hess Rise (Alegret and Thomas, 2005, 2009; Hull and Norris, 406 2011), and the mid-latitude South Pacific sections around Marlborough, South Island, New Zealand 407 (Hollis et al., 1995, 2003). The high export productivity at Marlborough appears to be the result of 408 increased upwelling along the continental margin (Hollis et al., 2003). Shatsky Rise and Hess Rise, 409 though, are open ocean sites on roughly the same paleolatitude as our study area and were generally 410 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 411 412 contrast with the overall global trend of reduced export production. But first we need to rule out other 413 possible explanations.

As discussed above, there is no evidence that changes in terrigenous Ba/Ti values influence the record at our Caribbean sites, and could not 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 or, more likely, ecological changes in the populations of phytoplankton and/or grazers in these gyres.

421 There are several possible mechanisms which could drive an increase in marine barite production422 while export production is kept steady. Different groups of plankton incorporate different amounts of Ba

423 into their biomass. For example, coccolithophores have less Ba in their cells than diatoms, which in turn 424 have less Ba in their cells than chrysophytes (gold algae), which have less Ba than chlorophytes (green 425 algae) (e.g., Paytan and Griffith, 2007). Calcareous nannoplankton suffered a severe extinction at the K-426 Pg, and if they were briefly replaced in oligotrophic gyres by any of these other groups, the biogenic Ba 427 flux to the seafloor would increase even if export production held steady. Alternatively (or additionally), 428 an increase in temperature or a shift in bacterial ecology at mesopelagic depths could have increased 429 bacterial remineralization and thus barite production. A reduction in the abundance of grazers which 430 break apart sinking POM or an increase in ballasting or the formation of aggregates (which have the 431 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 432 increased biogenic barium, since marine barite formation is a byproduct of the remineralization of organic 433 434 matter (Dehairs et al., 2008; Jacquet et al., 2011; Planchon et al., 2013) and quickly sinking POM has less 435 time to remineralize. On the other hand, a more robust grazer community at mesopelagic depths may have 436 broken apart more POM, slowed sinking and increased the time it was exposed to remineralization. Many 437 of these change (mesopelagic temperature increase, shifts in the grazer community or toward 438 phytoplankton with higher Ba abundance in their cells) are impossible to test with existing 439 paleoceanographic tools. What we can do, though, is look to other parts of the biological pump and see if 440 they indicate whether the observed increase in Ba/Ti was 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 values are associated with an interval of higher benthic

448 foraminiferal abundance, indicating increased export production was associated with increased food 449 supply to the seafloor (Lowery et al., 2021). We don't have benthic foraminifera data from Site 95 450 because it is difficult to tell reworked benthics from *in situ* ones, and we don't have benthic foraminifera 451 from Sites 999 and 1001 because of overall poor preservation of microfossils. On Shatsky Rise in the 452 North Pacific gyre benthic foraminifera from Site 1210 (from Alegret and Thomas, 2009) and barium 453 proxy data from the adjacent Site 577 (from Hull and Norris, 2011) are elevated for roughly the first 100 454 kyr after the extinction. On Hess Rise, also in the North Pacific gyre, no barium data exist but benthic 455 for a site 465 indicate a peak in post K-Pg burial flux within 100 kyr of the boundary (within 456 planktic foraminifer Zone Pa) (Alegret and Thomas, 2005). At the three sites with both Ba and benthic for aminifer data, they both indicate increased transport of POM out of the euphotic zone and to the 457 458 seafloor; we therefore interpret the Ba/Ti data at all our sites as primarily recording an increase in export 459 productivity.

460 In the Gulf of Mexico and Caribbean, the interval of highest export production ends right around 461 the $P\alpha/P1a$ zonal boundary at each site, roughly 300 kyr after the K-Pg boundary, followed by a general 462 decline over the next million years or so. The precise features 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 463 464 cores (Sites 999 and 1001). Likewise, Site 999 records very low values immediately above the K-Pg 465 boundary followed by a rapid recovery that is not evident at any of the other sites. Finally, the timing of 466 the sharp decline of these high productivity intervals varies by a few tens of kyrs between sites. Because 467 the age models are based on biostratigraphy or paleomagnetic reversals, with no higher resolution 468 techniques like orbital chronology, it is impossible to say whether these differences are real or merely 469 artifacts of the limits of the age models. These are superficial differences, though, and a clear overall 470 trend exists that export productivity was elevated across Gulf of Mexico and Caribbean (a distance of \sim 1700 km) for \sim 300 kyr after the K-Pg mass extinction, and began to decline thereafter. 471

472 The observed homogeneity in regional export productivity in the earliest Paleocene provides 473 important context for previous observations of global-scale heterogeneity determined with the Ba proxy. 474 Previous work had shown major differences in the amount of organic matter remineralized in the 475 mesopelagic zone between ocean basins, with an increase in export production in the middle of the North 476 Pacific, a decline in the western North Atlantic, western South Atlantic, and Southern Ocean, and no 477 change in the eastern South Atlantic (Hull and Norris, 2011). Those sites are widely separated and 478 represent different oceanographic environments (oligotrophic gyres, western boundary currents, eastern 479 boundary currents). With only one site in each region, it is hard to know whether these observations are 480 indicative of regional trends or more limited, local change. With the discovery that open ocean sites 481 within the Gulf of Mexico/Caribbean all exhibit the same trends (and, interestingly, the local change in 482 benthic foraminiferal diversity in nearshore environments Gulf of Mexico is also lower than many other 483 sites; Alegret et al., 2022), we can be more confident that previously observed regional differences are 484 real, and therefore conclude that oligotrophic open ocean sites were prone to increased export production 485 immediately after the K-Pg boundary, as suggested by Henehan et al. (2019). But what was the driver for this increased export production? 486

487 **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 μ m in size) like cyanobacteria and algae, but larger nano and micro phytoplankton (2-20 μ m and >20 μ m, respectively), though less numerous, account for the majority of productivity measured in incubation experiments (e.g., Marañón et al., 2003). Because picophytoplankton have no physical 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 magnitude, 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 502 503 all, if export increased then there would be a mechanism to remove nutrients from the euphotic zone and 504 NPP would necessarily decrease. Yet our work and that of others has found that high export production 505 was maintained in typically oligotrophic regions for 100-300 kyr (Alegret and Thomas, 2005, 2009; 506 Alegret et al., 2012, 2022; Hull and Norris, 2011). To explain this dichotomy, we suggest that POM 507 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 508 509 the euphotic zone is more refractory and difficult to metabolize (Legrendre and Michaud, 1998; de la 510 Rocha and Passow, 2007). This refractory organic matter is less likely to be completely remineralized by 511 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 512 513 of larger phytoplankton, then the export of refractory POM may have increased, as would the amount of 514 barite formation from that POM. Thus, even if only a small fraction of the refractory POM was 515 remineralized, the overall increase in POM sinking below the euphotic zone would have elevated total 516 remineralization and barite production. This also would explain why food supply increased to the 517 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

522 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 523 524 other groups, do not typically fossilize. Blooms of plankton like these may serve to increase export to the seafloor and also increase marine barite production without necessarily relying on a stronger microbial 525 526 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 527 528 can see some evidence for ecosystem changes associated with increased export productivity after the K-529 Pg.

530 4.3 Evidence of Ecosystem Changes

531 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-532 533 defined intervals of microcrystalline calcite ("micrite"). The widespread deposition of micrite in marine 534 settings after the K-Pg boundary was documented by Bralower et al. (2020), and proposed to have been 535 primarily formed by microbial blooms. The structure of individual micrite crystals is similar to that 536 produced by various cyanobacteria (Bralower et al., 2020) and the micrite layer itself at several sites is 537 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 538 likely formed by the backreaction of CaO or CaOH vaporized by the Chicxulub impact, but this process 539 540 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. 541

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

None of the published Pacific sites which show an increase in post-K-Pg export production have 552 553 both Ba/Ti data and micrite data (although we can compare nearby sites 1210 and 577 – see below). 554 Micrite is enriched at Shatsky Rise Site 1209 over a 6 cm interval above the boundary, and at 1210 over a 555 7 cm interval above the boundary (Bralower et al., 2020), associated with the ~ 100 kyr peak in benthic foraminifer proxies for burial flux (Alegret and Thomas, 2009) and the ~ 100 kyr interval of elevated 556 557 Ba/Ti at nearby Site 577 (Hull and Norris, 2011). At Hess Rise Site 465, micrite is enriched over a 24 cm interval above the boundary (Bralower et al., 2020), and benthic foraminifera likewise show a peak in 558 559 burial flux in this interval (Alegret and Thomas, 2005). It is important to point out that foraminifer 560 samples at both Sites 465 and 1210 were taken at a 10 cm resolution (Alegret and Thomas, 2005, 2009) 561 so a precise tie between the decline in export productivity and the end of micrite deposition is impossible 562 to make.

563 Although various types of "ballast," including calcite plankton shells, have been thought to influence export production in the modern ocean (Armstrong et al., 2001; Francois et al., 2002), it does 564 565 not seem likely that micrite itself, or more specifically the cyanobacteria that produced it, is the cause of 566 increased export production in the earliest Paleocene. Micrite is abundant at many sites which did not 567 experience elevated export production after the K-Pg. For example, Blake Nose Site 1049, which 568 experienced either a decline or no change in export production after the boundary (Alegret and Thomas, 569 2004), has a 30 cm thick micrite layer. Walvis Ridge Site 1262, which similarly experienced no change in 570 post-extinction export production based on benthic foraminifera (Alegret and Thomas, 2007), has a 1.82 m thick micrite layer. All told, Bralower et al. (2020) identified micrite layers at 31 sites globally; of 571

these, only 5 record elevated export production in the early Danian based on available proxies. All ofthese 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 across Pacific and Caribbean/Gulf of Mexico sites 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.

578 The dominance of picophytoplankton may have been the proximal cause of elevated post K-Pg 579 export production in tropical open ocean waters, but it is important to note that the timing was different 580 between the Caribbean and the central Pacific. The period of highest export production dropped off ~ 300 581 kyr after the K-Pg in the Gulf of Mexico and Caribbean but much earlier at Shatsky and Hess Rises, i.e., 582 after ~ 100 kyr (Alegret and Thomas, 2005, 2009; Hull and Norris, 2011). This is in line with previous 583 results which indicate a global diachroneity in the turnover of calcareous nannoplankton assemblages in 584 the earliest Paleocene (Jones et al., 2019), driven by transition from surface waters characterized by 585 efficient recycling of nutrients due to the prevalence of picophytoplankton feeding the microbial loop, to 586 surface waters characterized by less efficient recycling of nutrients caused by greater export of larger 587 plankton out of the euphotic zone (Jones et al., 2019; Lowery et al., 2021). At Shatsky Rise, disaster 588 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 589 590 continued until the final decline in export productivity about a million years after the K-Pg (Jones et al., 591 2019), and at Site 999, disaster taxa continued at least into Zone P1a >300 kyr after the K-Pg (Sigurdsson 592 et al., 1997). Whether the recovery in calcareous nannoplankton caused the observed change in export 593 production or if a reduction in export production spurred the local diversification of calcareous 594 nannoplankton remains an open question.

595 Conclusions

596 Our XRF-derived Ba/Ti export productivity proxy data from the Gulf of Mexico and Caribbean 597 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, then declining values for another ~ 700 kyr. This is a major improvement on 598 599 previous compilations of earliest Paleocene export productivity, which showed that post-extinction 600 changes in export production were globally heterogeneous on an ocean basin scale. Our results show that 601 broad regions followed similar trends. In particular, we find that most elevated export production in the 602 earliest Danian occurred 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). 603

604 At sites with elevated export production and at which preservation makes such observations 605 possible, the post K-Pg global micrite layer corresponds to the interval of elevated export production. We 606 interpret this as evidence that the dominance of picophytoplankton like cyanobacteria and chlorophyte algae, which appear to have been responsible for the micrite deposition (Bralower et al., 2020), altered the 607 608 dynamics of the biological pump to increase recycling of organic matter in the euphotic zone. Enhanced 609 recycling of organic matter left only refractory material, which is more difficult to recycle, to be exported 610 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 611 612 oligotrophic environments, this slight increase in efficiency of the biologic pump could have resulted in 613 overall higher export production; as larger phytoplankton recovered and more labile organic matter was 614 exported and grazed, enhanced export production would have subsided.

615 More datasets from a wider range of latitudes and ocean basins are needed to build a more 616 complete picture of post K-Pg export production to more fully understand how the marine biosphere 617 recovered from the most recent major mass extinction.

618 **Open Research**

619 XRF core scan data and age models are archived at the NCEI Paleoclimate Database (Lowery, 2021).

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628 preparing samples from Site 999 and 1001 for biostratigraphic analysis.

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.

635 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.

637 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

639 XRF data were collected (except for the photograph of the K-Pg boundary in Hole 1001B, which is from

- 640 the ODP photo archives). Mbsf = meters below sea floor, PFZ = Planktic Foraminifer Zone, Lith. =
- 641 lithology, PMag = Paleomagnetic polarity, E. Campanian = Early Campanian, Maas. = Maastrichtian, G.
- 642 *elevata* = *Globotruncanita elevata*, *A.m.* and *A. mayaroensis* = *Abathomphalus mayaroensis*.

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

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