Size-fraction specific isotopic variations as a framework for interpreting early Paleogene bulk sediment carbon isotope records

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November 21, 2022

Abstract

Carbon isotope (δ 13C) records from marine sediments have been extensively used in Cenozoic chemostratigraphy. The early Paleogene interval in particular has received exceptional attention because negative carbon isotope excursions (CIEs) documented in the sedimentary record, e.g. at the Paleocene Eocene Thermal Maximum (PETM), ca ~56 Ma, are believed to reflect significant global carbon cycle perturbations during the warmest interval of the Cenozoic era. However, while bulk-carbonate δ 13C values exhibit robust correlations across widely separated marine sedimentary sections, their absolute values and magnitude of CIEs vary spatially. Moreover, bulk-carbonates in open-marine environments are an ensemble of different components, each with a distinct isotopic composition. Consequently, a complete interpretation of the bulk δ 13C record requires an understanding of co-evolution of these components. In this study, we dissect sediments, from early Paleogene interval, at ODP Site 1209, Shatsky Rise, Pacific Ocean to investigate how an evolving bulk-carbonate ensemble influences the overall carbon isotope record. A set of 45 samples were examined for δ 13C and δ 18O compositions, as bulk and individual size fractions. We find a significant increase in coarse-fraction abundance across PETM, driven by a changing community structure of calcifiers, modulating the size of CIE at Site 1209 and thus making it distinct from those recorded at other open-marine sites. These results highlight the importance of biogeography in marine stable-isotope record, especially when isotopic excursions are driven by climate- and/or carbon-cycle changes. In addition, community composition changes will alter the interpretation of weight percent coarse fraction as conventional proxy for carbonate dissolution.

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10 Key points

12	1.	Co-evolution of different components within pelagic carbonate systems drive spatial
13		variations of bulk carbonate stable isotope records.

- 14 2. Increase in coarse fraction abundance across PETM at Shatsky Rise alters the15 conventional implications of using it as a dissolution proxy.
- 3. Size-fraction-specific isotopic variations can also significantly control the magnitude of
 carbon isotope excursions.

18 Abstract

Carbon isotope (δ^{13} C) records from marine sediments have been extensively used in 19 Cenozoic chemostratigraphy. The early Paleogene interval in particular has received exceptional 20 attention because negative carbon isotope excursions (CIEs) documented in the sedimentary record, 21 e.g. at the Paleocene Eocene Thermal Maximum (PETM), ca ~56 Ma, are believed to reflect 22 significant global carbon cycle perturbations during the warmest interval of the Cenozoic era. 23 However, while bulk-carbonate δ^{13} C values exhibit robust correlations across widely separated 24 marine sedimentary sections, their absolute values and magnitude of CIEs vary spatially. Moreover, 25 26 bulk-carbonates in open-marine environments are an ensemble of different components, each with a distinct isotopic composition. Consequently, a complete interpretation of the bulk $\delta^{13}C$ record 27 requires an understanding of co-evolution of these components. In this study, we dissect sediments, 28 from early Paleogene interval, at ODP Site 1209, Shatsky Rise, Pacific Ocean to investigate how an 29 evolving bulk-carbonate ensemble influences the overall carbon isotope record. A set of 45 samples 30 were examined for δ^{13} C and δ^{18} O compositions, as bulk and individual size fractions. We find a 31 significant increase in coarse-fraction abundance across PETM, driven by a changing community 32 structure of calcifiers, modulating the size of CIE at Site 1209 and thus making it distinct from those 33 34 recorded at other open-marine sites. These results highlight the importance of biogeography in marine stable-isotope record, especially when isotopic excursions are driven by climate- and/or 35 carbon-cycle changes. In addition, community composition changes will alter the interpretation of 36 37 weight percent coarse fraction as conventional proxy for carbonate dissolution.

38 Key words

- 39 Carbon Isotope Excursions, Chemostratigraphy, PETM, Hyperthermals, Coarse fraction, Bulk
- 40 Carbonates

41 **1. Introduction**

Carbon isotope records of the Cretaceous and Cenozoic are commonly obtained using 42 analysis of open marine carbonate sediments (e.g. Shackleton 1986; Shackleton et al., 1987; 43 Reghellin et al., 2015). A substantial amount of work using bulk carbonate δ^{13} C records focuses on 44 the early Paleogene period (e.g. Quillévéré et al., 2008; Slotnick et al., 2015; Luciani et al., 2016; 45 Westerhold et al. 2017), which had a hothouse climate and was the warmest interval of the 46 Cenozoic (e.g. Zachos et al., 2001; 2008). Temporal variations in bulk carbonate δ^{13} C values from 47 widely separated ocean sites are remarkably consistent during the early Paleogene, thus forming a 48 49 robust tool of stratigraphic correlation between marine sedimentary sections (e.g. Slotnick et al, 2012; Agnini et al, 2015; Westerhold et al, 2018; Barnet et al, 2019; D'Onofrio et al., 2020). 50 However, differences in their absolute values suggest that subtle differences in palaeoceanographic 51 context are also recorded alongside large-scale changes in carbon cycling and climate. 52

One manifestation of the palaeoceanographic context may be the community structure of 53 calcifiers, because bulk carbonates in open marine environments are generally an ensemble of 54 various biogenic components (Figure 1). At a simple level of classification, calcifiers can be readily 55 grouped as either pelagic or benthic. Calcareous nannoplanktons predominate the group of pelagic 56 57 calcifiers by abundance, followed by planktic foraminifers (e.g. Bralower et al., 2002; Reghellin et al., 2020). Benthic foraminifers, in contrast, generally constitute a small proportion of bulk 58 carbonates (Milliman, 1993; Sarmineto and Gruber, 2006; Cramer et al, 2009). Each of these 59 60 calcifying groups, further comprised of a multitude of genera, dwell at different depth in the water column and express different isotopic fractionation during carbonate precipitation; therefore, their 61 62 carbonate shells have distinct carbon and oxygen isotope signatures (Figure 1). Furthermore, these 63 calcifiers exhibit varying degrees of susceptibility to carbonate dissolution (e.g. Petrizzo et al., 2008;

Nguyen et al., 2009). All such factors contribute towards resultant heterogeneity in bulk carbonates
across time and space.

In the early Paleogene sediment sections of Shatsky Rise (in the tropical north-central 66 pacific; Supplementary Figure S1), Walvis Ridge (south Atlantic) and Cicogna (Tethys), an 67 excellent correlation of bulk carbonate δ^{13} C values has been documented (e.g. Agnini et al., 2015). 68 However, the average value of bulk carbonate $\delta^{13}C$, as well as the magnitude of carbon isotope 69 excursions (CIEs) at any given early Paleogene hyperthermal, e.g. the PETM ca. 56 Ma, varies from 70 one site to another. Major changes in global carbon cycling related to both long- and short-term 71 inputs of CO₂ (Dickens 1995; Dickens et al., 1997; Zachos et al., 2007; 2010) provide a first-order 72 explanation for the correlated changes in bulk carbonate δ^{13} C records, but the variability between 73 different sites and ocean basins requires a subtler examination of ocean circulation, biogeography, 74 environmental conditions, and diagenesis (Berger and Killingly, 1977; Reuning et al., 2005; 75 Tagliabue and Bopp, 2008, Agnini et al, 2015). In this regard, variations in the δ^{13} C values and mass 76 fractions of the different components within bulk carbonate may provide additional insight. 77

Here, we compare bulk- and size-fraction-specific isotopic compositions of 45 samples from 78 ODP Site 1209 in Shatsky Rise, north-central Pacific Ocean, accumulated between 58-50 Ma. Our 79 80 study documents a rise in coarse-fraction (>63 μ m) abundance during the PETM, and for several Myr afterwards, at Shatsky Rise. Sites at Walvis Ridge and many other open ocean environments, by 81 contrast, document a decrease in coarse fraction, owing to ocean acidification and thus an increase 82 83 in carbonate dissolution during the early Paleogene hyperthermals (e.g. Kelly et al., 2010). Therefore, our study indicates that weight percent coarse fraction is not general proxy for carbonate 84 dissolution. Moreover, we also suggest that the increase in coarse fraction at the PETM alters the 85 86 CIE magnitude at Shatsky Rise compared to other sites.

88 2.1 Site description

Shatsky Rise, a large igneous province in the north-central Pacific, was located at $\sim 15^{\circ}$ 89 latitude during early the Paleogene (Bralower et al, 2002; Dutton et al, 2005, Supplementary 90 Figure S1). Site 1209, drilled during ODP leg 198, lies on the Southern High of Shatsky Rise 91 and contains a continuous Cenozoic record of carbonate sediments. The early Paleogene interval 92 is comprised of clayey nannofossil ooze and nannofossil ooze with clay, along with foraminifers, 93 fish teeth, and biosilica (Bralower et al, 2002). Site 1209 was presumably in the lysoclinal depth 94 95 range during the early Paleogene, thus constituting a good record of long- and short-term changes in carbonate accumulation and dissolution in the tropical Pacific Ocean (Hancock and 96 Dickens, 2005; Colosimo et al., 2006; Bhattacharya and Dickens, 2020). 97

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99 2.2 Early Paleogene carbon and oxygen isotope records at Shatsky Rise

The basic aspects of carbon and oxygen isotope stratigraphy of the early Paleogene 100 interval at Shatsky Rise have been documented (Luciani et al., 2016; Westerhold et al., 2018; 101 Bhattacharya and Dickens, 2020). Between 58 Ma and 50 Ma, the bulk carbonate δ^{13} C record 102 consistently tracks that of benthic foraminifers, but with an offset of 1-2‰ (Figure 2). Such 103 differences arise because bulk carbonates at Site 1209 are dominated by calcareous nannofossils 104 (Bralower et al., 2002), which are generally finer than 25 µm (Broecker and Clark, 1999; 2009; 105 Reghellin et al, 2015). These nannofossils reflect the higher δ^{13} C values of inorganic carbon in 106 surface water (Figure 1; Reghellin et al., 2020; Bhattacharya and Dickens, 2020). Benthic 107 for a minifers, however, represent bottom-water conditions characterized by lower δ^{13} C values 108 (Figure 1), resulting in consistently lower δ^{13} C values than bulk carbonates (Figure 2). In 109

contrast, δ^{18} O values of bulk carbonates between 58 Ma and 54 Ma are lower than that of benthic 110 foraminifers (Figure 2), because bottom waters are generally cooler than surface waters (Figure 111 1). Between 54-51 Ma, the difference between bulk carbonate- and benthic foraminiferal δ^{18} O 112 values becomes negligible; a possible collapse in the temperature gradient in the stratified waters 113 of early Eocene has been implicated (e.g. Kaiho et al., 2006; Hines et al., 2017; Barnet et al., 114 2020). After 51 Ma, however, benthic for a miniferal δ^{18} O values become lower than those of bulk 115 carbonates. Here it is important to note that the carbonate sediments from Shatsky Rise show 116 significant diagenetic alterations that may have altered the bulk-carbonate δ^{18} O isotopic record 117 and thus its apparent relationship to benthic foraminiferal δ^{18} O values (Dutton et al., 2005; 118 Bhattacharya and Dickens, 2020). 119

In general, both planktic and benthic foraminifers in open marine sediments (e.g., Site 120 1209) constitute the bulk of the coarse fraction, which is generally $>63 \mu m$ (Chiu and Broecker, 121 2008; Frenz et al., 2005; Bassinot et al, 1994). However, due to diverse ecological niches, the 122 resultant isotopic compositions of the various genera, especially of the planktic foraminifers, 123 vary greatly (Figure 1; 2). Spinose planktic foraminifers like Morozovella sp. and Acarinina sp. 124 have higher δ^{13} C values than bulk carbonates, while non-spinose planktic foraminifers like 125 Subboting sp., have δ^{13} C values largely similar to that of the bulk carbonates (Figure 2). Such 126 differences in δ^{13} C value between these two dominant types of planktic foraminifers of the early 127 Paleogene are often attributed to differences in nutrient profile between the surface and 128 thermocline, which leads to a difference in inorganic carbon uptake and the resultant δ^{13} C value 129 (e.g. Boersma et al., 1987; Coxall et al., 2000; Makarova et al., 2017). In addition, so-called 130 "vital effects" on isotopic fractionation and photosymbiotic algal associations of mixed surface 131 planktic foraminifers contribute to their higher δ^{13} C values (e.g. Spero et al., 1991; D'Hondt et 132

al., 1994; Luciani et al., 2017; Penman et al., 2014; Gaskell and Hull, 2019). The difference in δ^{18} O values arises primarily from the vertical temperature gradient in the water column. Thus, isotopic differences between planktic foraminifers are thought to reflect growth habitats (**Figure 1**). Therefore, varying proportions of these planktic calcifiers through time may have important implications on the resultant bulk carbonate stable isotope records at any given location.

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139 **3. Methods**

140 **3.1. Samples and ages**

A total of 45 samples (**Supplementary Table 1**) were collected from cores recovered at Site 1209 using a 10 cm³ wedge. 42 samples are from hole 1209A and 3 samples are from hole 1209C. For this study we use a revised meter composite depth (rmcd) scale (Westerhold and Röhl, 2006). The samples belong to lithostratigraphic subunit IIA of Site 1209, ODP Leg 198 (Bralower et al., 2002) and range between 194.26 and 220.09 rmcd, with ages determined by a previously published astronomically tuned age model (Westerhold et al., 2018).

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148 **3.2 Sample processing**

All sediment samples were oven-dried at 60°C for 24 hours to remove residual pore water. Weight measurements before and after drying were recorded. Each dried sample was then split into two portions. One portion weighing ~3g was crushed and homogenized using an agate mortar and used for bulk sediment analyses. The other, weighing ~5g, was used for size-fractionspecific isotope analyses.

Dried samples for size-fraction studies were gently and thoroughly washed in deionized
water. The wet sediments were then separated using a stack of 4 sieves: 250 μm, 125 μm, 63 μm

and 25 μ m from top to bottom. Each of the five size fractions was then collected on filter paper and left to dry for 24-48 hours at room temperature, after which it was weighed. On an average there was 5.2 ± 4.2 % sample loss associated with the rinsing techniques, details of which can be found in the supplementary information.

Each size fraction was separated into two halves, one of which was crushed and homogenized with agate mortar and used for isotope analyses. The other part was used in stereoscopic and scanning electron microscope (SEM) imagery. Representative samples are shown in **Supplementary Figures S3** and **S4**.

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3.3 Stable isotope analyses

Crushed and homogenized bulk sediment samples and size-fraction separates were 166 analyzed for δ^{13} C and δ^{18} O values at the Stable Isotope Laboratory at Rice University. Weights of 167 the samples used for these analyses were adjusted to obtain approximately 150 µg of carbonate. 168 They were analyzed on a ThermoScientific Delta V Plus Isotope Ratio Mass Spectrometer 169 (IRMS) coupled with a Gasbench II device. Measurements are reported relative to the Vienna 170 PeeDee Belemnite standard (VPDB) using NBS-18, IAEA-603 and in-house KLS and YALS as 171 standards. The isotopic compositions of these standards are noted in Table 1. Analytical 172 precision was 0.05 ‰ and 0.08 ‰ for δ^{13} C and for δ^{18} O respectively. 173

174

175 **4. Results**

176 **4.1 Relative changes in size-fraction abundance**

The abundance by weight of each size fraction was normalized to the cumulative weight
of all size fractions and is tabulated in **Supplementary Table 2**. In our suite of early Paleogene

179 sediment samples, fine fraction (FF; <25 μ m), is the most abundant size fraction, followed by 180 coarse fraction (CF; >63 μ m), and then the intermediate fraction (IF; 25-63 μ m). Their 181 abundance by weight, on average, is 91 wt%, 7 wt%, and 2 wt%, respectively (see also **Figures** 182 **3, 4** and **Supplementary Figure S5**). Among the three sub-fractions of CF, the 125-250 μ m 183 fraction dominates (mean 5 wt%), followed by the 63-125 μ m fraction (mean 2 wt%), and then 184 the >250 μ m size fraction (mean 0.1 wt%).

The relative abundance of FF decreases notably near the PETM, where it reaches a minimum (from >95% to ~75 wt% at 56 Ma; see **Figure 3** and **Supplementary Figure S5**). This decrease in FF abundance coincides with a maximum in CF and IF abundances. These relative proportions persist until ~54 Ma. Between 53- and 51 Ma, the size-fraction abundances return to levels more characteristic of the 58-56 Ma time period.

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191 4.2 Carbon isotopic composition of bulk sediments and size fractions

The $\delta^{13}C$ composition of bulk carbonates and size fractions is tabulated in 192 Supplementary Table S3. All size fractions show a δ^{13} C trend similar to that of bulk carbonate 193 through the 58-50 Ma interval (i.e., that shown in Figure 2; see Supplementary Figure S6). A 194 prominent negative CIE of ~2.25 ‰ occurs at ~55.9 Ma. Another prominent negative CIE of 195 ~0.9 ‰ occurs at ~54 Ma. Between 56-53 Ma, the δ^{13} C values of the size fractions and bulk 196 sedimentary carbonates exhibit a decreasing trend up-section. After 52 Ma, there is a $\sim 1\%$ 197 increase in δ^{13} C values of bulk sedimentary carbonates as well as size-fraction separates, 198 followed by a broader δ^{13} C increase up-section. 199

200 The FF δ^{13} C value is similar to the bulk-carbonate δ^{13} C value, although the former is 201 generally slightly higher (**Figure 3**). The overall CF δ^{13} C value is ~0.5 ‰ lower than the bulkcarbonate δ^{13} C value before the PETM, but a notable change in the CF δ^{13} C trend occurs at ~55.9 Ma (**Figure 3**): immediately after the PETM, CF δ^{13} C values become consistently higher than the bulk-carbonate δ^{13} C values until ~54 Ma. Then, between 54-51 Ma, this difference tends to decrease up the section. Both the 63-125 µm and 125- 250 µm size fractions follow this trend; however, the δ^{13} C value of >250 µm size fractions is generally higher than bulk-carbonate δ^{13} C throughout the early Paleogene interval.

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4.3 Oxygen isotope composition of bulk sediments and size fractions

The δ^{18} O of bulk sediments and size fractions are tabulated in **Supplementary Table 4**. A negative oxygen isotope excursion of ~1 ‰ occurs at ~55.9 Ma for both bulk sediments and size fractions (**Supplementary Figure S6**). Between 54-51 Ma, the δ^{18} O values show a decrease up the section. However, significant amount of fluctuation occurs in the overall δ^{18} O data at Site 1209.

The bulk carbonate δ^{18} O is largely similar to FF δ^{18} O, and is generally lower than CF δ^{18} O (**Figure 4**). However, the sub-fractions of CF show different relationship with bulk carbonate δ^{18} O. The δ^{18} O value of the 63-125 µm fraction is less than that of bulk carbonate before the PETM, whereas it is higher at and immediately after the PETM. However, the δ^{18} O value of the 125-250 µm fraction shows an opposing trend: it is higher than that of bulk carbonate before the PETM, and generally lower immediately afterwards. Bulk carbonate δ^{18} O values are generally higher than those of the 125-250 µm fraction throughout the section.

222

223 5. Discussion

5.1 Coherence of δ^{13} C and δ^{18} O values in early Paleogene bulk carbonates and size fractions

- Isotopic mass balance for any given sample dictates that the bulk carbonate stable isotope composition should be equal to the weighted average of its components:
- 228

(1)

Where, *i* represents the different size fractions: $<25 \mu m$, 25-63 μm , 63-125 μm , 125-250 μm and $>250 \mu m$. The weighted mean isotopic composition of all size fractions is hereafter referred to as the reconstructed bulk isotopic composition.

For the present suite of samples, the average difference between reconstructed and 232 measured bulk δ^{13} C value is 0.01 ± 0.12 ‰ (1 σ) (Figure 5). Analytical precision of δ^{13} C 233 measurements is 0.05 ‰, so the reconstruction of bulk carbonate δ^{13} C value from the five size 234 fractions is analytically indistinguishable from the bulk carbonate. Any minor differences that 235 are present may arise from unaccounted mass loss during rinsing and wet sieve separation (~5% 236 by weight), the presence of clays, and/or some differences in homogenization of samples before 237 analysis. For oxygen, the average difference between reconstructed and measured bulk δ^{18} O 238 value is 0.17 ± 0.25 ‰ (1 σ) (Figure 5), larger than that for carbon isotopes, yet still analytically 239 indistinguishable from the bulk carbonate samples. We note that δ^{18} O values can be altered due 240 to isotope exchange during sample rinsing and wet sieve separation processes, perhaps leading to 241 a larger variability in the reconstructed δ^{18} O value. The quantitative consistency between bulk 242 243 and size-fraction separates, however, suggests that these effects do not affect the interpretations below. 244

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5.2 Complexity of coarse-fraction abundance as a proxy for carbonate dissolution

The abundance of $>63\mu m$ fraction in pelagic sediments, which constitutes the coarse 247 fraction (CF, same as defined in 4.1) has been commonly used as a proxy for carbonate 248 dissolution in paleoceanography (e.g. Bassinot et al., 1994; Kelly et al., 2010). It generally co-249 varies with lysoclinal depth changes, which control the preservation of planktic foraminifers in 250 pelagic sediments (Broecker and Clark, 1999; Kelly et al, 2005; Littler et al, 2014). Planktic 251 252 foraminifers show higher vulnerability to carbonate dissolution than benthic foraminifers (e.g. Nguyen et al., 2009); and because benthic foraminifers form only a minor fraction of pelagic 253 carbonate sediments (e.g. Rothwell, 2016), planktic foraminifers constitute the major portion of 254 255 coarse (or foraminiferal) fraction. During an ocean acidification event, e.g. the PETM or another early Paleogene hyperthermal, enhanced fragmentation and dissolution of planktic foraminiferal 256 tests results in a decrease in CF (Berger et al. 1982; Chiu and Broecker, 2008). Such a response 257 is observed Walvis Ridge in south Atlantic, where a dark colored sediment layer, with low 258 carbonate content and CF, marks the PETM interval (e.g. Zachos et al., 2005; Stap et al., 2009; 259 Kelly et al., 2010). 260

However, studies from other open marine sites have indicated that the CF abundance to 261 does not consistently respond to carbonate dissolution in this manner. At ODP Site 865 in the 262 263 equatorial Pacific, it remains unusually high in the upper Paleocene and lower Eocene sediment strata and has been attributed to increased winnowing activity by water currents (Arreguin-264 Rodriguez et al., 2016). Moreover, our results and previous work (Hancock and Dickens, 2005; 265 266 Westerhold et al., 2018) show an inverted trend in the CF abundance in the early Paleogene sediments at Shatsky Rise (Figure 6). In the late Paleocene, CF remains <5 wt %, and reaches a 267 high of ~25 wt % at PETM, and remains substantially high for the next 2 My (Figure 6). 268

269 An anomalous increase in the test size of certain Morozovellid group planktic foraminifers in the PETM interval at Shatsky Rise has been noted earlier (Kaiho et al., 2006). 270 Presence of algal photosymbionts in these spinose planktic foraminifers possibly give them an 271 ecological advantage in the nutrient-deficient and thermally stratified ocean waters of the PETM 272 (Kaiho et al., 2006). At Site 1209, the absolute abundance of such muricate groups of planktic 273 foraminifers was also high during the PETM, while that of mixed surface dwelling Subbotinids 274 decreased (Petrizzo et al., 2008). Studies show that different groups of planktic foraminifers have 275 a varied response to carbonate dissolution; muricate taxa like *Morozovella* and *Acarinina* are less 276 277 vulnerable to fragmentation and subsequent dissolution than Subbotina (Petrizzo et al., 2008; Nguyen et al., 2011). This resilience could have resulted in enhanced preservation of these 278 photosymbiont-bearing (and possibly thermocline dwelling) planktic foraminifers, even amidst 279 intense ocean acidification and increased carbonate dissolution. Hence, the increase in CF 280 abundance during and after the PETM at Shatsky Rise may be associated with both an increased 281 competitive advantage for photosymbiont-bearing planktic foraminifers and their enhanced 282 preservation. 283

The environmental conditions that led to such a response of a particular group of planktic 284 foraminifers during the PETM may have been localized, therefore leading to differences in CF 285 abundance in the PETM interval of various open marine sites. Shatsky Rise and Walvis Ridge, 286 for example, were situated in different latitudes during the early Paleogene (Supplementary 287 288 Figure 1). Shatsky Rise, in the tropics, could have experienced higher oligotrophy than Walvis Ridge in the midlatitudes. Greater environmental stress and nutrient deficiency might have made 289 290 the photosymbiotic relationship in planktic foraminifers an adaptive pathway (Kaiho et al., 2006), resulting in their proliferation at Shatsky Rise. A greater amount of water column 291

denitrification related to enhanced suboxia in the north-central Pacific has also been suggested for Shatsky Rise during early Eocene (Kast et al., 2019), consistent with nutrient stress at that site. Thus, CF abundance can respond not only to changes in carbonate dissolution but also changes in plankton community composition.

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297 5.3 Partitioning size-fraction contributions to the bulk δ^{13} C composition and implications 298 for carbon isotope excursions

299 5.3.1 Fine fraction

Bulk-carbonate δ^{13} C values are similar to FF δ^{13} C values throughout the early Paleogene 300 section at Shatsky Rise (Figure 3), primarily because the FF is the primary component of bulk 301 carbonate. This observation is similar to that found in the Neogene sediments from the eastern 302 equatorial Pacific (Reghellin et al., 2020) and Paleogene sediments of the Cicogna section 303 (Agnini et al., 2015). The fine fraction, which comprises calcareous nannofossils, tends to record 304 conditions in the upper water column (e.g. Okada and Honjo, 1973; Ennyu et al., 2002), so bulk-305 carbonate δ^{13} C values in the early Paleogene interval at Shatsky Rise likely reflect the conditions 306 and δ^{13} C values of inorganic carbon in surface waters. The IF and CF δ^{13} C values tend to be 307 markedly different from the bulk δ^{13} C value. These size fractions contain both planktic and 308 benthic foraminifers, the so their δ^{13} C values reflect a mixed signal of surface- and bottom-water 309 carbon-isotope composition (Figure 1). 310

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312 5.3.2 Intermediate fraction

Because most calcareous nannofossils are $<25 \ \mu m$ in test size, and foraminifers are generally $>63 \ \mu m$, the IF is likely comprised of juvenile and fragmented adult foraminifers. However, because IF is a mix of both planktic and benthic foraminifers, interpreting its δ^{13} C value is less straightforward.

The bulk carbonate δ^{13} C is generally higher than IF δ^{13} C, possibly because of the presence of small sized benthic foraminifers. During early Paleogene hyperthermals, deep-sea benthic foraminifers underwent significant extinction, loss in diversity and reduction in test size (Kaiho et al., 2006; Thomas, 2007; Alegret et al., 2009; Foster et al., 2013), and could constitute a major proportion of the IF, resulting in lower δ^{13} C values, compared to the bulk carbonate (**Figure 3**).

Within the PETM interval, the IF abundance increases (Figure 3). The widespread ocean 323 acidification and shoaling of carbonate saturation horizons associated with the PETM could have 324 resulted in increased planktic foraminiferal fragmentation (e.g. Hancock and Dickens, 2005; 325 Colossimo et al., 2006; Bhattacharya and Dickens, 2020), and the breakage of larger 326 foraminiferal tests could increase IF abundance at the PETM interval. In our data, the difference 327 between IF and bulk-carbonate δ^{13} C values shrinks at the PETM (Figure 3), consistent with a 328 larger contribution from ¹³C-enriched planktic foraminifer fragments. We note that another 329 increase in IF abundance is evident between 54.5 and 53.5 Ma. Despite a low sampling 330 resolution of this study, this increase in IF is also plausibly explained by enhanced carbonate 331 dissolution and foraminiferal fragmentation around the H1/ETM2 hyperthermal event. 332

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334 **5.3.3 Coarse fraction**

The change in CF δ^{13} C value from lower than to higher than the bulk carbonate δ^{13} C value across the PETM at Shatsky Rise (**Figure 7**) is particularly striking. It may result from two key changes to foraminiferal communities that occurred. First, the PETM caused significant

benthic foraminiferal extinction (e.g. Thomas, 2007; Alegret et al., 2009). Benthic foraminifers 338 have lower δ^{13} C values than the calcareous nannoplanktons and planktic foraminifers (Figure 1), 339 so removal of benthic foraminiferal mass increases the bulk δ^{13} C values toward those of the 340 planktic species. Second, a marked increase in the CF abundance at Shatsky Rise (Figure 6) may 341 result from an increase in relative abundance and size, and better preservation of photosymbiont-342 bearing planktic foraminifers, e.g. Morozovella (Kaiho et al., 2006; Petrizzo et al., 2008; Ngyuen 343 et al., 2011), which have the highest δ^{13} C value among all the components of bulk carbonates 344 (Figures 1 and 2). An increase in Morozovellids and Acarinids from 200/g to 2900/g of bulk 345 sediments was reported across the PETM at Site 1209 in Petrizzo et al. (2008). This increase in 346 the proportion of high- δ^{13} C components in the bulk carbonate system across the PETM interval 347 would increase the resultant bulk-carbonate δ^{13} C value. 348

Here we examine the importance of this effect using the mass-balance framework (Eq. 1) 349 for the FF, IF, and CF components. For this quantitative analysis, we further divide CF into three 350 sub-components: benthic foraminifers (B in Figure 8A), planktic foraminifers with 351 photosymbionts (e.g. Morozovella sp. and Acarinina sp.; M/A in Figure 8A), and planktic 352 foraminifers without photosymbionts (e.g. Subbotina sp.; S in Figure 8A). All three sub-353 components have known δ^{13} C values before, during, and after the PETM (Dutton et al., 2005; 354 Westerhold et al., 2018). These common early Paleogene varieties of planktic foraminifers have 355 distinct carbon isotope compositions (Figure 2 and Makarova et al., 2017; Gaskell and Hull, 356 2019). Thus, we can now define the $\delta^{13}C_{CF}$ mass balance in the same way as in Eq. 1: 357

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(2)

with (wt%) here representing the weight percent within the coarse fraction only. While (wt%)_B, (wt%)_{M/A}, and (wt%)_S are unknown, the known δ^{13} C values of the three sub-components are 361 listed in Table 2. We determined plausible relative weight percent of the three components that can reproduce the measured $\delta^{13}C_{CF}$ value before, during, and after the PETM. An increase in 362 $(wt\%)_{M/A}$ and decrease in $(wt\%)_B$ within the CF system was, indeed, necessary (Table 2; Figure 363 8): a decline in (wt%)_B without an increase in (wt%)_{M/A} cannot reproduce the measured $\delta^{13}C_{CF}$ 364 value at the PETM. It is important to note here that this simplified representation of the CF mass 365 balance omits several other genera of planktic foraminifers that existed in early Paleogene 366 oceans. Though imprecise, our results broadly corroborate the plausibility of the M/A increase in 367 the PETM scenario presented above for Shatsky Rise and the isotopic data do not rule out such a 368 planktonic community shift. Thus, it also suggests that size fraction abundances can strongly 369 influence bulk sedimentary δ^{13} C values in the early Paleogene. 370

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5.3.4 The magnitude of PETM carbon isotope excursion at Shatsky Rise

Changing community structures of marine calcifiers during the anomalous warmth of the 373 PETM as seen at Shatsky Rise may have further implications on carbon isotope excursions. Here 374 we revisit the bulk δ^{13} C record of the PETM interval at Shatsky Rise (Dickens and Backman, 375 2013; Luciani et al., 2016; Bhattacharya and Dickens, 2020), Walvis Ridge (Kelly et al., 2010; 376 Westerhold et al., 2017), and Cicogna (Agnini et al., 2015). The bulk δ^{13} C values of the three 377 sites are offset, as are the magnitudes of the PETM CIEs: the difference between average $\delta^{13}C$ 378 values before the CIE (from 56.1-55.93 Ma) and the lowest δ^{13} C value measured within the CIE 379 interval, are 3.1‰ at Walvis Ridge, 2.75‰ at Cicogna and 2.25‰ at Shatsky Rise (Figure 6C). 380

381 Multiple factors could have contributed to these differences in the bulk δ^{13} C values. Site 382 depth and location are both important. For example, the Cicogna section was deposited in water 383 depths <1000m, in a mid-lower bathyal setting (Giusberti et al., 2007; 2016), which is proximal to organic matter rich terrigenous sediment source; hence, the δ^{13} C values of the carbonates there can differ from those in open marine environments. This discrepancy in depositional environment could result in consistently lower δ^{13} C values in the Cicogna bulk carbonates than at Shatsky Rise and Walvis Ridge. In addition, the latitude and location within an ocean basin can influence δ^{13} C values of dissolved inorganic carbonate: modern upwelling regions, for example, have lower δ^{13} C values than in the oligotrophic ocean (e.g. Tagliabue and Bopp, 2008).

The interplay of these factors can lead to differences in the makeup of bulk carbonates 390 and thus spatial variations in the bulk carbonate δ^{13} C values, especially during CIEs. For 391 example, across the PETM onset interval, the CF abundance drops from 4 wt.% to 1 wt.% at 392 Walvis Ridge, but rises from 7 wt.% to 20 wt.% at Shatsky Rise (Figure 6B), presumably due to 393 the proliferation of Morozovellids and other photosymbiont-bearing planktic foraminifera. The 394 pronounced increase in these communities during the PETM in the north-central Pacific Ocean 395 (Figure 8) may have dampened the magnitude of the Paleocene-Eocene CIE at Shatsky Rise 396 because they exhibit the highest δ^{13} C values amongst all the components of pelagic carbonates; 397 increasing their abundance in the bulk carbonate system would result in a higher δ^{13} C value (i.e., 398 a less negative excursion) within the CIE interval. While the precise evolution of relative 399 community abundances is not well constrained by the isotopic data, a change in the proportion of 400 planktic and benthic foraminifera (by mass) during the PETM is required to explain the 401 magnitude of the CIE at Shatsky Rise (see Table 2). 402

403

404 5.4 Interpreting size-fraction specific δ^{18} O variations

405 Unlike the δ^{13} C record, size-fraction specific δ^{18} O variations at Shatsky Rise are 406 complicated by post-depositional effects. In the hothouse (ice-free) climate state of the early

Paleogene (Zachos et al., 2001; Zachos et al., 2008; Westerhold et al., 2020), bulk carbonate δ^{18} O 407 values are expected to reflect upper ocean temperatures because FF (calcareous nannofossils) 408 constitutes its major component (Figure 4A; see also Supplementary information). While FF 409 δ^{18} O values indeed track those of bulk carbonate, the IF δ^{18} O value is higher than that of bulk 410 carbonate within the PETM interval. One possible explanation for this difference could be a size 411 reduction of benthic foraminifers at PETM, which increases their abundance in the IF and 412 decreases their abundance in the CF (e.g. Kaiho et al., 2006; Thomas, 2007). However, both the 413 FF and IF δ^{18} O values show fluctuations up section that are similar in magnitude to the PETM 414 change (Figure 4), suggesting that the latter may be spurious. 415

With increasing numbers of photosymbiont-bearing planktic foraminifers and a 416 decreasing abundance of benthic foraminifers within the CF across the PETM interval at Shatsky 417 Rise (Figure 8), the difference between CF and bulk δ^{18} O values is expected to decrease. 418 However, CF δ^{18} O values remain higher than those in bulk carbonate (Figure 4C). In addition, 419 δ^{18} O values of the >250 µm fraction are consistently lower than those of bulk carbonate (Figure 420 **4F**), which is the opposite of what is expected: the coarsest component in the bulk carbonates 421 constitutes large planktic foraminifers like muricate Morozovellids (Kaiho et al., 2006), which 422 are believed to dwell in the thermocline, where cooler temperatures should yield higher $\delta^{18}O$ 423 values, not lower. Consequently, size-fraction specific changes in δ^{18} O values do not obviously 424 reflect the ecological trends inferred from of δ^{13} C values; other factors are important. 425

Dissolution and re-precipitation of carbonates in bulk sediments affects oxygen isotopes greatly in low-latitude open-ocean sites and could increase their δ^{18} O values (Scholle and Arthur, 1980; Schrag et al., 1995). Indeed, evidence of authigenic calcite and recrystallization of planktic foraminiferal tests have been reported in sediments from Site 1209 (Dutton et al., 2005; Bhattacharya and Dickens, 2020). The degree of calcite recrystallization varies in different groups of calcifiers, which makes these effects difficult to quantify. Furthermore, calcifiers in the surface oceans (e.g., in the fine fraction) will record a wide range of temperature throughout the year due to seasonal gradients in sea surface temperature, while bottom dwellers will reflect smaller variations in temperature. Consequently, the size-fraction-specific δ^{18} O values can neither corroborate nor invalidate the interpretations derived from δ^{13} C values at present.

436

437 6. Conclusions

Our study from Shatsky Rise presents variations in bulk carbonate and size fraction δ^{13} C 438 and δ^{18} O isotope record and changes in relative abundance of different size fractions in the early 439 Paleogene interval between 58 and 50 Ma. Bulk carbonate δ^{13} C values have been commonly 440 used in chemostratigraphic correlation of widely separated marine sedimentary sections. 441 Shackleton and Hall (1995) made a pioneering study showing coherency of bulk carbonate $\delta^{13}C$ 442 and δ^{18} O in the Cenozoic; such records show significant offsets in absolute values through space. 443 While many factors contribute to the spatial variations, our study reveals an additional potential 444 driver of early Paleogene bulk carbonate stable isotope records, namely, variations in the 445 abundances of calcifiers that comprise the bulk carbonates in pelagic depositional environments. 446 The main findings of this study can be hereby summarized: 447

448

- Size fraction stable isotope records show comparable temporal trends to those of the bulk carbonates through the early Paleogene interval at Shatsky Rise.
- Consistent with previous studies, bulk δ^{13} C values primarily track those of surfacedwelling calcareous nannofossils, which yield surface-water signals.

 At Shatsky Rise, an increase in coarse fraction abundance is observed at the PETM, ca.
 56 Ma, and persists until ~54 Ma. This increase is associated with an increased abundance of photosymbiont-bearing planktic foraminifers, in contrast to what has been documented in Walvis Ridge in the south Atlantic and in contrast to the simple expectation of increased fragmentation (and therefore a decrease in CF abundance) during ocean acidification events. This observation at Shatsky Rise challenges the generality of CF abundance as a proxy for carbonate dissolution.

Significant community changes of marine calcifiers during early Paleogene may be a significant driver for resultant heterogeneity in bulk carbonate isotope records across
 space, even though their temporal trends show good stratigraphic correlation.

• The magnitude of carbon isotope excursions can be modulated by variable abundances of different groups of marine calcifiers at different deep-sea locations. Such effects, along with other factors like latitude and location of site within the ocean basin, can strongly influence the magnitude of a CIE at any given early Paleogene hyperthermal.

466

467 Acknowledgement

We thank the scientists and staff at Gulf Coast Repository at College Station for sample collection. This work was partially supported by NSF grant awarded to Cin-Ty Lee, Gerald R. Dickens and colleagues at Rice University and by the 'Program of studying abroad for young scholars' awarded to Lin Cong by Northeast Petroleum University. All data in the manuscript are available in Tables in the main text and as Supplementary Tables in supporting information during review process. All data will be finally deposited into Pangaea database upon acceptance of the manuscript.

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Tables and table captions

Table 1: Carbon and oxygen isotopic composition of standard reference materials used.

Standard material	NBS-18	IAEA-603	In House-KLS	In House-YALS
Standard material	1125 10	11 IEA 1 005	III HOUSE ILLS	In House THES
name				
Material	calcite	calcite	limestone	limestone
description				
description				
$s^{13}C_{0}$ (VDDD)	5.01	2.46	0.22	1 15
0 C (VPDB)	-3.01	2.40	0.35	1.13
δ^{18} O‰ (VPDB)	_22.97	_2 37	-20.08	-6.08
0 0/00 (VIDD)	-22.91	-2.37	-27.98	-0.08
name Material description δ^{13} C‰ (VPDB) δ^{18} O‰ (VPDB)	-5.01 -22.97	calcite 2.46 -2.37	0.33 -29.98	limestone 1.15 -6.08

Table 2: Values of the known and unknown variables in Eqn 2. The δ^{13} C of CF (measured), B, M/A, and S are known variables. The wt% of B, M/A, and S are generated by optimization of modeled δ^{13} C_{CF}.

726				
720		pre-PETM	at-PETM	post-PETM
777				
121	$\delta^{13}C_B$ / ‰	0.5	-0.75	0.75
728				
	$\delta^{13}C_{M/A}$ / ‰	3.20	1.25	2.50
729				
	$\delta^{13}C_S$ / ‰	2.25	0.50	1.75
730				
	Modeled (wt%) _B	45	20	20
731				
	Modeled (wt%) _{M/A}	47	78	73
732				
/02	Modeled (wt%) _S	8	2	7
733				
	$\delta^{13}C_{CF}$ / ‰ (modeled)	1.91	0.84	2.10
734				
,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	$\delta^{13}C_{CF}$ / ‰ (measured)	1.93	0.72	2.14
735				

736 Figures and figure captions

737

738 Figure 1





740

Constituents of bulk carbonate in deep marine carbonate records and their variable δ^{13} C compositions. Pelagic components (primarily originating from mixed surface waters and thermocline) constitute calcareous nannofossils and planktic foraminifers. Benthic foraminifers, constituting the benthic factory, are bottom dwellers. The orange and purple lines show variations in modern day DIC δ^{13} C in the Pacific and Atlantic oceans respectively. The black line shows change in temperature with depth in ocean water column.

748 Figure 2



750

749



and Shackleton et al., 1985) stable carbon and oxygen isotope record at Shatsky Rise.



Variations in size fraction abundance and their δ^{13} C values with respect to bulk carbonate 760 δ^{13} C values across the early Paleogene interval at Shatsky Rise. Changes in abundance 761 (wt %) are color coded for each of the size fractions. The difference between size fraction-762 specific δ^{13} C value and bulk carbonate δ^{13} C value at each sample interval is plotted over time. 763 (A) i-iii show the data for fine fraction FF (<25 µm), IF intermediate fraction (25-63 µm) and 764 coarse fraction CF (>63 μm). (B) in iv-vi, CF is subdivided into three size fractions: 63-125 μm, 765 125-250 µm and >250 µm. The yellow line denotes PETM interval. The black line provides a 766 visual reference for no difference between size fraction-specific and bulk carbonate $\delta^{13}C$ value. 767



Variations in size fraction abundance and their δ^{18} O values with respect to bulk carbonate 773 δ^{18} O values across the early Paleogene interval at Shatsky Rise. Changes in abundance 774 (wt %) are color coded for each of the size fractions. The difference between size fraction δ^{18} O 775 and bulk δ^{18} O at each sample interval is plotted across time. (A) i-iii show the data for fine 776 fraction FF (<25 µm), IF intermediate fraction (25-63 µm) and coarse fraction CF (>63 µm). (B) 777 in iv-vi, CF is subdivided into three size fractions: 63-125 μ m, 125-250 μ m and >250 μ m. The 778 yellow line denotes PETM interval. The black line provides a visual reference for no difference 779 between size fraction-specific and bulk carbonate δ^{18} O value. 780



783

Difference between measured and size-fraction reconstructed bulk carbon and oxygen isotopes. Left panel shows measured bulk isotope record from Shatsky Rise (solid circles; δ^{13} C in A and δ^{18} O in B) and the reconstructed bulk isotope values from weighted sums of size fractions (solid rhombs). The right panel shows the difference between measured and reconstructed bulk isotope values.

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790 Figure 6
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Bhattacharya et al.

Coarse fraction abundance and the PETM CIE at Shatsky Rise and elsewhere. (A) Change in weight percent coarse fraction (WPCF) at Site 1209 between 58-50 Ma. The data from this study is represented by black line with red rhombs, while the grey line in the background constitutes data from Westerhold et al. (2018). (B) Comparison of WPCF at Shatsky Rise and Walvis Ridge across the PETM interval. (C) Comparison of the PETM CIE magnitude for three different open ocean sites: Shatsky Rise (red dashed line), Walvis Ridge (blue line) and Cicogna section in Italy (grey line). 800 Figure 7



803 The δ^{13} C record of bulk carbonate at Shatsky Rise from 57 – 55 Ma compared to those of 804 individual constituents: benthic foraminifera, fine fraction (calcareous nannofossils), 805 intermediate fraction (fragments and juvenile foraminifers), coarse fraction (mixture of planktic 806 and benthic foraminifers), and larger photosymbiont-bearing planktic foraminifers (>250 µm).

807 Figure 8



- 808
- 809
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811 Influence of relative changes in size fraction abundances on the bulk carbonate $\delta 13C$ 812 record at Shatsky Rise. (A) Three samples from before, during, and after the PETM CIE 813 interval at Site 1209, as seen under SEM. Benthic foraminiferal abundance decreases sharply at

and after the PETM, while larger planktic foraminifers increase in abundance. (B) Abundance of benthic foraminifers, photosymbiont-bearing planktic foraminifers, and photosymbiont-free planktic foraminifers for pre-PETM, at-PETM and post-PETM intervals that can quantitatively explain the measured positive shift in CF δ 13C value (see 5.3.3).

1	Supporting information for	
2	Size-fraction specific isotopic variations as a framework for interpreting early Paleo	ogene bulk sediment carbon
3		
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9		
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11	Supplementary Tables and table captions	
12	Supplementary Figures and figure captions	
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ı isotope records

Supplementary Table 1. Change in weights of sediments before and after wet sieve separation process.

Sample ID	MBSF m	rmcd m	Age (Ma)	Sediment loss upon rinsing (wt %)
198-1209-A-19-5-121	176.56	194.26	50.68	7.43
198-1209-A-19-5-146	177.16	194.86	50.72	8.65
198-1209-A-19-6-38	177.17	194.87	50.78	8.53
198-1209-A-19-6-86	177.88	195.58	50.87	-0.89
198-1209-A-19-7-26	178.26	195.96	50.93	8.62
198-1209-C-9-4-11	178.86	197.05	51.09	-3.70
198-1209-A-20-1-6	179.56	198.72	51.22	3.22
198-1209-A-20-2-21	181.06	200.22	51.50	0.33
198-1209-C-9-6-17	181.31	199.50	51.51	2.84
198-1209-A-20-2-111	182.36	201.52	51.74	3.32
198-1209-C-9-7-41	182.64	200.83	51.87	9.59
198-1209-A-20-3-136	183.56	202.72	52.09	-0.15
198-1209-A-20-4-11	183.81	202.97	52.15	9.29
198-1209-A-20-6-39	187.09	206.25	52.76	2.20
198-1209-A-20-6-74	187.44	206.60	52.81	23.00
198-1209-A-20-6-106	187.76	206.92	52.89	4.90
198-1209-A-21-1-19	188.89	208.99	53.33	7.44
198-1209-A-21-1-81	189.51	209.61	53.46	9.59
198-1209-A-21-1-121	189.91	210.01	53.54	8.66
198-1209-A-21-1-127	189.97	210.07	53.55	4.38
198-1209-A-21-1-143	190.13	210.23	53.58	7.07
198-1209-A-21-2-66	190.86	210.96	53.76	2.17
198-1209-A-21-2-106	191.26	211.36	53.87	1.84
198-1209-A-21-3-4	191.74	211.84	53.96	4.29
198-1209-A-21-3-33.5	192.04	212.14	54.01	4.65
198-1209-A-21-3-62	192.32	212.42	54.08	9.77
198-1209-A-21-3-92	192.62	212.72	54.21	9.26
198-1209-A-21-3-116	192.86	212.96	54.32	7.00
198-1209-A-21-4-7	193.27	213.37	54.49	7.73
198-1209-A-21-4-46	193.66	213.76	54.65	6.73
198-1209-A-21-4-68	193.88	213.98	54.73	4.94
198-1209-A-21-4-103	194.23	214.33	54.89	6.90
198-1209-A-21-5-11	194.81	214.91	55.04	5.18
198-1209-A-21-5-83	195.53	215.63	55.25	1.24
198-1209-A-21-5-123	195.93	216.03	55.37	0.81
198-1209-A-21-6-31	196.51	216.61	55.57	2.62
198-1209-A-21-6-116	197.36	217.46	55.78	2.43
198-1209-A-21-6-143	197.63	217.73	55.83	2.20
198-1209-A-21-7-4	197.74	217.84	55.86	5.24
198-1209-A-21-7-11	197.81	217.91	55.89	5.76
198-1209-A-21-7-13	197.83	217.93	55.89	6.70
198-1209-A-21-7-32	198.02	218.12	55.94	3.69
198-1209-A-22-1-10	198.30	219.74	56.46	3.61
198-1209-A-22-1-25	198.45	219.89	56.73	0.43
198-1209-A-22-1-50	198.65	220.09	57.11	4.80

19 Supplementary Table 2. Abundance by weight percent of the five size fractions.

Sample ID	MBSF m	rmed m	Age (Ma)	FF < 25 µm wt %	IF 25-63 µm wt %	63-125 um wt %	125-250 um wt %	>250 µm wt %	CE >63 µm
198-1209-A-19-5-121	176 56	194.26	50.68	97.02	0 370	0.49	2 09	0.03	2 61
198-1209-A-19-5-146	177.16	194.86	50.72	96.37	0.567	0.63	2.38	0.06	3.07
198-1209-A-19-6-38	177.17	194.87	50.78	98.09	0.383	0.40	1.13	0.00	1.52
198-1209-A-19-6-86	177.88	195.58	50.87	97.11	0.559	0.76	1.56	0.01	2.33
198-1209-A-19-7-26	178.26	195.96	50.93	97.50	0.506	0.82	1.18	0.00	2.00
198-1209-C-9-4-11	178.86	197.05	51.09	97.99	0.188	0.47	1.33	0.02	1.82
198-1209-A-20-1-6	179.56	198.72	51.22	96.18	0.430	0.79	2.60	0.00	3.39
198-1209-A-20-2-21	181.06	200.22	51.50	97.97	0.390	0.06	1.57	0.01	1.64
198-1209-C-9-6-17	181.31	199.50	51.51	96.55	0.728	0.84	1.86	0.02	2.72
198-1209-A-20-2-111	182.36	201.52	51.74	95.31	1.434	0.99	2.27	0.00	3.26
198-1209-C-9-7-41	182.64	200.83	51.87	93.88	1.538	1.65	2.90	0.03	4.58
198-1209-A-20-3-136	183.56	202.72	52.09	94.60	0.668	1.06	3.62	0.06	4.73
198-1209-A-20-4-11	183.81	202.97	52.15	96.01	1.101	0.98	1.90	0.01	2.89
198-1209-A-20-6-39	187.09	206.25	52.76	94.24	0.867	1.04	3.78	0.07	4.89
198-1209-A-20-6-74	187.44	206.60	52.81	90.34	1.720	2.21	5.10	0.64	7.94
198-1209-A-20-6-106	187.76	206.92	52.89	93.75	1.574	1.53	3.00	0.14	4.67
198-1209-A-21-1-19	188.89	208.99	53.33	92.34	1.208	1.05	5.35	0.05	6.45
198-1209-A-21-1-81	189.51	209.61	53.46	89.11	1.808	3.14	5.91	0.02	9.08
198-1209-A-21-1-121	189.91	210.01	53.54	93.39	1.075	1.86	3.64	0.03	5.53
198-1209-A-21-1-127	189.97	210.07	53.55	94.45	1.100	1.02	3.36	0.07	4.45
198-1209-A-21-1-143	190.13	210.23	53.58	93.21	1.241	1.39	4.08	0.08	5.55
198-1209-A-21-2-66	190.86	210.96	53.76	87.14	2.770	3.73	6.29	0.07	10.09
198-1209-A-21-2-106	191.26	211.36	53.87	93.02	1.077	2.39	3.48	0.04	5.90
198-1209-A-21-3-4	191.74	211.84	53.96	92.88	1.373	3.02	2.70	0.02	5.74
198-1209-A-21-3-33.5	192.04	212.14	54.01	91.35	1.648	1.88	5.05	0.06	7.00
198-1209-A-21-3-62	192.32	212.42	54.08	92.29	0.979	1.72	4.89	0.13	6.73
198-1209-A-21-3-92	192.62	212.72	54.21	83.74	2.627	3.51	9.91	0.22	13.63
198-1209-A-21-3-116	192.86	212.96	54.32	81.55	3.467	3.67	11.26	0.06	14.98
198-1209-A-21-4-7	193.27	213.37	54.49	89.32	1.506	2.75	6.38	0.04	9.18
198-1209-A-21-4-46	193.66	213.76	54.65	83.11	2.662	4.80	9.39	0.03	14.23
198-1209-A-21-4-68	193.88	213.98	54.73	82.51	3.414	4.81	9.21	0.06	14.07
198-1209-A-21-4-103	194.23	214.33	54.89	84.84	2.911	4.28	7.88	0.09	12.25
198-1209-A-21-5-11	194.81	214.91	55.04	79.86	3.976	5.41	10.71	0.04	16.17
198-1209-A-21-5-83	195.53	215.63	55.25	85.92	3.120	4.32	6.61	0.03	10.95
198-1209-A-21-5-123	195.93	216.03	55.37	87.98	2.315	3.66	6.01	0.03	9.71
198-1209-A-21-6-31	196.51	216.61	55.57	88.23	2.305	3.71	5.73	0.02	9.46
198-1209-A-21-6-116	197.36	217.46	55.78	87.99	2.192	3.91	5.88	0.03	9.82
198-1209-A-21-6-143	197.63	217.73	55.83	87.73	2.630	4.09	5.43	0.13	9.64
198-1209-A-21-7-4	197.74	217.84	55.86	84.54	3.637	4.88	6.78	0.17	11.82
198-1209-A-21-7-11	197.81	217.91	55.89	78.15	3.908	7.84	9.90	0.20	17.94
198-1209-A-21-7-13	197.83	217.93	55.89	75.63	4.130	8.63	11.59	0.01	20.23
198-1209-A-21-7-32	198.02	218.12	55.94	90.24	2.005	2.72	5.02	0.01	7.75
198-1209-A-22-1-10	198.30	219.74	56.46	98.70	0.589	0.43	0.27	0.00	0.71
198-1209-A-22-1-25	198.45	219.89	56.73	99.23	0.415	0.19	0.16	0.01	0.36
198-1209-A-22-1-50	198.65	220.09	57.11	99.14	0.420	0.23	0.21	0.00	0.44

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22 Supplementary Table 3. Bulk carbonate- and size fraction $\delta^{13}C$ composition.

MBSF m	rmcd m	Age (Ma)	CaCO3%	Measured Bulk δ13C (‰)	FF <25μm δ13C ‰	IF 25-63μm δ13C ‰	63-125μm δ13C ‰	125-250 μm δ13C ‰	>250 μm δ13C ‰	CF >63 μm δ13C ‰	Reconstructed Bulk δ13C (‰)
176.56	194.26	50.68	92.47	1.82	1.83	0.65	1.40	1.69	1.98	1.64	1.69
177.16	194.86	50.72	94.62	1.88	1.88	1.99	2.00	1.90	3.04	1.94	1.78
177.17	194.87	50.78	97.89	1.87	1.88	1.80	2.04	1.63	1.93	1.74	1.84
177.88	195.58	50.87	89.03	0.83	1.01	1.58	1.17	1.27	2.13	1.24	0.91
178.26	195.96	50.93	93.60	1.74	1.75	1.42	1.70	2.00	1.88	1.87	1.65
178.86	197.05	51.09	94.30	1.48	1.62	1.30	1.61	1.83	2.27	1.78	1.53
179.56	198.72	51.22	91.29	0.77	1.47	1.40	1.47	1.76	2.64	1.69	1.36
181.06	200.22	51.50	90.82	1.14	1.40	1.15	1.30	1.42	2.11	1.42	1.27
181.31	199.50	51.51	88.91	1.18	1.30	0.74	1.05	1.42	1.46	1.31	1.16
182.36	201.52	51.74	95.40	0.99	1.09	0.60	1.27	1.45	2.36	1.40	1.05
182.64	200.83	51.87	88.34	1.20	1.32	0.51	1.04	1.51	2.23	1.35	1.17
183.56	202.72	52.09	96.71	1.11	1.22	1.45	0.97	1.47	2.84	1.38	1.19
183.81	202.97	52.15	95.01	1.56	1.56	1.10	1.12	1.91	2.86	1.65	1.48
187.09	206.25	52.76	96.56	1.03	1.05	1.15	1.07	1.35	2.32	1.31	1.03
187.44	206.60	52.81	97.03	1.02	1.12	0.98	0.99	1.08	2.27	1.15	1.09
187.76	206.92	52.89	95.12	1.18	1.28	0.55	0.66	0.98	2.80	0.93	1.19
188.89	208.99	53.33	88.70	1.24	1.51	1.43	1.55	1.77	2.46	1.74	1.36
189.51	209.61	53.46	92.50	1.28	1.37	1.12	1.30	1.80	2.39	1.63	1.30
189.91	210.01	53.54	93.20	1.24	1.36	0.79	0.98	1.44	1.72	1.29	1.26
189.97	210.07	53.55	93.40	1.15	1.19	0.91	1.16	1.45	2.41	1.39	1.12
190.13	210.23	53.58	90.75	1.04	1.16	1.07	1.13	1.80	2.47	1.64	1.09
190.86	210.96	53.76	93.00	0.85	1.02	1.65	1.48	1.93	2.91	1.77	1.05
191.26	211.36	53.87	94.00	1.38	1.58	1.31	1.35	2.10	2.62	1.80	1.50
191.74	211.84	53.96	92.30	1.28	1.40	0.69	0.78	1.73	1.97	1.23	1.28
192.04	212.14	54.01	96.30	1.27	1.51	1.00	1.07	1.79	2.12	1.60	1.45
192.32	212.42	54.08	91.00	1.28	1.35	1.17	1.16	1.44	1.75	1.37	1.24
192.62	212.72	54.21	94.70	1.85	1.79	1.30	1.08	1.66	2.90	1.53	1.66
192.86	212.96	54.32	92.80	1.59	1.69	1.36	1.52	1.65	2.92	1.62	1.57
193.27	213.37	54.49	88.20	1.43	1.47	1.27	1.50	1.91	2.43	1.79	1.34
193.66	213.76	54.65	92.30	1.38	1.43	1.50	1.75	2.09	3.09	1.98	1.42
193.88	213.98	54.73	93.00	1.74	1.99	1.26	1.38	1.57	2.78	1.51	1.78
194.23	214.33	54.89	89.45	1.72	1.82	1.62	1.82	2.30	3.17	2.14	1.69
194.81	214.91	55.04	82.94	1.67	1.81	1.54	1.95	2.62	2.91	2.40	1.65
195.53	215.63	55.25	96.80	2.04	2.13	1.60	1.93	2.49	3.35	2.27	2.07
195.93	216.03	55.37	94.20	1.75	1.67	1.33	1.84	2.52	3.33	2.26	1.63
196.51	216.61	55.57	86.90	1.94	1.95	1.66	2.12	3.16	3.28	2.76	1.80
197.36	217.46	55.78	94.90	1.96	2.07	1.94	1.78	2.54	3.12	2.24	1.99
197.63	217.73	55.83	93.80	1.58	1.62	1.27	1.36	2.34	2.29	1.93	1.55
197.74	217.84	55.86	82.10	1.21	1.35	0.96	1.01	1.63	1.50	1.37	1.13
197.81	217.91	55.89	81.50	0.92	1.16	0.96	0.94	1.16	1.64	1.07	0.97
197.83	217.93	55.89	80.80	0.58	0.66	0.54	0.65	0.78	1.60	0.72	0.57
198.02	218.12	55.94	88.00	2.53	2.83	1.64	1.85	2.18	2.61	2.07	2.44
198.30	219.74	56.46	97.76	3.22	3.32	3.00	3.26	2.61	3.92	3.01	3.24
198.45	219.89	56.73	95.10	3.23	3.33	3.13	2.62	2.44	3.77	2.57	3.16
198.65	220.09	57.11	93.20	3.32	3.52	3.00	3.10	2.61	No sample	2.86	3.27

Supplementary Table 4. Bulk carbonate- and size fraction δ^{18} O composition.

Sample ID	MBSF m	rmcd m	Age (Ma)	CaCO3%	Measured Bulk δ18O (‰)	FF <25 μm δ18O ‰	IF 25-63μm δ18O ‰	63-125μm δ18O ‰	125-250 μm δ18O ‰	>250 μm δ18O ‰	CF >63 μm δ18O ‰	Reconstructed Bulk δ 18O (‰)
198-1209-A-19-5-121	176.56	194.26	50.68	92.47	-0.59	-0.42	-1.71	-1.44	-1.20	-1.93	-1.17	-0.42
198-1209-A-19-5-146	177.16	194.86	50.72	94.62	-1.19	-1.09	-0.15	-0.54	-1.40	-0.65	-0.44	-1.03
198-1209-A-19-6-38	177.17	194.87	50.78	97.89	-0.60	-0.18	-1.25	-1.15	-0.84	-2.55	-0.85	-0.19
198-1209-A-19-6-86	177.88	195.58	50.87	89.03	-0.59	-0.21	-0.06	-0.37	-0.95	-2.27	-0.25	-0.20
198-1209-A-19-7-26	178.26	195.96	50.93	93.60	-0.38	-0.45	-0.18	-0.24	-0.84	-1.30	-0.14	-0.43
198-1209-C-9-4-11	178.86	197.05	51.09	94.30	-0.75	0.05	-0.62	-0.44	-0.61	-0.70	-0.33	0.04
198-1209-A-20-1-6	179.56	198.72	51.22	91.29	-1.31	-0.40	-0.64	-0.86	-0.86	-0.82	-0.66	-0.39
198-1209-A-20-2-21	181.06	200.22	51.50	90.82	-0.29	-0.09	-0.54	-1.74	-2.81	-0.75	-1.69	-0.13
198-1209-C-9-6-17	181.31	199.50	51.51	88.91	-1.46	-1.88	-0.67	-0.58	-1.47	-1.19	-0.41	-1.65
198-1209-A-20-2-111	182.36	201.52	51.74	95.40	-0.50	-0.37	-0.79	-0.44	-1.03	-1.00	-0.31	-0.37
198-1209-C-9-7-41	182.64	200.83	51.87	88.34	-1.02	-0.29	-0.57	-0.62	-1.39	-0.92	-0.40	-0.30
198-1209-A-20-3-136	183.56	202.72	52.09	96.71	-0.65	-0.62	-0.83	0.49	0.60	-0.72	0.38	-0.55
198-1209-A-20-4-11	183.81	202.97	52.15	95.01	-0.39	-0.10	-1.12	-0.46	-1.10	-1.31	-0.31	-0.13
198-1209-A-20-6-39	187.09	206.25	52.76	96.56	-0.68	-0.39	-0.23	-0.39	-0.77	-1.83	-0.31	-0.39
198-1209-A-20-6-74	187.44	206.60	52.81	97.03	-0.43	-0.23	-0.36	-0.22	-0.53	-0.91	-0.19	-0.25
198-1209-A-20-6-106	187.76	206.92	52.89	95.12	-0.49	-0.47	-0.77	-0.66	-1.44	-1.51	-0.47	-0.48
198-1209-A-21-1-19	188.89	208.99	53.33	88.70	-0.83	-0.10	-0.42	-0.18	-0.54	-1.38	-0.15	-0.12
198-1209-A-21-1-81	189.51	209.61	53.46	92.50	-0.41	-0.29	-0.05	-0.49	-1.37	-0.60	-0.32	-0.34
198-1209-A-21-1-121	189.91	210.01	53.54	93.20	-0.20	-0.04	0.28	0.33	-1.49	-0.50	0.21	-0.08
198-1209-A-21-1-127	189.97	210.07	53.55	93.40	-0.75	-0.98	-0.17	-0.69	-0.69	-0.72	-0.53	-0.90
198-1209-A-21-1-143	190.13	210.23	53.58	90.75	-0.37	-0.27	0.22	0.01	-0.77	-0.56	0.00	-0.25
198-1209-A-21-2-66	190.86	210.96	53.76	93.00	-0.45	-0.26	-2.91	-0.51	-2.58	-1.44	-0.33	-0.48
198-1209-A-21-2-106	191.26	211.36	53.87	94.00	-0.34	-0.22	-0.75	-0.08	-1.47	-0.80	-0.06	-0.25
198-1209-A-21-3-4	191.74	211.84	53.96	92.30	-0.54	-0.16	-0.12	-0.30	-0.88	-1.47	-0.14	-0.17
198-1209-A-21-3-33.5	192.04	212.14	54.01	96.30	-0.34	0.29	0.21	-0.17	-0.41	-0.57	-0.13	0.23
198-1209-A-21-3-62	192.32	212.42	54.08	91.00	-0.70	-0.52	-0.16	-0.45	-0.90	-1.63	-0.34	-0.50
198-1209-A-21-3-92	192.62	212.72	54.21	94.70	-0.48	-0.41	-0.17	0.07	-0.52	-0.85	0.05	-0.38
198-1209-A-21-3-116	192.86	212.96	54.32	92.80	-0.82	-0.84	-0.56	-0.54	-1.20	-1.13	-0.41	-0.81
198-1209-A-21-4-7	193.27	213.37	54.49	88.20	-0.81	-0.76	-0.88	-0.79	-1.52	-1.28	-0.56	-0.73
198-1209-A-21-4-46	193.66	213.76	54.65	92.30	-0.73	-0.83	-0.59	-0.52	-0.80	-1.02	-0.34	-0.75
198-1209-A-21-4-68	193.88	213.98	54.73	93.00	-1.06	-0.85	-1.76	-0.67	-1.74	-2.99	-0.45	-0.91
198-1209-A-21-4-103	194.23	214.33	54.89	89.45	-0.90	-0.78	-0.71	-0.82	-0.82	-1.12	-0.54	-0.71
198-1209-A-21-5-11	194.81	214.91	55.04	82.94	-0.73	-0.56	-0.58	-0.84	-1.55	-0.60	-0.56	-0.60
198-1209-A-21-5-83	195.53	215.63	55.25	96.80	-0.91	-0.82	-1.01	-0.62	-0.97	-0.77	-0.38	-0.81
198-1209-A-21-5-123	195.93	216.03	55.37	94.20	-1.00	-0.78	-2.02	-0.91	-1.38	-1.77	-0.57	-0.81
198-1209-A-21-6-31	196.51	216.61	55.57	86.90	-1.06	-1.08	-0.21	-0.53	-1.13	-1.48	-0.33	-0.92
198-1209-A-21-6-116	197.36	217.46	55.78	94.90	-0.84	-0.92	-1.05	-0.07	-1.45	-1.69	-0.05	-0.88
198-1209-A-21-6-143	197.63	217.73	55.83	93.80	-0.60	-0.57	0.34	-0.06	-0.72	-0.60	-0.05	-0.51
198-1209-A-21-7-4	197.74	217.84	55.86	82.10	-0.70	-0.70	-0.40	0.01	-0.42	-1.07	0.00	-0.53
198-1209-A-21-7-11	197.81	217.91	55.89	81.50	-0.96	-1.21	-0.48	-1.01	-0.82	-1.30	-0.57	-0.95
198-1209-A-21-7-13	197.83	217.93	55.89	80.80	-1.09	-0.98	-0.47	-1.14	-2.08	-2.29	-0.66	-0.96
198-1209-A-21-7-32	198.02	218.12	55.94	88.00	-0.20	-0.41	-0.34	-0.88	-0.65	-1.60	-0.57	-0.39
198-1209-A-22-1-10	198.30	219.74	56.46	97.76	-0.60	-0.69	-0.25	-0.90	0.04	-2.19	-0.34	-0.67
198-1209-A-22-1-25	198.45	219.89	56.73	95.10	-0.38	-0.55	-0.39	-0.44	-0.09	-1.02	-0.20	-0.52
198-1209-A-22-1-50	198.65	220.09	57.11	93.20	-0.35	-0.54	-0.17	-0.65	-0.10	No sample	-0.31	-0.50

Supplementary Table 5. Correlation coefficient between isotope composition of bulk carbonates and size fractions.

r	Bulk vs (<25)	Bulk vs (25-63)	Bulk vs (63-125)	Bulk vs (125-250)	Bulk vs (>250)
δ ¹³ C	0.98	0.80	0.86	0.70	0.63
δ ¹⁸ Ο	0.70	0.20	0.23	0.15	0.19

Supplementary Table 6. Relation (r^2) between bulk carbonate- and size fraction $\delta^{13}C$ at three intervals, pre-PETM, at PETM and post-PETM.

r^2	Bulk vs (<25)	Bulk vs (25-	Bulk vs (63-125)	Bulk vs (125-250)	Bulk vs (>250)
		63)			
Pre-PETM	0.98	0.14	0.01	0.13	1
PETM	1	1	1	1	1
post-PETM	0.95	0.85	0.76	0.44	0.97

Supplementary Figure S1



S1. Map showing location of Shatsky Rise in north-central Pacific, Walvis Ridge in south Atlantic and Cicogna section in Italy (paleo-Tethys). This map was generated at https://www.odsn.de/odsn/services/paleomap/paleomap.html.



S2. Difference between weight of original bulk sample and the summed weights of size fractions. Upon sample washing, sieving, drying and settling, there is an average sample loss of about 5%. Highlighted data points show error bars ranging 1σ , calculated from replicate analysis.

44 Supplementary Figure S3



45

46

47 **S3**. Stereoscopic images of representative samples' size fractions. The fine fraction appears lumpy because they retain more moisture and have colloidal properties. (See Text T1).

>250 µm





S4. SEM images of representative samples' size fractions as seen under scanning electron microscope. Three samples from before PETM, at PETM and after PETM intervals show the decrease in benthic foraminiferal abundance and increase in spinose planktonic foraminiferal abundance across PETM.

Supplementary Figure S5 54



S5. Weight percent (WP) of size fractions. Panel A shows changes in WP fine fraction, intermediate Fraction and coarse fraction with time, between 58- and 50 Ma. Panel B similarly shows three subdivisions of WP of coarse fractions. 56





fractions.

61 **Text T1**

62	Change in mass after sediment rinsing
63	The weights of dry samples ($Wt_{dry sample}$) and individual size fractions after were measured. The sum of weights of five size fractions ($\Sigma_i Wt_i$) were then compared wi
64	Sample loss after rinsing= $Wt_{dry sample} - \Sigma_i Wt_i$ (1)
65	i= <25 μ m, 25-63 μ m, 63-125 μ m, 125-250 μ m and >250 μ m
66	On an average 5% sample loss is recorded (Supplementary Figure S2). Wet sieve separation process of rinsing sediment samples inevitably always causes some
67	lower mass and higher settling times (Reghellin et al, 2015). Sample weight loss can also be attributed to presence of salts in marine sediments (Kendrick, 2018) which are of salts (Kendrick, 2018)
68	However, occasionally our data shows $\Sigma_i Wt_i > Wt_{dry sample}$. This is because extra moisture could have been present in the fine fractions during weight measurement
69	clays get incorporated in the fine fractions, whose colloidal properties results in moisture retention (Meyer, 1934).
70	
71	Text T2
72	Correlation between bulk carbonate- and size fraction $\delta^{13}C$ and $\delta^{18}O$
73	The correlation coefficient (r) between bulk carbonate- and size fractions δ^{13} C and δ^{18} O are displayed in Table 5 .
74	Readily clear, δ^{13} C values of bulk carbonate and size fractions show greater correlation than δ^{18} O. Fine fraction and bulk carbonates show maximum correlation. Fin
75	any change in δ^{13} C in the fines will be almost equally reflected in bulk carbonate, resulting in their excellent correlation.
76	Important to note here, that a study by Hupp et al. (2019) suggested a possible role of size dependent sediment mixing in controlling the stratigraphic position of CIE
77	precise timing of a CIE e.g. PETM, in the stratigraphic record at any open marine setting. In our study at Site 1209, such an effect is not altering any implications because
78	much lower sampling resolution before, at and after the CIE, compared to that by Hupp et al. (2019), and do not emphasize on the exact timing of PETM here, rather we
79	δ^{13} C before, at and after PETM. Second, when we compare r ² values of individual size fraction δ^{13} C and bulk carbonate δ^{13} C at three different intervals: before PETM,
80	carbonate - fine fraction and bulk carbonate - >250 μ m size fractions is significantly higher than the others. There is no gradational increase in r ² values between bulk carbonate
81	the scale and perspective at which we conduct this study, taphonomic effects are not being considered further.
82	
83	References
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ith starting weight for each sample, using the following relation:

sample loss. The loss is higher for fine fractions, because of their dissolved during wet sieve separation process.

nts. The fine fractions require more time for drying. This is because

ne fractions comprise a major portion of bulk carbonates, and hence

E at Site 690. Such an effect is highly relevant when determining the e, first, the study we present here extends from 58- to 50 Ma, with a explore contributions of size fractions in controlling bulk carbonate at PETM and after PETM (**Table 6**), we find that r^2 between bulk rbonate and increasing size of the sediment fractions. Therefore, for

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