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Orbital phasing of the Paleocene-Eocene Thermal Maximum

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21 Highlights

- Orbital controls influenced Paleocene-Eocene Thermal Maximum triggering.
- The Paleocene-Eocene Thermal Maximum appeared close to a long eccentricity
 maximum.

The Paleocene-Eocene Thermal Maximum appeared close to a short eccentricity
 maximum.

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The Paleocene-Eocene Thermal Maximum contained multiple lysocline shoaling events.

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30 Abstract

31 Paleocene-Eocene sedimentary archives record a series of global warming events called 32 hyperthermals. These events occurred across a long-term increasing temperature trend and 33 were associated with light carbon injections that produced carbon isotope excursions (CIEs). 34 Early Eocene hyperthermals occurred close to both long (~405 kyr) and short (~100 kyr) 35 eccentricity maxima. It has been proposed that under long-term global warming, orbital 36 forcing of climate crossed a thermodynamic threshold that destabilized carbon reservoirs and 37 produced Early Eocene hyperthermals. However, orbital control on triggering of the largest hyperthermal, the Paleocene-Eocene Thermal Maximum (PETM), remains unclear. 38 39 Identification of the precise orbital phasing of the PETM has been hindered by extensive 40 calcium carbonate (CaCO₃) dissolution, which introduces uncertainty into PETM age models. 41 Here, we report orbital signatures in marine sediments from Contessa Road (Italy), a western 42 Tethyan section with reduced PETM CaCO₃ dissolution compared to other deep ocean sites. 43 Orbitally controlled lysocline depth adjustments and orbital phasing of the PETM CIE onset 44 close to both long and short eccentricity maxima are documented here. Precession-based age 45 models from the well-resolved PETM section of Ocean Drilling Program (ODP) Site 1262 46 (South Atlantic) confirm these results and reveal that the PETM CIE onset was partially triggered by an orbitally controlled mechanism. Climate processes associated with orbital 47 forcing of both long and short eccentricity maxima played an important role in triggering the 48 49 carbon cycle perturbations of all Paleocene-Eocene CIE events.

50 Keywords: Paleocene-Eocene Thermal Maximum (PETM), orbital control, CaCO₃
51 dissolution, long eccentricity maximum, short eccentricity maximum.

52 **1. Introduction**

53 Late Paleocene-early Eocene climate records (~58-52 Ma) contain evidence of a series of light carbon injections that produced negative carbon isotope excursions (CIEs) (Cramer et 54 55 al., 2003; Zachos et al., 2010; Westerhold et al., 2020). Some of these short-lived (<200 kyr) carbon cycle perturbations were associated with global warming events called hyperthermals 56 57 (Cramer et al., 2003; Zachos et al., 2010). The Paleocene-Eocene Thermal Maximum 58 (PETM, ~56 Ma) was the largest hyperthermal, and was followed by early Eocene 59 hyperthermals-i.e., the Eocene Thermal Maximum (ETM) 2 (~54 Ma) and ETM 3 (~53 Ma)-60 and smaller carbon cycle perturbations-i.e., the H2, I1 and I2 events (Lourens et al., 2005; 61 Westerhold et al., 2007; Zachos et al., 2010; Zeebe and Lourens, 2019). All of these events occurred across a long-term increasing temperature trend (Westerhold et al., 2020). Under 62 63 gradual long-term warming and orbital forcing of long (~405 kyr) and short (~100 kyr) 64 eccentricity maxima, climate is thought to have crossed a thermodynamic threshold that destabilized carbon reservoirs and triggered light carbon releases to the climate system (Fig. 65 1a; Lunt et al., 2011; DeConto et al., 2012; Kirtland Turner et al., 2014). This driving 66 67 mechanism explains the origins of early Eocene hyperthermals, all of which appeared close to 68 long eccentricity maxima (Galeotti et al., 2010; Zachos et al., 2010; Kirtland Turner et al., 69 2014; Laurin et al., 2016). However, the influence of this orbitally controlled mechanism on 70 PETM CIE triggering remains unclear.

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The PETM had a ~170-220 kyr duration that has been related to at least two light carbon
injections (Röhl et al., 2000, 2007; Murphy et al., 2010; Westerhold et al., 2018; Zeebe and
Lourens, 2019; van der Meulen et al., 2020). The initial PETM light carbon injection has

75 been partially interpreted to have resulted from thermogenic methane releases associated with North Atlantic Igneous Province activity (Svensen et al., 2004; Sluijs et al., 2007; Kender et 76 77 al., 2021). Volcanic activity has been suggested to have promoted widespread warming 78 before the PETM, which may have subsequently destabilized carbon reservoirs and triggered 79 the PETM CIE (Sluijs et al., 2007; Frieling et al., 2019; Kender et al., 2021). However, North 80 Atlantic Igneous Province activity was reduced at the PETM CIE onset (Kender et al., 2021), which suggests that additional positive carbon cycle feedbacks, likely related to other 81 82 mechanisms-i.e., orbitally controlled processes (Lourens et al., 2005; Lunt et al., 2011; 83 DeConto et al., 2012; Zeebe and Lourens, 2019)-may have also played a role in PETM CIE 84 triggering.

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86 Carbon releases following the PETM CIE onset produced a long (>100 kyr) lysocline shoaling event with extensive calcium carbonate (CaCO₃) dissolution (Fig. 1b; Zeebe et al., 87 2009; Zeebe, 2013; Bowen, 2013; Frieling et al., 2016; Lyons et al., 2019). This prolonged 88 89 CaCO₃ dissolution interval has not been identified in succeeding early Eocene CIEs. Some 90 early Eocene carbon cycle perturbations were paired events associated with two different 91 carbon injections. These carbon releases caused CaCO₃ dissolution layers that coincided with 92 consecutive maxima of short eccentricity cycles-i.e., the ETM 2 and H2, and I1 and I2 93 events (Cramer et al., 2003; Zachos et al., 2010; Laurin et al., 2016; Westerhold et al., 2018). 94 Extensive PETM CaCO₃ dissolution produced poor recording of orbitally controlled CaCO₃ 95 dissolution cycles in marine sediments, which has affected the accuracy of Paleocene-Eocene 96 astrochronological age models and hindered assessments of orbital controls on PETM CIE 97 triggering.

99 The PETM CaCO₃ dissolution interval duration has been debated due to limitations of astrochronological age models and temporal differences of lysocline depth variations at 100 101 diverse locations (Zeebe et al., 2009). Age model calibrations have been carried out to 102 estimate the PETM CaCO₃ dissolution interval duration at the well-resolved PETM section from the South Atlantic Ocean Drilling Program (ODP) Site 1262 (Fig. 1c; ~3600 m 103 104 paleowater depth). A ~120 kyr duration for the PETM CaCO₃ dissolution interval at ODP Site 1262 was estimated using precession-based age models and age calibrations between 105 106 terrestrial and marine records (Zachos et al., 2005; Aziz et al., 2008; Westerhold et al., 2018; 107 van der Meulen et al., 2020). Alternatively, orbital tuning of ODP Site 1262 records to the 108 recent ZB18a astronomical solution (Zeebe and Lourens, 2019) indicates a 170 \pm 30 kyr 109 duration for the same time interval, despite uncertain astronomical solutions beyond ~50 Ma 110 (e.g., Laskar et al., 2004; Zeebe and Lourens, 2019). These Paleocene-Eocene chronologies reveal a period of CaCO₃-rich sedimentation, enhanced CaCO₃ burial, and carbon 111 112 sequestration following the PETM CaCO₃ dissolution interval (Kelly et al., 2010; Luo et al., 113 2016; Penman et al., 2016). However, differences among Paleocene-Eocene age models 114 hinder identification of orbital phasing in relation to the PETM CIE onset. The PETM CIE 115 onset has been suggested to lie close to a long eccentricity maximum (Lourens et al., 2005; 116 Galeotti et al., 2010; Zeebe and Lourens, 2019) or with a quarter of a period offset after a 117 long eccentricity maximum (Westerhold et al., 2007). These contrasting interpretations do not 118 allow clear recognition of the possible influence of an orbitally controlled driving mechanism 119 on PETM CIE triggering.

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Marine sedimentary sections with reduced PETM $CaCO_3$ dissolution may preserve better orbital signals across the PETM $CaCO_3$ dissolution interval, which might enable more accurate estimation of the duration of this interval. Orbital signals from these locations are 124 accompanied by amplitude modulation (AM) and frequency modulation (FM) patterns (see 125 Materials and methods) that can refine Paleocene-Eocene chronologies and reveal orbital 126 phasing of the PETM CIE onset. Modeling experiments suggest that Tethys Ocean sediments 127 experienced less extensive PETM CaCO₃ dissolution compared to other locations (Zeebe et al., 2009). These results are confirmed by PETM records from the western Tethyan Contessa 128 129 Road section, Italy (Fig. 1c-d; ~1000-1500 m paleowater depth). Two marly horizons separated by a limestone layer cover the PETM CaCO₃ dissolution interval at Contessa Road 130 131 (Fig. 2a-b; Galeotti et al., 2000; Giusberti et al., 2009; Galeotti et al., 2010). The lowest 132 CaCO₃ contents across the first and second Contessa Road marly horizons are ~35% and 133 ~65%, respectively (Fig. 2c; Giusberti et al., 2009), which contrast with CaCO₃ values from 134 other marine sections that are close to 0%-i.e., ODP Site 1262 (Fig. 1b; Zachos et al., 2005). 135 Here, we use the exceptionally well-preserved PETM records from Contessa Road to 136 constrain the PETM CaCO₃ dissolution interval duration at this section. We assess AM and 137 FM patterns in orbital signals from Contessa Road to identify orbital phasing of the PETM 138 CIE onset. We also generate a probabilistic estimate of orbital phasing of the PETM CIE 139 onset using a new refined chronology for ODP Site 1262, which provides a broader 140 perspective on the orbital configuration in which the PETM CIE onset occurred.

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142 **2. Materials and methods**

143 2.1 Amplitude and frequency modulation

Astrochronological age models, and associated AM and FM patterns of precession and short eccentricity can help to reveal orbital phasing of the PETM. These approaches are independent of uncertain astronomical solutions beyond ~50 Ma (Laskar et al., 2004; Zeebe and Lourens, 2019). Orbital precession (~21 kyr) and short eccentricity are tied to short and long eccentricity phases, respectively (Berger and Loutre, 1991). Hence, AM of precession 149 and short eccentricity indicate cyclicity in their signal modulators (Laurin et al., 2005, 2016, 150 2021; Meyers et al., 2015). These modulations include orbital components of 19 and 23 kyr 151 for precession, and 95 and 124 kyr for short eccentricity (Laskar et al., 2004). Systematic 152 shifts in frequencies of orbital components are described as FM patterns (Laurin et al., 2016, 2021). FM defines positive and negative interference of orbital frequencies in wavelength 153 154 components of evolutive harmonic analysis (EHA) (Rial, 1999; Meyers et al., 2001; Laurin et al., 2016). Negative interference of FM is associated with bifurcations of wavelength 155 156 components, which indicates minimal conditions of the modulator-i.e., bifurcations of 157 precession components (known as P1 and P2) reveal short eccentricity minima, and 158 bifurcations of short eccentricity components (known as E2 and E3) indicate long eccentricity 159 minima (Laurin et al., 2016). In contrast, positive interference of FM, which is identified by 160 junctions of wavelength components, suggests modulator maxima-i.e., junctions of precession components reveal short eccentricity maxima and junctions of short eccentricity 161 162 components indicate long eccentricity maxima (Laurin et al., 2016).

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164 2.2 Contessa Road

The Contessa Road section (lat. 43°22'47''N; long. 12°33'50''E) exposes Paleocene-Eocene 165 166 rocks of the Scaglia Rossa Formation (Galeotti et al., 2000, 2010). This sedimentary unit 167 consists of reddish limestones and marls that were deposited in the western Tethyan Umbria-168 Marche Basin (Giusberti et al., 2009). Contessa Road sedimentation mainly consisted of 169 pelagic CaCO₃ deposition with minimal detrital mineral inputs from northern Africa and southwestern Europe (Fig. 1d; Coccioni et al., 2019). The detrital fraction of Contessa Road 170 171 carbonates includes quartz, hematite, barite, magnetite, and clay minerals (Giusberti et al., 172 2009; Galeotti et al., 2010; Coccioni et al., 2019). However, some studies have hypothesized that magnetite and barite are biomineralization products (Giusberti et al., 2009; Coccioni etal., 2019).

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176 Contessa Road has well-developed magnetostratigraphic and biostratigraphic age constraints that allowed identification of the Cretaceous/Paleogene boundary. This major geological 177 178 event has been assigned as 0 m depth at Contessa Road (e.g., Galeotti et al., 2000, 2010), and was followed by an extensive record of Paleocene-Eocene carbon cycle perturbations that 179 180 mainly appeared between Chron 25n and 24n.1n, and between calcareous nannofossil zones NP8/NP9 and NP11 (Fig. 2a; Galeotti et al., 2010; Coccioni et al., 2019). These age 181 182 constraints correspond to the 26-46 m depth interval at Contessa Road, which contains 183 multiple CaCO₃ dissolution horizons that have been associated with Paleocene-Eocene 184 carbon cycle perturbations (Fig. 2a; Galeotti et al., 2000, 2010). The CaCO₃ dissolution 185 layers have also been used to generate early Eocene cyclostratigraphic frameworks that are interpreted to indicate orbital control on CaCO3 dissolution cycles (Galeotti et al., 2010). 186 187 Orbital control of CaCO₃ sedimentation has been identified from inverse relationships between CaCO₃ and terrigenous input indicators-i.e., magnetic susceptibility (Galeotti et al., 188 189 2010; Francescone et al., 2018); however, orbital controls have not been assessed for the 190 Contessa Road PETM record. Contessa Road presents anti-correlation of quartz and CaCO₃ 191 records, which is interpreted to indicate that siliciclastic sedimentation depended exclusively 192 on continental detrital inputs (Giusberti et al., 2009) with no important biogenic Si 193 contribution.

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195 Paleocene-Eocene carbon cycle perturbations recorded in the Scaglia Rossa Formation appear 196 in different outcrops across Contessa Road. The outcrop that contains the ~30-33 m interval 197 of this section has two marly horizons separated by a limestone layer within magnetochron 198 C24r and calcareous nannofossil biozone NP10, which allowed recognition of the PETM 199 CaCO₃ dissolution interval at Contessa Road (Fig. 2a-c; Galeotti et al., 2000, 2010). Previous 200 and succeeding CIE events are identified in other outcrops (e.g., Galeotti et al., 2010). PETM 201 marly layers at Contessa Road resulted from lysocline shoaling events that brought about different faunal changes (Giusberti et al., 2009). These lysocline shoaling events were 202 203 separated by a lysocline deepening period that is indicated by limestones (Fig. 2b; Galeotti et 204 al., 2000; Giusberti et al., 2009). The first marly horizon coincides with the PETM CIE onset 205 ~31.26 m above the Cretaceous/Paleogene boundary. The PETM CIE onset is followed by low stable carbon isotope (δ^{13} C) values that started increasing during the second PETM marly 206 207 layer (Fig. 2d; Giusberti et al., 2009).

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209 2.3 X-ray fluorescence measurements

For this study, we sampled the PETM outcrop at Contessa Road (30-33 m interval) 210 211 continuously at 1-cm resolution for X-ray fluorescence (XRF) analyses. Samples were cut to 212 expose flat surfaces for measurements. These were made using a third generation Avaatech 213 XRF Core Scanner at 10 kV (current = 0.5 mA, count time = 60 s, and no filter) with a 16 214 mm² sample area. XRF data were acquired using a Canberra X-PIPS silicon drift detector. 215 Samples were cleaned before measurement and were fixed over plastic holders for discrete 216 measurement of each sample. Sample spacing in the core scan table was 20 cm to avoid 217 interference between measurements. Contessa Road carbonate samples are lithified and do 218 not release dust when in contact with the detector. Analyses of raw X-ray spectra were made 219 by iterative least squares analysis in the Win Axil software from Canberra Eurisys. Standards 220 were run multiple times between measurement sets to test measurement reliability, and to 221 identify possible detector contamination. 105 replicate measurements were carried out for 222 probabilistic uncertainty assessment. Standard deviation (1σ) of these measurements correspond to 2.7%, 1.6%, and 3.0% for Fe, Ca, and Si, respectively. All experiments were
performed at the Australian National University.

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226 2.4 Probabilistic uncertainty assessments and spectral analysis of Contessa Road records

Probabilistic uncertainty assessments for Contessa Road Fe, Ca, and Si records were used to 227 228 develop astrochronological age models using Monte Carlo simulations. Initially, logarithmic 229 transformation was applied to Fe and Si records to minimize the effects of large variability 230 between the marly interval and pre-marly and post-marly intervals. Logarithmic 231 transformation has also been applied to different Paleocene-Eocene XRF records from 232 pelagic carbonate sections (e.g., Westerhold et al., 2007), which indicates that logarithmic 233 transformation allows clear recognition of orbitally controlled CaCO₃ dissolution cycles. 234 Then, Fe, Ca, and Si records were assigned standard deviations (1σ) . A standard deviation 235 (1σ) was assigned for depth as half the spacing between successive samples $(1\sigma = 0.5 \text{ cm for})$ 236 XRF data), and standard deviations (1σ) for XRF data were estimated for each element using 237 replicate measurements. Individual data points were sampled randomly within their 238 uncertainties. 10,000 Monte Carlo simulations were produced to generate empirical distributions from which the mean and standard error (SE) were estimated at each depth. To 239 240 avoid depth reversals, the stratigraphic order of samples was reviewed after Monte Carlo 241 simulations. Mean and SE were then interpolated to fixed depth points.

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To carry out spectral analysis of Contessa Road records, Fe, Ca, and Si records were detrended with a locally estimated scatterplot smoothing (LOESS) filter that uses 35% of the entire record length for each local regression window. Data variability indicates that detrending should be carried out via subtraction of non-parametric, rather than parametric, trends (*see Results*; Fig 2e-g). Power spectra were generated using the Fast Fourier transform 248 (FFT) and discrete Fourier transform (DFT) routines of the Power Spectrum VI function of 249 LabView 2019. The power spectrum S_{xx} (*f*) of a function *x*(*t*) is indicated by:

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$$S_{xx}(f) = X(f)X(f)^* = |X(f)|^2,$$

251 where X(f) is the Fourier transform (F) product of x(t), and $X(f)^*$ indicates the complex 252 conjugate of X(f). The Power Spectrum VI function of LabView 2019 produces similar 253 power spectra to those obtained using the periodogram and multi-taper methods in the Acycle 254 software (Li et al., 2019), which validates our approach (see Supplemental information). Spectral analyses of detrended records were made for each Monte Carlo iteration, which 255 256 enables generation of empirical distributions from which the mean and SE were estimated. 257 Data were then reviewed to avoid reversals and interpolated to fixed frequencies which 258 allowed production of probabilistic-based power spectra for Contessa Road XRF records.

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First-order order autoregressive (AR1) processes were fitted to the background mean power spectrum using a Monte Carlo approach (Li et al., 2019; Husson, 2022). This method allowed estimation of 90% and 95% confidence levels from the AR1 fits. The power spectrum of the AR1 process for a frequency f is indicated by:

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$$S(f) = S_0 \frac{1 - \rho_1^2}{1 - 2\rho_1 \cos \pi(\frac{f}{f_N}) + \rho_1^2}$$

where f_N is the Nyquist frequency and the average value of a power spectrum related to the white-noise variance (S₀) is given by:

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$$S_0 = \frac{\sigma^2}{1 - \rho_1^2}$$

268 where ρ_1 corresponds to the lag-one autocorrelation coefficient, and σ^2 is the variance of a 269 white-noise sequence ε (Mann and Less, 1996).

271 Frequency components associated with orbital signals from probabilistic-based power spectra 272 were isolated using Gaussian bandpass filters also using LabView 2019. Each Monte Carlo 273 iteration from detrended records was filtered, which allowed generation of empirical 274 distributions from which the mean and SE were estimated. The stratigraphic order of samples was reviewed after Monte Carlo simulations to avoid depth reversals and data were then 275 276 interpolated to fixed depth points. This process allowed isolation of probabilistic-based filtered orbital signals such as mean short eccentricity and mean precession with their 277 278 respective uncertainty envelopes (2SE).

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EHA (Meyers et al., 2001; Laurin et al., 2016, 2021) was carried out using the Fast Fourier Transform LAH (FFT LAH) method within the Acycle software (Li et al., 2019). Sliding windows that move in consecutive steps are used for EHA estimation. Details of the values used for sliding windows and steps in each analysis are given in the respective figure captions.

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286 2.5 Contessa Road age models and AM patterns

Filtered mean precession and short eccentricity signals were used to identify AM patterns 287 288 using the Amplitude Modulation tool of the Acycle software (Li et al., 2019). Filtered mean 289 precession signals of the different XRF records were also used to produce astrochronological 290 age models. Each precession cycle was assigned a 21 kyr period to produce a different 291 chronology for each Contessa Road XRF record. Filtered precession signals from Contessa 292 Road contain uncertainty envelopes that result from the error propagation. However, only the 293 filtered mean precession signals were used for Contessa Road age model development. All 294 datasets from Contessa Road were transferred into the time domain and were then set to 0 at the PETM CIE onset. Contessa Road records were then interpolated every 2.5 kyr, whichcorresponds to the average age spacing between samples, to produce age-domain EHA.

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298 **3. Results**

299 3.1 Orbital signatures of the Contessa Road records

300 PETM marly layers, and thinner horizons with partial CaCO₃ dissolution, coincide with Fe 301 and Si concentration increases and Ca reductions at Contessa Road (Fig. 2e-g). Depth-domain 302 EHA of XRF records reveal a dominant wavelength component that has a frequency range of ~2 cvcles m⁻¹ across pre-PETM and post-PETM limestones, and a frequency range of ~3.5 303 304 cycles m⁻¹ across the PETM marly horizons (dashed white lines; Fig. 2c-f). This wavelength 305 component variation suggests sedimentation rate changes across Contessa Road (see below); 306 therefore, to avoid impacts from sedimentation rate variations on the time-series, we divided 307 the Contessa Road record into pre-marly (30.00-31.25), marly (31.20-31.75 m), and post-308 marly (31.70-33.00 m) intervals (Fig. 2b-g) and performed spectral analysis on each segment. 309

310 Power spectra of Fe, Ca, and Si records contain spectral peaks with means that exceed the 311 95% confidence level (Fig. 3). This indicates that on average Monte Carlo iterations of these 312 time series contain statistically significant components (Mann and Lees, 1996). 313 Magnetochron C24r had a ~3.2 Myr duration and is recorded over a ~12.6-m interval at the 314 Contessa Road section (Galeotti et al., 2010; Francescone et al., 2018). Therefore, an average sedimentation rate of ~0.4 cm kyr⁻¹ for C24r at Contessa Road can be estimated. Spectral 315 316 analysis of the whole Contessa Road section indicates spectral peaks with ~0.36 m, ~0.09 m, and ~ 0.07 m periods. These peaks correspond to, based on the average sedimentation rate, 317 318 ~90 kyr, ~22 kyr, and ~17 kyr periods, respectively (Fig. 3a), and can be associated with 319 short eccentricity and precession. Other spectral peaks with frequencies between ~5 and 10 320 cycles m⁻¹ exceed the 95% confidence level in power spectra for the entire Contessa Road 321 section; however, these spectral peaks are not regularly identified in power spectra for the 322 respective Contessa Road pre-marly, marly, and post-marly intervals. Hence, signals 323 associated with these peaks are not discussed further.

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325 The pre-marly and post-marly intervals have similar compositional characteristics, and wavelength component frequencies (Fig. 2b-g). Therefore, spectral peak periods for these 326 intervals were estimated using an average ~ 0.4 cm kyr⁻¹ sedimentation rate. Considering this 327 328 average sedimentation rate, our 1-cm sampling resolution corresponds to an average sample 329 spacing of ~2.5 kyr, which indicates a ~300 kyr duration for each interval. Spectral peaks 330 with ~0.42 m and ~0.43 m periods for the pre-marly and post-marly intervals, respectively, 331 can be attributed to short eccentricity due to their ~100-kyr periods (Fig. 3b, d). We note, 332 however, that short eccentricity in the post-marly interval is weak in the Ca and Si records and do not reach the 95% confidence level (Fig. 3d). Spectral peaks with ~0.09 m periods in 333 334 the pre-marly and post-marly intervals can be related to precession because of their ~22 kyr 335 periods (Fig. 3b, d). The marly interval has spectral peaks with ~0.29 m and ~0.06 periods (Fig. 3c). Periodicity variations of the dominant spectral peaks of the marly, pre-marly and 336 337 post-marly intervals (a spectral peak with a ~0.29 m period versus spectral peaks with ~0.42-0.43 m periods) suggest a sedimentation rate drop. The ~1.5 cycles m^{-1} difference of the 338 339 dominant wavelength component between PETM marly horizons and pre-PETM and post-340 PETM limestones (Fig. 2e-g) confirms this assumption. These frequency changes in spectral 341 peaks and wavelength components allow estimation of a sedimentation rate drop due to PETM CaCO₃ dissolution from ~0.4 cm kyr⁻¹ to ~0.3 cm kyr⁻¹ across the marly interval. This 342 343 estimate indicates a ~3.3 kyr sample spacing across the marly interval, which reveals a ~180 kyr duration for this interval. Considering the reduced sedimentation rate, spectral peaks in 344

345 the marly interval indicate cycles with ~94 kyr and ~23 kyr periods that can be related to 346 short eccentricity and precession, respectively (Fig. 3b-d).

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348 Gaussian bandpass filters with bandwidths of $2.38 \pm 1.20 (1\sigma)$ cycles m⁻¹ (~70-210 kyr), 3.56 \pm 1.20 cycles m⁻¹ (~70-141 kyr), and 2.29 \pm 1.20 cycles m⁻¹ (~70-230 kyr) for the pre-marly, 349 350 marly, and post-marly intervals, respectively, were used to isolate short eccentricity signals. 351 Short eccentricity signals were isolated for the Ca and Si records for the post-marly interval 352 despite their poorly developed short eccentricity signal. Comparisons of probabilistic power 353 spectra to periodograms of these records (see Supplementary information) indicate that the Si 354 record contains a statistically significant peak that can be associated with short eccentricity in 355 the post-marly interval. The Ca record in the post-marly interval periodogram also contains a 356 week short eccentricity signal (see Supplementary information); however, the well-identified 357 anti-correlation between Fe and Ca indicated by probabilistic uncertainty assessments (Fig. 358 2e-f) and filtered short eccentricity signals (Fig. 4a-b) reveal that the Contessa Road Ca 359 record may also contain short eccentricity signals in the post-marly interval. Nevertheless, 360 our interpretations of Ca in the post-marly interval do not depend exclusively on this record 361 because we also compare the filtered short eccentricity signal of Fe and Si. Precession signals were extracted using Gaussian bandpass filters with bandwidths of 11.10 ± 3.70 cycles m⁻¹ 362 $(\sim 17-34 \text{ kyr})$, $14.25 \pm 5.00 \text{ cycles m}^{-1}$ ($\sim 17-36 \text{ kyr}$), and $11.45 \pm 3.50 \text{ cycles m}^{-1}$ ($\sim 17-31 \text{ kyr}$) 363 for the pre-marly, marly, and post-marly intervals, respectively. Application of such wide 364 365 Gaussian bandpass filters was based on short eccentricity and precession periodicities and 366 ensures that all short eccentricity and precession components were captured. Isolated orbital 367 signals have good visual correlation with detrended records (Fig. 4, 5a, c, e), which validates 368 the consistency of the Gaussian bandpass filter bandwidths.

370 **4. Discussion**

371 3.1 Duration of the PETM CaCO₃ dissolution interval at Contessa Road

372 The inverse relationship between filtered orbital signals from Ca and detrital elements reflects 373 previously identified orbitally controlled CaCO₃ dissolution cycles at Contessa Road (Fig. 5; Galeotti et al., 2010). The PETM CIE onset at this section coincided with a lysocline shoaling 374 375 event that caused partial CaCO₃ dissolution over a ~42 kyr duration (precession cycles 0 and 1 in Fig. 5a, c, e). This event was followed by a lysocline deepening period that reestablished 376 377 pre-PETM CaCO₃-rich sedimentation (Fig. 5c; Giusberti et al., 2009). Fe and Si records 378 indicate that the PETM lysocline deepening at Contessa Road lasted nearly three precession 379 cycles (precession cycles 2, 3, and 4 in Fig. 5a, e). Alternatively, orbital signals extracted 380 from the Ca record reveal poor development of precession cycle 3, which suggests that only 381 two precession cycles covered this interval (precession cycles 2 and 4 in Fig. 5c). This 382 lysocline deepening period at Contessa Road was punctuated by a second, less extensive, lysocline shoaling event (Giusberti et al., 2009) that spanned one and a half precession cycles 383 384 (precession cycles 5 and 6 in Fig. 5a, c, e). After this second partial CaCO₃ dissolution 385 interval, pre-PETM CaCO₃-rich sedimentation was reestablished, and extensive PETM CaCO₃ dissolution ended. Considering differences between filtered precession signals at 386 387 Contessa Road, we estimate that the PETM CaCO₃ dissolution interval lasted ~5.5-6.5 388 precession cycles at this section.

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390 *3.2 Was the PETM close to a short eccentricity maximum?*

391 Orbital signals within Contessa Road pelagic carbonates allow clear recognition of AM and 392 FM patterns. AM of precession (purple dashed lines in Fig. 5a, c, d) correlates relatively well 393 with filtered short eccentricity signals. However, this relationship is less clear between 394 precession cycles 8 and 12 (Fig. 5a, c, e). Considering a ~116-137 kyr PETM CaCO₃ 395 dissolution interval duration, and a total PETM duration of ~170-220 kyr (Röhl et al., 2007; 396 Murphy et al., 2010; Westerhold et al., 2018; Zeebe and Lourens, 2019; van der Meulen et 397 al., 2020), cycles 8 to 12 coincide with a carbon sequestration period with enhanced CaCO₃ 398 burial. This interval records accelerated CaCO₃-rich sedimentation that may have been 399 related partially to either accelerated chemical weathering (Kelly et al., 2010; Penman et al., 400 2016) and/or biological carbonate compensation (Luo et al., 2016), which are non-orbitally 401 controlled processes that may have slightly disturbed AM patterns. Alternatively, FM 402 patterns obtained from filtered precession signals reveal two precession components (P1 and 403 P2; Fig. 5) that indicate negative interference patterns associated with short eccentricity 404 minima between precession cycles 7 and 9, and between precession cycles 13 and 14 (Fig. 5). 405 These patterns correlate well with filtered short eccentricity signals, which clarifies the 406 orbital configuration across this interval of enhanced CaCO₃ burial and carbon sequestration. 407

408 FM patterns allow recognition of the orbital phasing of PETM marly horizons at Contessa 409 Road. Junctions of the P1 and P2 components reveal that these layers appeared close to short 410 eccentricity maxima (Fig. 5b, d, f). Well-developed AM of precession and filtered short 411 eccentricity signals confirm this observation, and indicate that the PETM marly horizons 412 occurred in ascending flanks of short eccentricity cycles, close to short eccentricity maxima 413 (Fig. 5a, c, e). The CaCO₃-rich sedimentation interval that separates the PETM marly 414 horizons at Contessa Road coincided with a short eccentricity minimum, which is identified 415 by negative interference of P1 and P2 components, AM of precession, and filtered short 416 eccentricity signals (Fig. 5). These patterns reveal orbital controls on lysocline depth 417 variations, which promoted development of the same sedimentation patterns as other early 418 Eocene CIE events at Contessa Road-i.e., the ETM 2 and H2 events (Galeotti et al., 2010). 419 This evidence also suggests that the PETM marly horizons at Contessa Road had a similar 420 orbital phasing as other early Eocene hyperthermals in terms of short eccentricity (Zachos et421 al., 2010).

422

423 Identification of orbital phasing of the PETM with respect to short eccentricity has been also assessed at ODP Site 1262 (Westerhold et al., 2007; Zachos et al., 2010). Orbital signals from 424 425 ODP Site 1262 redness over greenness (a*) and Fe records have increased values preceding the PETM, which has been used to suggest that the PETM CIE onset likely coincided with a 426 427 short eccentricity maximum (Zachos et al., 2010). Orbitally controlled lysocline depth 428 variations recorded by Contessa Road pelagic carbonates allow recognition of the orbital 429 phasing of the PETM CIE onset with respect to short eccentricity. This event, according to 430 AM of precession patterns, preceded a short eccentricity maximum by half a precession cycle 431 (Fig. 5a, c, e). Alternatively, if only filtered short eccentricity signals are considered, the 432 PETM CIE occurred one precession cycle before a short eccentricity maximum (Fig. 5a, c, e). 433 This evidence suggests that the PETM CIE onset may have appeared only ~11-21 kyr before 434 a short eccentricity maximum, which confirms orbital phasing of the PETM CIE onset close 435 to a short eccentricity maximum (Zachos et al., 2010).

436

437 *3.3 Was the PETM close to a long eccentricity maximum?*

438 Spectral analyses of Contessa Road records do not allow extraction of long eccentricity 439 signals; however, AM and FM patterns of short eccentricity help to identify orbital phasing of 440 the PETM CIE onset with respect to long eccentricity. AM of short eccentricity indicates that 441 the PETM CIE onset appeared in the ascending flank of a long eccentricity cycle, close to a 442 long eccentricity maximum (dashed red line in Fig. 5a, c, e). Irregular AM patterns of short 443 eccentricity cycles between different Contessa Road records hinder accurate numerical 444 estimation of the PETM CIE onset with respect to long eccentricity. Depth-domain EHA of filtered short eccentricity signals reveal that the PETM CIE onset coincided with positive interference of two short eccentricity components (E2 and E3; Fig. 6a-c), which is a common pattern of long eccentricity maxima (Laurin et al., 2016) that confirms orbital phasing of the PETM CIE onset close to a long eccentricity maximum.

449

450 Age-domain EHA of detrended Contessa Road records reveal two short eccentricity components (E2 and E3; Fig. 6d-f) that allow identification of negative interference ~200-451 452 300 kyr after the PETM onset (Fig. 6d-f). Recognition of the long eccentricity minimum 453 associated with these FM patterns is hindered by signal distortion, which is likely related to 454 enhanced CaCO₃ sedimentation following the PETM CaCO₃ dissolution interval (Kelly et al., 455 2010; Luo et al., 2016; Penman et al., 2016). In contrast, well-developed negative 456 interference of E2-E3 components before the PETM allow better recognition of long eccentricity minima. Bifurcations of short eccentricity components reveal a long eccentricity 457 minimum between ~-170 and ~-240 kyr (Fig. 6d-f), which indicates a long eccentricity 458 459 maximum between ~-40 and ~30 kyr at Contessa Road. The PETM CIE onset at Contessa Road occurred close to the center of a long junction of E2 and E3 components in the range of 460 461 a long eccentricity maximum, which implies that the PETM CIE onset occurred close to a 462 long eccentricity maximum (Lourens et al., 2005; Zeebe and Lourens, 2019).

463

464 Precession-based age models for the ODP Site 1262 a* and Fe records were developed to 465 estimate numerically orbital phasing of the PETM CIE onset with respect to long eccentricity 466 (*see Supplementary information*). These records were used previously to develop 467 astrochronological age models for ODP Site 1262 (Westerhold et al., 2007, 2018); however, 468 those chronologies assumed a ~120 kyr PETM CaCO₃ dissolution interval duration. The 469 ~116-137 kyr PETM CaCO₃ dissolution interval duration estimate from Contessa Road 470 reveals that extensive CaCO₃ dissolution should have lasted for longer in deep ocean sites– 471 i.e., ODP Site 1262. Although this assumption requires further research due to the different 472 paleogeographic positions of Contessa Road and ODP Site 1262 (Fig. 1c), different estimates 473 of 170 ± 30 kyr and $167^{+32}/_{-24}$ kyr for the PETM CaCO₃ dissolution interval at South Atlantic 474 sites validate the inference that extensive CaCO₃ dissolution at ODP Site 1262 may have 475 lasted longer than ~120 kyr (Murphy et al., 2010; Zeebe and Lourens, 2019). This suggests 476 that the ODP 1262 astrochronological age model can be refined.

477

478 Precession-based chronologies for ODP Site 1262 a* and Fe records allow identification of 479 long eccentricity signals in power spectra (see Supplementary information). Filtered long 480 eccentricity signals of the ODP Site 1262 a* and Fe records are now separated by the 170 \pm 481 30 kyr PETM CaCO₃ dissolution interval which refines the precession-based age model for 482 this site. Long eccentricity signals have good visual correlation with detrended records (Fig. 483 7). However, these signals do not provide a unique estimate for the long eccentricity 484 maximum of the cycle that contains the PETM (cycle 0 in Fig. 7) because this cycle is 485 punctuated by the PETM CaCO₃ dissolution interval.

486

487 The filtered long eccentricity signal of the a* record enables identification of a long 488 eccentricity maximum at ~-33 kyr for cycle 0 (blue circle in Fig. 7a). However, a long eccentricity minimum at ~-227 kyr for cycle 0 indicates a long eccentricity maximum at ~-25 489 490 kyr. The long eccentricity maximum of cycle -1, which preceded the PETM CIE onset 491 appeared at ~-419 kyr, which implies a long eccentricity maximum at ~-14 kyr for cycle 0 492 (Fig. 7a). Filtered long eccentricity signals of the a* record indicate a long eccentricity 493 minimum at ~200 kyr, which suggest that the long eccentricity maximum of cycle 0 appeared 494 at \sim -3 kyr. Considering the ±30 kyr uncertainty of the PETM CaCO₃ dissolution interval at 495 ODP Site 1262, this estimate for the age of the long eccentricity maximum of cycle 0 ranges 496 between ~-33 kyr and ~28 kyr (Fig. 7a). A similar estimate can be obtained using the long 497 eccentricity maximum of cycle 1, which appeared at ~400 \pm 30 kyr (considering the 498 uncertainty of the PETM CaCO₃ dissolution interval) and reveals a long eccentricity 499 maximum for cycle 0 at -5 ± 30 kyr. All of these values, after probabilistic assessments (see 500 Supplementary information), produce a -11 ± 15 kyr (median and 95% confidence interval) 501 estimate for the age of the long eccentricity maximum of cycle 0 in the floating chronology of 502 the a* record (Fig. 7a).

503

504 The filtered long eccentricity signal of the Fe record can also be used to estimate the age of 505 the long eccentricity maximum of cycle 0. These estimates, however, are limited by poor 506 development of the long eccentricity minimum of cycle 1 after the PETM CaCO₃ dissolution 507 interval (Fig. 7b). The filtered long eccentricity signal of the Fe record reveals a long 508 eccentricity maximum at ~-13 kyr (blue circle in cycle 0; Fig. 7b). However, cycle 0 has a 509 well-developed long eccentricity minimum at ~-209 kyr, which indicates a long eccentricity 510 maximum at ~-7 kyr. The long eccentricity maximum of cycle -1, which precedes cycle 0, 511 appeared at ~-407 kyr (Fig. 7b), which allows identification of a long eccentricity maximum 512 at ~-2 kyr for cycle 0. Alternatively, the long eccentricity maximum of cycle 1 at -364 ± 30 513 kyr (considering the uncertainty of the PETM CaCO₃ dissolution interval; Fig. 7b) indicates a 514 long eccentricity maximum at -41 ± 30 kyr. Estimates of the long eccentricity maximum of 515 cycle 0 in the Fe record reveal lags between the a* and Fe records. These differences, which 516 are also identified in previous cyclostratigraphic framewords (Westerhold et al., 2007), may be associated with terrigenous material input shifts promoted by hydrological cycle variations 517 518 under global warming (e.g., Woodard et al., 2011; Jin et al., 2021). However, estimates of the 519 long eccentricity maximum of cycle 0 for both records are similar (Fig. 7). Combined estimates of the age of the long eccentricity maximum of cycle 0 in the Fe record (*see* Supplementary information) produce a -24 ± 19 kyr age estimate for this long eccentricity maximum (Fig. 7b).

523

Our estimates of the orbital phasing of the PETM coincide with those from the ZB18a 524 525 astronomical solution (Zeebe and Lourens, 2019). In the ZB18a astronomical solution, the PETM CIE onset occurred at 56.01 \pm 0.05 Ma and a long eccentricity maximum appeared at 526 527 ~56.04 Ma. These overlapping estimates confirm that the PETM was an orbitally paced event 528 (Lourens et al., 2005; Zeebe and Lourens, 2019). This evidence implies that the orbitally 529 controlled mechanism that promoted early Eocene light carbon releases may have also been 530 activated at the Paleocene/Eocene boundary (Lunt et al., 2011; DeConto et al., 2012; Kirtland 531 Turner et al., 2014). This mechanism depended strongly on early Eocene long-term 532 background temperatures, which are interpreted to have been higher than pre-PETM temperatures (Fig. 1a; Westerhold et al., 2020). Therefore, crossing of a thermodynamic 533 534 threshold and subsequent destabilization of carbon reservoirs at the PETM onset may have 535 required an exceptionally large temperature increase. Volcanic-related positive carbon cycle 536 feedbacks before the PETM CIE onset promoted temperature increases (Sluijs et al., 2007; 537 Frieling et al., 2019; Kender et al., 2021). These processes coincided with orbital phasing of 538 the PETM CIE onset close to both long and short eccentricity maxima. This indicates an 539 orbital configuration that produced persistently high eccentricity values with minimal 540 variation across the time interval during which the PETM CIE onset occurred (Laskar et al., 541 2004; Zeebe et al., 2017; Zeebe and Lourens, 2019). Maximal seasonal contrast associated 542 with both long and short eccentricity maxima may have promoted a larger temperature 543 increase than may have occurred with only volcanic-related carbon emissions. Increased temperatures, and associated ocean circulation changes due to global warming, may have led 544

545 the climate to cross a thermodynamic threshold that produced light carbon injections due to thermal destabilization of methane hydrates (Lunt et al., 2011). This scenario is compatible 546 with orbital control on the PETM CIE onset, as our data indicate; however, other processes 547 548 associated with organic carbon feedbacks may have also been involved in PETM CIE triggering. Orbitally controlled temperature increases may have accelerated decomposition of 549 550 soil organic carbon from terrestrial permafrost (DeConto et al., 2012). Although light carbon 551 releases produced by this mechanism may have occurred, evidence for major Paleocene-552 Eocene permafrost soil carbon stocks is controversial; therefore, disturbed biospheric carbon 553 stocks, and light carbon releases associated with decomposed terrestrial organic matter due to 554 global warming in diverse latitudes have been suggested to play a role in PETM CIE 555 triggering (Bowen, 2013). Any of these carbon reservoirs may have been destabilized by a 556 drastic orbitally controlled and volcanic-related temperature increase that triggered the initial 557 PETM light carbon release.

558

559 **5.** Conclusions

560 AM and FM patterns provide evidence in a relative sense, i.e., independent of absolute orbital 561 tuning and astronomical solutions, that the PETM CIE commenced close to both long and 562 short eccentricity maxima. Orbital signatures within Contessa Road pelagic carbonates indicate that this event occurred ~11-21 kyr before a short eccentricity maximum, which 563 564 confirms the orbital phasing of the PETM close to a short eccentricity maximum (Zachos et 565 al., 2010). Orbital forcing of short eccentricity played a central role in lysocline depth 566 fluctuations at Contessa Road. This produced PETM sedimentation patterns similar to those 567 of other early Eocene carbon cycle perturbations such as the ETM 2 and H2 events (Galeotti 568 et al., 2010; Zachos et al., 2010).

570 FM patterns from Contessa Road and precession-based age models from ODP Site 1262 571 reveal that the PETM CIE onset occurred close to a long eccentricity maximum. This 572 evidence indicates that the PETM was an orbitally paced event that was, at least, partially 573 triggered by an orbitally controlled mechanism. Similarities between the orbital phasing of 574 the PETM and other early Eocene carbon cycle perturbations suggest that these events were 575 driven by a common mechanism that produced light carbon releases from a carbon reservoir 576 that was thermally destabilized-i.e., methane hydrates, permafrost soil, and/or other 577 terrestrial organic matter. Maximal seasonal contrast of the orbital configuration in which the PETM occurred, and volcanic-related positive carbon cycle feedbacks may have triggered the 578 579 PETM CIE and contributed to the exceptionally large PETM magnitude.

580

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816 **Figure captions**

Fig. 1. (a) Model results of orbital variations (forcing) with imposed long-term global temperature trends. Hyperthermals are represented by temperature peaks that cross a thermodynamic threshold (black dashed line) (Kirtland Turner et al., 2014). (b) ODP Site 1262 CaCO₃ record indicating the PETM CaCO₃ dissolution interval. (c) Paleogeographic reconstruction at ~56 Ma (Pogge von Strandmann et al., 2021) with locations of the Contessa Road section and ODP Site 1262. (d) Paleogeographic reconstruction of sedimentary environments across the western Tethys Ocean (Aguirre-Palafox et al., 2019).

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825 Fig. 2. (a) Schematic stratigraphic summary of the Contessa Road through the interval 26-46 826 m above the K/Pg boundary. The purple rectangle indicates the studied outcrop interval. (b) 827 Lithological variations in the studied Contessa Road outcrop interval (Giusberti et al., 2009; Galeotti et al., 2010). (c) CaCO₃ record (Giusberti et al., 2009). (d) δ^{13} C record (Giusberti et 828 829 al., 2009). Elemental concentration records and EHA for (e) Log₁₀Fe, (f) Ca, and (g) Log₁₀Si. 830 Dashed white lines in EHA plots indicate wavelength component variability. EHA were 831 obtained using 80 cm sliding windows that move in 1 cm steps for the means of the Log₁₀Fe, 832 Ca, and Log₁₀Si records. Pre-marly, marly, and post-marly intervals are indicated. The marly 833 interval represents the PETM CaCO₃ dissolution interval at Contessa Road. Gray rectangles 834 define marly horizons. The rest of the sequence consists of limestones. The PETM CIE onset 835 is indicated by a dashed green line in all plots.

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Fig. 3. Log₁₀Fe, Ca, and Log₁₀Si power spectra for the (a) whole section, (b) pre-marly, (c)
marly, and (d) post-marly intervals at Contessa Road. Color bands represent frequency ranges
that contain orbital signatures. Average periods for each orbital signature are also indicated.

Fig. 4. Filtered orbital signals for the Contessa Road sequence, including (a) Log₁₀Fe, (b) Ca,
and (c) Log₁₀Si. Detrended data (gray) correlate well with filtered short eccentricity (green)
and filtered precession (purple) signals.

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845 Fig. 5. Filtered orbital signatures for Contessa Road (a, b) Log₁₀Fe, (c, d) Ca, and (e, f) 846 Log₁₀Si. Short eccentricity (gray) and precession (blue) are presented in terms of mean and standard error (SE). AM of precession and short eccentricity are indicated by dashed purple 847 848 and dashed red lines, respectively. EHA plots were generated using the filtered precession 849 signals with 30 cm sliding windows that move in 1 cm steps. P1 and P2 correspond to 850 precession components. Precession cycles are numbered. Marly horizons are pink shaded 851 rectangles. The rest of the sequence consists of limestones. The PETM CIE onset is indicated 852 by a dashed green line.

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854 Fig. 6. Depth-domain EHA for filtered short eccentricity signals from Contessa Road (a) 855 Log₁₀Fe, (b) Ca, and (c) Log₁₀Si. Depth-domain EHA were obtained using 150 cm sliding 856 windows that move in 5 cm steps. Age-domain EHA of detrended records for Contessa Road (d) Log₁₀Fe, (e) Ca, and (f) Log₁₀Si. Age-domain EHA were obtained using 250 kyr sliding 857 858 windows that move in 2.5 kyr steps. Records were set to 0 kyr at the PETM CIE onset (i.e., 859 negative ages correspond to pre-PETM ages). Short eccentricity components (E2 and E3), 860 precession (P), and lithologies (right) are indicated. The PETM CIE onset is indicated by a 861 white bar.

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Fig. 7. Age-domain detrended records (gray) and filtered long eccentricity signals (blue) for ODP Site 1262 (a) a* and (b) $Log_{10}Fe$ records. Long eccentricity cycles are numbered. Cycle 0 contains the PETM. Black bars represent the 170 ± 30 kyr PETM CaCO₃ dissolution 866 interval duration, which separates the pre-PETM (Paleocene) and post-PETM (Eocene) 867 intervals at this site. Records were set to 0 kyr at the PETM CIE onset (negative ages 868 correspond to pre-PETM ages). Blue circles represent long eccentricity maxima of the 869 filtered time-domain long eccentricity signals. Estimates of the age of the long eccentricity 870 maximum of cycle 0 are indicated in fuchsia, in terms of median \pm 95% confidence interval. 871 The estimate for the age of the long eccentricity maximum of cycle 0 at Contessa Road is 872 indicated in orange. All estimates coincide within uncertainties. The PETM CIE onset is indicated with a green dashed line. 873













