

1 **Constraints on the numerical age of the Paleocene/Eocene boundary**

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10

11 **Abstract**

12 Here we present combined radio-isotopic dating (U-Pb zircon) and cyclostratigraphic analysis of
13 the carbon isotope excursion at the Paleocene/Eocene (P/E) boundary in Spitsbergen, to
14 determine the numerical age of the boundary. Incorporating the total uncertainty from both
15 radio-isotopic and cyclostratigraphic datasets gives an age ranging from 55.728-55.964 Ma,
16 within error of a recently proposed astronomical age of ~55.93 Ma. Combined with the
17 assumption that the Paleocene Epoch spans twenty-five 405 kyr cycles, our new age for the
18 boundary suggests an age of ~66 Ma for the Cretaceous/Paleogene (K/Pg) boundary.
19 Furthermore, our P/E boundary age is consistent with the hypothesis that the onset of the
20 Paleocene-Eocene thermal maximum (PETM) at the boundary occurred on the falling limb of a
21 405 kyr cycle, suggesting the event was initiated by a different mechanism to that which
22 triggered the other early Eocene hyperthermals.

23 **Keywords:** Paleocene, Eocene, PETM, cyclostratigraphy, radio-isotopic dating, Spitsbergen

24

25 **1. Introduction**

26 The early Cenozoic was an interval of globally warm climate [e.g. *Zachos et al.*, 2001, 2008;
27 *Pearson et al.*, 2007; *Sluijs et al.*, 2008; *Bijl et al.*, 2009], punctuated by a series of short-term
28 global-scale transient warming events known as hyperthermals [*Kennett and Stott*, 1991; *Zachos*
29 *et al.*, 2001, 2008; *Cramer et al.*, 2003; *Lourens et al.*, 2005; *Nicolo et al.*, 2007; *Agnini et al.*,
30 2009; *Galeotti et al.*, 2010]. The most pronounced hyperthermal, the Paleocene-Eocene thermal
31 maximum (PETM), reflects global-scale warming of both surface and bottom waters by ~5°C
32 [*Kennett and Stott*, 1991; *Zachos et al.*, 2003; *Tripati and Elderfield*, 2005; *Sluijs et al.*, 2006].
33 Negative carbon isotope excursions (CIEs) and carbonate dissolution horizons have been shown
34 to be coeval with warming during both the PETM and other hyperthermals [*Lourens et al.*, 2005;
35 *Zachos et al.*, 2005, 2010], implying that a significant quantity of isotopically light carbon was
36 injected into the exogenic system to cause the observed warming [*Dickens et al.*, 1995; 1997;
37 *Sluijs et al.*, 2007; *Panchuk et al.*, 2008; *Zeebe et al.*, 2009]. However, the trigger mechanism for
38 carbon release at the PETM is controversial, with several hypotheses proposed (see *Sluijs et al.*
39 [2007] for a review). Several authors have suggested that insolation maxima during the peak of
40 100 and 405 kyr eccentricity cycles resulted in warming of oceanic deep waters, causing the
41 dissociation of methane hydrates, thus instigating the warming event(s) [*Cramer et al.*, 2003;
42 *Lourens et al.*, 2005; *Sluijs et al.*, 2007]. Conversely it has also been suggested that the methane
43 and carbon dioxide which initiated the PETM were generated from contact metamorphism of
44 organic-rich sediments around intrusions in North Atlantic sedimentary basins [*Svensen et al.*,
45 2004, 2010; *Storey et al.*, 2007]; a trigger requiring no orbital forcing but coeval magmatism. An
46 understanding of the causative mechanism(s) for the PETM and later Eocene hyperthermals
47 therefore requires a precise and accurate temporal framework within which the various records
48 can be integrated in order to assess potential drivers (geologic and/or astronomical). Much

49 progress has been made through the construction of high-resolution proxy and lithologic
50 records from various OPD and IODP sites [Zachos *et al.*, 2001; 2003; 2005; 2008; Sluijs *et al.*,
51 2007; 2008], and the construction of orbitally-tuned timescales for these intervals have helped
52 elucidate the relative timing/sequencing of different events [Lourens *et al.*, 2005; Westerhold *et*
53 *al.*, 2007; 2009; Westerhold and Röhl, 2009; Galeotti *et al.*, 2010]. However, an outstanding
54 issue relates to the numerical age of key events, such as the PETM, which are currently
55 considered to be 'floating' – i.e. the age models contain only relative ages with respect to
56 certain stratigraphic markers. This issue is the result of four factors: (1) the 'unstable' nature of
57 the astronomical solutions in the early Paleogene, meaning that numerical ages derived from
58 tuning geological datasets to astronomical solutions carry high uncertainty [Laskar *et al.*, 2004];
59 (2) a gap in cyclostratigraphic records in the middle Eocene, meaning composite
60 cyclostratigraphic records for the entire Eocene cannot currently be constructed [Hilgen, 2008;
61 Pälike and Hilgen, 2008]; (3) disagreement surrounding the length of the Paleocene Epoch as
62 derived from floating cyclostratigraphic timescales, with the presence of either twenty-four or
63 twenty-five 405 kyr eccentricity cycles proposed [Kuiper *et al.*, 2008; Westerhold *et al.*, 2008;
64 2009; Hilgen *et al.*, 2010], and (4) a lack of geologically well constrained radio-isotopic dates, for
65 both the P/E and K/Pg boundaries and associated magneto-chrons. This is largely a result of
66 uncertainty in the $^{40}\text{Ar}/^{39}\text{Ar}$ dating methods [Kuiper *et al.*, 2008; Renne *et al.*, 2010; Channell *et*
67 *al.*, 2010] that are used to underpin Cenozoic timescales (note this uncertainty also prevents the
68 accurate determination of the number of 405 kyr cycles in the Paleocene).

69 The current astronomical solutions are unstable prior to ~40 Ma owing to the chaotic nature of
70 the orbits [Laskar, 1999; Varadi *et al.*, 2003; Laskar *et al.*, 2004; Pälike *et al.*, 2004]; therefore,
71 unlike the Neogene timescale, construction of a numerical geologic timescale for the Paleogene
72 relies on radio-isotopic dating (primarily $^{40}\text{Ar}/^{39}\text{Ar}$ and/or U-Pb) of minerals (sanidine and/or

73 zircon) from volcanic ash layers [e.g. *Wing et al.*, 2000; *Luterbacher et al.*, 2004]. Time-series
74 analysis of various proxy records (color, elemental, isotopic) permits identification of cyclicity
75 within sedimentary records that can be attributed to orbital (Milankovitch) forcing, which has
76 permitted the development of floating timescales for the early Paleogene [*Lourens et al.*, 2005;
77 *Westerhold et al.*, 2007, 2008, 2009; *Westerhold and Röhl*, 2009; *Galeotti et al.*, 2010]. Such
78 floating timescales can be constrained via radio-isotopic dating of minerals from volcanic layers,
79 either directly or by correlation (using bio- and/or magneto-stratigraphy). At present $^{40}\text{Ar}/^{39}\text{Ar}$
80 dates underpin much of the Cenozoic timescale. However the accuracy of these dates is relative
81 to ages of the mineral standard used in their calibration - typically the Fish Canyon sanidine (FCs)
82 standard, in addition to the potassium decay constants [*Renne et al.*, 1998], both of which have
83 been the focus of ongoing research. Attempts to calibrate the age of FCs using sanidines from
84 multiple tuff layers with both $^{40}\text{Ar}/^{39}\text{Ar}$ and astronomical ages, has resulted in an age of 28.201
85 ± 0.046 Ma [*Renne et al.*, 1998; *Kuiper et al.*, 2008]. *Renne et al.* [2010] derive an age of 28.305
86 ± 0.036 Ma for the FCs based upon a dataset of paired $^{238}\text{U}/^{206}\text{Pb}$ (zircon) and $^{40}\text{Ar}/^{39}\text{Ar}$ (sanidine
87 and biotite) dates for rocks where the minerals should give equivalent dates. Furthermore,
88 *Channell et al.* [2010] used astronomical ages for Quaternary magnetic reversals, also dated by
89 $^{40}\text{Ar}/^{39}\text{Ar}$, to derive an age of ~ 27.93 Ma for FCs. These age estimates for the FCs do not overlap
90 within their quoted uncertainties, and combined indicate that the accuracy of $^{40}\text{Ar}/^{39}\text{Ar}$ dates is
91 (at present) limited to $\sim 1\%$. In contrast, the accuracy of U-Pb dates is relative to isotopic tracers
92 which can be accurately calibrated to SI units, and the decay constants that are known through
93 counting experiments [*Jaffey et al.*, 1971]. Precise isotope ratio determinations can therefore
94 result in $^{238}\text{U}/^{206}\text{Pb}$ (zircon) dates with total uncertainties of $< 0.2\%$ [*Jaffey et al.*, 1971; *Condon et*
95 *al.*, 2007]. Furthermore, transformation of mineral dates into eruption/stratigraphic dates

96 requires interpretation of mineral date populations and consideration of petrology (i.e., magma
97 chamber processes, mineral closure temperature for retention of isotopes systematics).

98 Compounding the problem of Paleogene timescale calibration is the issue that the geological
99 context of radio-isotopically dated samples is somewhat uncertain with respect to the proxy
100 records being constrained. As a result, recent numerical ages derived for the P/E boundary
101 using the recalibrated $^{40}\text{Ar}/^{39}\text{Ar}$ radio-isotopic data and cyclostratigraphic datasets have yielded
102 inconsistent ages for the boundary [Kuiper *et al.*, 2008; Westerhold *et al.*, 2008, 2009],
103 preventing consensus on the duration of the Paleocene epoch and the exact temporal
104 relationship of the PETM to potential geologic/orbital triggers [e.g. Svensen *et al.*, 2004, 2010;
105 Storey *et al.*, 2007]. More robust constraints on the numerical age of the P/E boundary are
106 therefore required in order to (1) constrain the duration of the Paleocene Epoch, to ascertain
107 the number of 405 kyr cycles within it and permit the accurate correlation of IODP, ODP and
108 DSDP cores, (2) anchor currently floating cyclostratigraphic records, and (3) constrain the exact
109 temporal relationship between the PETM and potential triggers.

110 The P/E boundary is defined at the base of the 2.5-6 ‰ negative CIE [Dupuis *et al.*, 2003], coeval
111 with the PETM. Typically, previous studies have only indirectly derived a numerical age for the
112 P/E boundary [e.g. Wing *et al.*, 2000; Luterbacher *et al.*, 2004; Westerhold *et al.*, 2007, 2008,
113 2009; Kuiper *et al.*, 2008], owing to the absence of ash layers within the PETM CIE (the exception
114 being Jaramillo *et al.* [2010]; see Section 4.1). Here we document a U-Pb (zircon) date from a
115 bentonite layer *within* the PETM CIE from the Longyearbyen section in the Central Basin of
116 Spitsbergen. We combine this date with cyclostratigraphic datasets, from both the
117 Longyearbyen section [Harding *et al.*, 2011] and core BH9/05 (drilled near Sveagruba,
118 Spitsbergen; Dypvik *et al.* [2011]), to constrain the age of the P/E boundary.

119

120 **2. Materials and methods**

121 *2.1 Geological succession*

122 The study localities are located in the Paleogene Central Basin of Spitsbergen, the largest island
123 in the Svalbard Archipelago, situated on the NW corner of the Barents Shelf (Figure 1; *Dallman*
124 *et al.* [1999]; *Harland* [1997]). *Harland* [1997; and references therein] provides a comprehensive
125 overview of the stratigraphy of the Central Basin and the other Paleogene successions on
126 Spitsbergen. The stratigraphic nomenclature used in this report adheres to that proposed by
127 *Dallman et al.* [1999]. During the Paleogene Spitsbergen was situated at ~75°N [*Harland, 1997*],
128 adjacent to the NE corner of Greenland, but with the progressive opening of the northern North
129 Atlantic a predominantly transpressional dextral strike-slip motion between the two continental
130 masses was initiated in the Paleocene (Figure 1; *Bruhn and Steel* [2003]). For the remainder of
131 the Paleogene the Central Basin developed as a subsiding foreland basin [*Kellogg, 1975; Helland-*
132 *Hansen, 1990; Müller and Spielhagen, 1990; Harland, 1997*], the sediment shed from the rising
133 West Spitsbergen Orogenic Belt resulting in a thick sedimentary succession (up to 2.5 km:
134 *Helland-Hansen* [1990]).

135 Two sections were studied: the Longyearbyen outcrop section and core BH9/05. At
136 Longyearbyen the PETM lies within the Gilsonryggen Member of the Frysjaodden Formation
137 [*Harding et al., 2011*], a unit of around 250 m of homogeneous mudstones. A -4 ‰ organic
138 carbon isotope excursion ($\delta^{13}\text{C}_{\text{TOC}}$) is present between 3 and 28 m above the top of the
139 Hollendardalen Formation, with the coeval presence of the PETM-diagnostic dinoflagellate cyst
140 *Apectodinium augustum* [*Harding et al., 2011*]. Two conspicuous bentonite horizons occur at

141 10.90 and 14.60 m above the top of the Hollendardalen Formation, within the PETM CIE (Figure
142 2).

143 The Frysjaodden Formation is identified from 551-110 m depth in core BH9/05 [Dypvik *et al.*,
144 2011], drilled NW of the town of Sveagrauva near Urdkollbreen. The cored succession cannot be
145 divided into members due to the fine grained nature of the lithologies [Dallman *et al.*, 1999].
146 The mudstone-dominated succession is continuous across the upper Paleocene-lower Eocene
147 interval, with only minor amounts of carbonate detected in XRD analyses [Dypvik *et al.*, 2011]. A
148 ~4.2 ‰ organic carbon isotope ($\delta^{13}\text{C}_{\text{TOC}}$) excursion is present at the base of the Frysjaodden
149 Formation in core BH9/05 (534-487 metres depth, see Figure 2; Cui [2010]), again coincident
150 with two bentonite horizons lying at 517.20 and 511.10 metres depth respectively [Dypvik *et al.*,
151 2011].

152

153 Insert Figures 1 and 2 here

154

155 2.2 Palynological processing

156 Sixty-six samples were processed in order to constrain the $\delta^{13}\text{C}_{\text{TOC}}$ excursion in core BH9/05
157 using dinoflagellate cyst (dinocyst) biostratigraphy. Sample processing methods were identical
158 to those of Harding *et al.* [2011], with the exception that no samples were subject to ultrasonic
159 treatment. Concentrations of dinocysts were generated by counting 300 specimens where
160 possible, with normalisation against the out-of-count *Lycopodium* spike [Stockmarr, 1971].
161 Dinocyst taxonomy follows that of Fensome and Williams [2004]. The appearance of the
162 dinocyst *Apectodinium augustum* at the start of the $\delta^{13}\text{C}_{\text{TOC}}$ excursion firmly identifies the PETM

163 in core BH9/05, illustrating that the bentonite horizons in both the Longyearbyen section and
164 core BH9/05 are coeval (Figure 2). The PETM CIE from core BH9/05 is plotted in Figure 3 to
165 illustrate the different phases of the CIE in Spitsbergen, with respect to ODP sites 690 and 1263.

166

167 2.3 Radio-isotopic dating

168 Analysis of the lower bentonite layer in the Longyearbyen section (sample SB01-1; Figure 2), was
169 carried out at the he NERC Isotope Geosciences Laboratory (NIGL), UK. Zircons were isolated
170 from around 300 grams of sample SB01-1, using conventional mineral separation techniques.
171 Prior to isotope dilution thermal ionization mass spectrometry (ID-TIMS) analyses zircons were
172 subject to a modified version of the chemical abrasion technique [Mattinson, 2005]. For details
173 of sample pre-treatment, dissolution and anion exchange chemistry at NIGL the reader is
174 referred to Sláma *et al.* [2008]. Our U-Pb ID-TIMS analyses utilized the EARTHTIME ^{205}Pb - ^{233}U -
175 ^{235}U (ET535) tracer solution. Measurements at the NERC Isotope Geosciences Laboratory were
176 performed on a Thermo Triton TIMS. Pb analyses were measured in dynamic mode on a
177 MassCom SEM detector and corrected for $0.14 \pm 0.04\%$ u. mass fractionation. Linearity and
178 dead-time corrections on the SEM were monitored using repeated analyses of NBS 982, NBS 981
179 and U500. Uranium was measured in static Faraday mode on 10^{11} ohm resistors or for signal
180 intensities <15 mV, in dynamic mode on the SEM detector. Uranium was run as the oxide and
181 corrected for isobaric interferences with an $^{18}\text{O}/^{16}\text{O}$ composition of 0.00205 (IUPAC value and
182 determined through direct measurement at NIGL). U-Pb dates and uncertainties were calculated
183 using the algorithms of Schmitz and Schoene [2007], combined with a $^{235}\text{U}/^{205}\text{Pb}$ ratio of 100.18
184 and $^{233}\text{U}/^{235}\text{U}$ double spike ratio of 0.99464 for the ET535 tracer. All common Pb in the analyses
185 was attributed to the blank and subtracted based on the isotopic composition and associated

186 uncertainties analyzed over time. The $^{206}\text{Pb}/^{238}\text{U}$ ratios and dates were corrected for initial ^{230}Th
187 disequilibrium using a $\text{Th}/\text{U}_{[\text{magma}]}$ of 4 ± 1 applying the algorithms of *Schärer* [1984] resulting in
188 an increase in the $^{206}\text{Pb}/^{238}\text{U}$ dates of ~ 100 kyrs and an additional uncertainty contribution of
189 ~ 10 kyrs. Errors for U-Pb dates are reported in the following format: $\pm X(Y)[Z]$, where X is the
190 internal or analytical uncertainty in the absence of all systematic error (tracer calibration and
191 decay constants), Y includes the quadratic addition of tracer calibration error (using a
192 conservative estimate of the 2σ standard deviation of 0.1% for the Pb/U ratio in the tracer), and
193 Z includes the quadratic addition of both the tracer calibration error and additional ^{238}U decay
194 constant errors of *Jaffey et al.* [1971]. All analytical uncertainties are calculated at the 95%
195 confidence interval. These $^{238}\text{U}/^{206}\text{Pb}$ dates are traceable back to SI units via the gravimetric
196 calibration of the EARTHTIME U-Pb tracer and the determination of the ^{238}U decay constant
197 [*Jaffey et al.*, 1971; *Condon et al.*, 2007].

198

199 Insert Figure 3 here

200

201 2.4 XRF time-series

202 Fe and Mn time-series were generated for core BH9/05 using a Niton UK XL3t portable XRF
203 scanner. Measurements ($n=1195$; Auxiliary Table 1) were taken every 20 cm throughout that
204 part of the core section recording the $\delta^{13}\text{C}_{\text{TOC}}$ excursion (550 m to 480 m core depth) and every
205 40 cm outside this interval (Figure 4). Twelve samples were analyzed using wavelength
206 dispersive (WD) XRF, to calibrate results from the Niton UK scanner. These samples were
207 crushed to a fine powder and air dried at 105°C . The sample ($0.5 \text{ g} \pm 0.0003$) was mixed with 5

208 ±0.003 g lithium tetraborate flux (Fluxana GmbH, Germany) and fused at ~1100 °C using a
209 Vulcan fusion system (HD Elektronik und Elektrotechnik GmbH, Germany) to provide a 1:10 glass
210 bead. The glass beads were analysed using a Philips MAGIX-PRO automatic sequential
211 wavelength dispersive X-ray fluorescence spectrometer fitted with a 4 kW Rh X-ray tube. Loss on
212 ignition (LOI) was estimated from the function (100 %- Σ XRF oxides) since the original XRF major
213 element calibration was constructed on this basis. We obtained correlation coefficients (r^2)
214 between the WD XRF and the Niton UK scanner of 0.76 for Fe and 0.89 for Mn (Figure 5).

215

216 *2.5 Time-series analysis*

217 Both Fe and Mn time-series were first smoothed using a 5-point moving average in order to
218 reduce noise. Log Fe and Mn values were used in order to stabilize cycle variance, with the data
219 also normalized and detrended before spectral analysis [Weedon, 2003]. Gaussian filtering and
220 tuning were carried out using Analyseries version 1.1 [Paillard *et al.*, 1996]. In order to generate
221 both wavelet and multi-taper method power spectra, both Fe and Mn time-series were re-
222 sampled using a constant sample spacing, *via* linear interpolation using Analyseries. Multi-taper
223 method power spectra [Thompson, 1982] were calculated using SSA-MTM toolkit [Dettinger *et*
224 *al.*, 1995; Ghil *et al.*, 2002] with a red noise model to assess confidence levels. Wavelet spectra
225 were calculated using the Matlab script of Torrence and Compo [1998]. The time-series was
226 zero padded to reduce edge effects, with a red noise model to assess confidence levels
227 [Torrence and Compo, 1998].

228

229 Insert Figure 4 here

230

231 3. Results

232 3.1 Radio-isotopic dating

233 Zircon separated from bentonite sample SB01-1 were small (<50 μm) with aspect ratios of ~ 3 to
234 ~ 7 . Thirteen single grains were analyzed, and the resulting data are presented in Auxiliary Table
235 2. Three of the thirteen analysis produced discordant U-Pb data with Paleozoic $^{207}\text{Pb}/^{206}\text{Pb}$
236 dates. The remaining ten analyses yielded $^{206}\text{Pb}/^{238}\text{U}$ dates between 57.08 and 55.71 Ma (Figure
237 6). U-Pb ages for volcanic ash beds are determined by the interpretation of U-Pb dates from
238 single zircon crystals. Utilization of the chemical abrasion pre-treatment technique [Mattinson,
239 2005] for the effective elimination of Pb-loss means that we consider each zircon $^{206}\text{Pb}/^{238}\text{U}$ date
240 accurate (i.e., they do not reflect post-crystallization Pb-loss). Detailed studies of zircons and
241 other minerals dateable by the U-Pb system often indicate a protracted interval of zircon
242 crystallization in a magmatic system, demonstrating the possibility that some zircon in a given
243 ash layer record ages of the eruption (i.e., those that crystallized immediately prior to eruption)
244 and some older ages which reflect the pre-eruptive crystallization (and residence) of zircons
245 [Schoene *et al.*, 2010]. In such samples the age of the youngest zircon (or zircon population) is
246 considered to best approximate the age of the ash layers with older zircon dates reflecting pre-
247 eruptive crystallization. Excluding obvious inheritance of Paleozoic zircon, we observe a range of
248 zircon $^{206}\text{Pb}/^{238}\text{U}$ dates in sample SB01-1 from 57.08 ± 0.06 to 55.71 ± 0.14 Ma, with the five
249 youngest analyses yielding a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date of $55.785 \pm 0.034(0.066)[0.086]$ Ma
250 (MSWD = 0.88, calculated using Isoplot 3.0 [Ludwig, 1991]) which is interpreted as being the
251 best estimate for the zircons of this sample. We consider this date to best approximate the age
252 of sample SB01-1 and the older zircon $^{206}\text{Pb}/^{238}\text{U}$ dates to reflect analyses of xenocrystic and/or

253 zircons that have experienced pre-eruptive magma residence, with the single analysis precision
254 of ~100 kyr permitting de-convolution of the mixed age population. An alternative to the
255 conventional approach of taking a weighted mean date based upon a coherent population of
256 youngest $^{206}\text{Pb}/^{238}\text{U}$ dates would be to interpret the single zircon dates. As the youngest five
257 analyses form a coherent population this would have no discernable effect on the interpreted
258 $^{206}\text{Pb}/^{238}\text{U}$ date for SB01-1 and would increase the total uncertainty by an additional ~20 kyrs,
259 and as such our proposed date for SB01-1 is insensitive to different approaches to zircon date
260 interpretation.

261

262 Insert Figure 5 here

263

264 *3.2 Cyclostratigraphic analysis*

265 A detailed description of the cyclostratigraphic age model for the Longyearbyen section can be
266 found in *Harding et al.* [2011]. Here, numerical ages from Longyearbyen [*Harding et al.*, 2011]
267 were corrected using the numerical age of the bentonite. However, we also generated Fe and
268 Mn time-series from core BH9/05, with cyclostratigraphic analysis of this data discussed below.

269

270 *3.2.1 Records in the depth domain*

271 In order to build an orbital age model for core BH9/05, it was first necessary to ascertain if the
272 cycles present in the time-series were derived from orbital forcing [*Weedon, 2003; Bailey, 2009*].
273 Comparison of the Fe/Mn time-series of core BH9/05 with the TOC record from Longyearbyen

274 illustrates that the same cycles are present in the depth domain in both different parameters
275 and localities within Spitsbergen [Figure 2]. This confirms the cycles present in the PETM are not
276 predominantly the result of stochastic noise [Weedon, 2003].

277 The BH9/05 time-series (Figure 4) illustrate a strong cyclicity within the interval from the base of
278 the Frysjaodden Formation to the top of the PETM (551-487 m), with two dominant cycle
279 lengths of 4-6 m (~ 0.2 cycles/m) and 20 m (0.05 cycles/m) above 95 % confidence level (Figure 4;
280 note that the short stratigraphic thickness of this interval with respect to the cycle wavelengths
281 being analyzed results in a wide bandwidth for the power spectra shown in Figure 4d, which has
282 the effect of smearing out the spectral peaks). Above this interval the cycle wavelength
283 increases, with components at 0.12 and 0.024 cycles/m representing 8 m and 42 m cycles
284 respectively (Figure 4). The wavelet spectra therefore suggest that the sedimentation rate
285 increases above the PETM (as cycle wavelength increases when sedimentation rates rise). This is
286 in contrast to other PETM continental margin sections, which typically show an increase in
287 sedimentation rates within the PETM [e.g. *John et al.*, 2008; *Sluijs et al.*, 2008]. However, the
288 Central Basin lies adjacent to the West Spitsbergen Orogeny, and thus the high volume of
289 sediment shed off the growing orogenic belt at this time [*Harland, 1997; Dallman, 1999*]
290 probably overprinted any climatically induced changes in sedimentation. The increase in
291 sedimentation rates above the PETM is also consistent with the gradual infilling of the basin
292 through time, eventually leading to deposition of the overlying shelf margin delta and terrestrial
293 formations (Battfjellet and Aspelintoppen Formations respectively [see *Dallman, 1999*]).

294 In order to estimate the duration of the Fe and Mn cycles, an independent estimate of the
295 sedimentation rate is required. Outside the PETM interval, no such constraints are currently
296 available. Therefore, the rest of this study will focus on the interval between the base of the

297 Frysjaodden Formation and the end of the PETM (551–487 m), where the PETM CIE acts as an
298 external constraint on cycle durations. Note that the PETM CIE is a valid external constraint for
299 the following reasons: (1) The CIE inflection points in $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{13}\text{C}_{\text{n-alkane}}$ records in core
300 BH9/05 are at stratigraphically equivalent heights [Cui, 2010], indicating changes in organic
301 matter assemblage did not alter the stratigraphic position of the CIE inflection points. (2) The
302 abundance of reworked pre-Cenozoic palynomorphs is low throughout the lower Frysjaodden
303 Formation [Harding *et al.*, 2011], indicating reworking of such material did not significantly alter
304 the $\delta^{13}\text{C}_{\text{TOC}}$ record. Furthermore the consistent stratigraphy between Spitsbergen sites (Figure
305 2), suggests localized reworking of Paleocene organic matter did not significantly affect our
306 records (as differential reworking of isotopically heavy pre-PETM material would alter the
307 carbon isotope stratigraphy between sites; Harding *et al.*, [2011]).

308 The stratigraphic thickness of the PETM CIE in core BH9/05 (onset to the end of recovery phase
309 II: 533.66 m to 487.00 m) was combined with previously published data for the duration of this
310 interval to calculate the sedimentation rate during the PETM. However, different estimates for
311 the duration of the PETM CIE currently exist. Röhl *et al.* [2007] used cycles in Fe, Ca and Ba at
312 ODP sites 1263 (Walvis Ridge) and 690 (Weddell Sea) to derive a PETM duration of 170 kyr (8.5
313 precession cycles), which is similar to cyclostratigraphic results from the Bighorn Basin (157 kyr,
314 7.5 precession cycles; Abdul Aziz *et al.* [2008]). A recent re-appraisal of the ^3He age model of
315 Farley and Eltgroth [2003] led to estimates from 90 ± 10 to 140 ± 30 kyr for the duration of the
316 PETM CIE at ODP Site 690 [Sluijs *et al.*, 2007], with the upper estimate consistent with recent
317 cyclostratigraphic results. As similar durations for the PETM CIE have been derived from both
318 low (Walvis Ridge), mid (Bighorn Basin) and high (Weddell Sea) latitudes it is reasonable to
319 assume that the duration of the event would have been the similar in the Arctic (170 kyr, *sensu*
320 Röhl *et al.* [2007]). Given the 46.6 m thickness of the CIE (Figure 2) and assuming that its

321 duration is 170 kyr yields a sedimentation rate of 27.4 cm/kyr (4660 cm/170 kyr). Using this
322 sedimentation rate the 4-6 m and 20 m cycles within the PETM represent 15-22 kyr and 73 kyr
323 cycles respectively.

324 However, recently *Murphy et al.* [2010] derived a duration of 217 +44/-31 kyr for the PETM CIE
325 (onset to the end of recovery phase II) from ODP Site 1266 using an extraterrestrial ³He age
326 model. Potential reasons for the difference between this age model and that of *Röhl et al.*
327 [2007] were previously discussed in *Murphy et al.* [2010]. Using a duration of 217 kyr for the
328 PETM CIE (onset to the end of recovery phase II) together with the stratigraphic thickness of the
329 same interval from core BH9/05 gives sedimentation rates of 21.5 cm/kyr (4660 cm/ 217 kyr). In
330 this scenario, the 4-6 m and 20 m cycles would have durations of 19-28 kyr and 93 kyr
331 respectively. The duration of the 4-6 m cycles using either the *Röhl et al.* [2007] or *Murphy et al.*
332 [2010] age models is therefore consistent with their derivation from precession forcing. The
333 ratio between the 4-6 and 20 m cycles suggests the 20 m cycle represents the short eccentricity
334 component (~100 kyr), consistent with the cycle duration derived using the *Murphy et al.* [2010]
335 age model. The dominance of precession and eccentricity with a minor obliquity component in
336 late Paleocene/early Eocene sediments is typical and has been observed at numerous sites on a
337 global scale [e.g. *Westerhold et al.*, 2007; 2008; *Abdul Aziz et al.*, 2008; *Sluijs et al.* 2008].

338 Because of the different age models for the duration of the PETM CIE, we present two options
339 for the interpretation of the cycles within core BH9/05 (Section 3.2.2). We extracted the
340 Gaussian filter outputs from the Fe and Mn time-series in the depth domain at wavelengths of
341 4.2 m (0.24 ±0.07 cycles/m), and 20 m (0.05 ±0.01 cycles/m; Figure 7). The 4.2 m and 20 m filters
342 represent the precession and short eccentricity components respectively, with precession cycles
343 numbered according to *Röhl et al.* [2007]. Figure 7 shows that a minimum of 8.5 precession

344 cycles are present within the PETM CIE (from onset to end of recovery phase II), consistent with
345 the cyclostratigraphic age model of *Röhl et al.* [2007]. If we consider the *Röhl et al.* [2007] age
346 model to be the most accurate, the precession cycles labeled 1 to 3 in Figure 7 (i.e. excluding
347 those marked with an asterisk) correspond to one short eccentricity (20 m) cycle. However,
348 between 4-6 precession cycles (typically 5) should be present for every one short eccentricity
349 cycle [e.g. *Pälike, 2005*], and thus it is difficult to reconcile the two filter outputs in this interval.
350 Furthermore, we identify three additional cycles with low amplitude in the time-series and filter
351 outputs in the PETM interval (marked with asterisks) when compared to the *Röhl et al.* [2007]
352 age model (Figure 7). If these cycles are interpreted as low-amplitude precession cycles, the
353 duration of the PETM CIE is consistent with that obtained from the ^3He age model of *Murphy et*
354 *al.* [2010; i.e. 11 precession cycles]. Using this approach the short eccentricity:precession cycle
355 ratio is 1:5, consistent with orbital cycle ratios [e.g. *Pälike, 2005*]. Two of the additional
356 precession cycles occur within the interval between the PETM CIE onset and the end of recovery
357 phase I (making a total of 7 cycles; Figure 7), which is equivalent to the clay layer interval in ODP
358 Leg 208 sites (Figure 3). This is consistent with the hypothesis of *Röhl et al.* [2007], who argued
359 that 5-7 precession cycles must be present within the clay layer interval of Leg 208 sites, in order
360 to maintain the phase of the 405 kyr eccentricity cycle extracted from Site 1262.

361

362 Insert Figure 6 here

363

364 *3.2.2 Records in the time domain*

365 Here we construct two separate cyclostratigraphic age models for core BH9/05 (from 551-487
366 m), each based on the different options for the duration of the PETM CIE from *Röhl et al.* [2007]
367 and *Murphy et al.* [2010]. Option A, matching the BH9/05 records to the *Röhl et al.* [2007] age
368 model, was carried out by matching the Fe concentration record from BH9/05 to that of ODP
369 Leg 208, Site 1263 (*Westerhold et al.* [2007]; corrected after *Röhl et al.* [2007]; Auxiliary Table 4),
370 using the PETM CIE as an external constraint. The duration of the PETM CIE from the ^3He age
371 model of *Murphy et al.* [2010] is longer than recent cyclostratigraphic estimates of the PETM CIE
372 [e.g. *Röhl et al.*, 2007; *Abdul Aziz et al.*, 2008], and therefore tuning the BH9/05 record to
373 another site consistent with this ^3He age model is currently not possible. Therefore, in order to
374 build an age model for core BH9/05 consistent with the results of *Murphy et al.* [2010], we
375 assigned a 21 kyr duration to the interval between each precession cycle peak, for each cycle
376 identified in the filter output of Figure 7c (following a similar approach by *Westerhold et al.*
377 [2007] and *Röhl et al.* [2007]). Note that this approach assumes sedimentation rates remained
378 constant between precession cycle peaks. Cycle peaks were assigned ages relative to cycle -1 in
379 Figure 7c, with the resultant age model (Option B) shown in Auxiliary Table 4. However, we note
380 that precession cyclicity is quasi-periodic, with cycle durations ranging from 19-24 kyr in
381 duration [e.g. *Pälike*, 2005]. Therefore we estimate an error of ± 3 kyr for each precession cycle
382 peak utilized in age model Option B.

383

384 *3.3 The numerical age of the Paleocene/Eocene boundary*

385 The P/E boundary is defined as the base of the PETM CIE [*Dupuis et al.*, 2003] and we therefore
386 integrate the age of the bentonite with time-series datasets to constrain the age of the P/E
387 boundary (and by inference the onset age for the PETM CIE). Numerical ages for both the

388 cyclostratigraphic age models from Section 3.2.2 and the record from the Longyearbyen section
389 [Harding *et al.*, 2011] were corrected using the age of the bentonite. In order to constrain the
390 age of the P/E boundary, the relative duration between the dated bentonite horizon and the
391 onset of the PETM CIE is required. No grain size fluctuations or abrupt shifts in carbon isotope
392 values were observed within this interval in either the Longyearbyen section or core BH9/05
393 (Figure 2), implying that sedimentation was continuous between the onset of the CIE and the
394 lower bentonite horizon.

395 Figure 8 shows the duration between the bentonite and base of the PETM CIE using age model
396 Option A for core BH9/05 together with the cyclostratigraphic age model from the
397 Longyearbyen section [Harding *et al.*, 2011]. Cycle counting using the Gaussian filter output of
398 precession illustrates a 40 and 45 kyr duration between the lower bentonite and the base of the
399 PETM CIE in core BH9/05 and at Longyearbyen respectively; which results in numerical ages of
400 55.827 ± 0.086 Ma (BH9/05) and 55.831 ± 0.086 Ma (Longyearbyen) for the P/E boundary (Figure
401 8). As each section was tuned independently, the 5 kyr difference between the ages derived
402 from each section partly represents the error associated with the tuning process. However, as
403 the time-series from each section are constructed from different parameters (TOC% in
404 Longyearbyen; Fe and Mn concentrations in core BH9/05), part of the 5 kyr offset may result
405 from differences in how the individual parameters were incorporated into the sedimentary
406 record. Therefore we incorporate the 5 kyr offset into the error for the age the P/E boundary.
407 Further error results from tuning the cyclostratigraphic records from Spitsbergen to the Fe
408 record of ODP Site 1263, because carbonate dissolution at the base of the PETM clay layer at
409 Site 1263 results in a minor hiatus in this section [Zachos *et al.*, 2005; McCarren *et al.*, 2008]. It is
410 estimated that the duration of missing time owing to carbonate dissolution is on the order of 10
411 kyr [Röhl *et al.*, 2007], which we incorporate into the error, producing an age of 55.829 ± 0.101

412 Ma (Figure 8). Conversely, using age model Option B for core BH9/05 results in a duration of 81
413 kyr between the bentonite and the base of the PETM CIE (Figure 9), giving an age of 55.866
414 ± 0.098 Ma for the P/E boundary. The error based on age model Option B includes ± 0.086 Myr
415 from U-Pb dating of bentonite SB01-1, and ± 0.012 Myr error from cycle counting [4 precession
416 cycles at ± 3 kyr per cycle; Section 3.2.2]). Note that no error for carbonate dissolution is applied
417 to Option B because this approach required no tuning to Site 1263, and the near absence of
418 carbonate in the Frysjaodden Formation [*Dypvik et al.*, 2011; *Harding et al.*, 2011] implies that
419 carbonate dissolution did not alter the Spitsbergen PETM records. The difference between age
420 model option A and B for the age of the P/E boundary is thus ~ 37 kyr, and both options are
421 within error of one another because the accuracy of the radio-isotopic date dominates the
422 uncertainty of our derived P/E boundary age. Therefore the age of the boundary inferred here
423 is not significantly altered by large changes in the duration of the PETM CIE used to derive the
424 respective age models. Taking into account both the cyclostratigraphic options and their
425 uncertainty, together with the uncertainty from the radio-isotopic dating of sample of SB01-1,
426 we derive an age range of 55.728-55.964 Ma for the P/E boundary (Figure 10).

427

428 Insert Figure 7 here

429

430 **4. Discussion**

431 *4.1 Comparison with recent age estimates for the P/E boundary*

432 Owing to the lack of direct radio-isotopic dating of the P/E boundary (other than *Jaramillo et al.*
433 [2010], see below), earlier studies have derived numerical ages indirectly using either
434 astronomical solutions and/or cycle counting from stratigraphic horizons which are themselves
435 constrained by radio-isotopic dating. Three different astronomical age options have recently
436 been proposed for the P/E boundary [*Westerhold et al.*, 2007; 2008]. These options were
437 derived by extracting the 405 kyr cycle from both Fe and a* records from ODP Site 1262 (Leg
438 208, Walvis Ridge; *Westerhold et al.* [2007]). Combined with broad radio-isotopic age
439 constraints the correlation of the extracted 405 kyr cycle to astronomical solutions [*Varadi et al.*,
440 2003; *Laskar et al.*, 2004] yields three different options each separated by one 405 kyr cycle
441 (option one: ~55.53 Ma; option two: ~55.93 Ma; option three: ~56.33 Ma). Note that three
442 options were proposed due to the uncertainties associated with both astronomical solutions
443 and $^{40}\text{Ar}/^{39}\text{Ar}$ radio-isotopic dating [*Westerhold et al.*, 2007; 2008]. The error associated with
444 each option is ± 20 kyr [*Westerhold et al.*, 2007], derived from the error associated with the
445 extremely stable 405 kyr eccentricity cycle as calculated from astronomical modeling [*Laskar et*
446 *al.*, 2004].

447 Recent ages for the P/E boundary derived *via* cycle counting from radio-isotopic horizons have
448 utilized $^{40}\text{Ar}/^{39}\text{Ar}$ (sanidine) dating of the K/Pg boundary [*Kuiper et al.*, 2008; *Westerhold et al.*,
449 2008; *Hilgen et al.*, 2010], and ash – 17 in the Fur Formation of Denmark [*Storey et al.*, 2007;
450 *Westerhold et al.* [2009]. As outlined in Section 1, the ~1 % uncertainty in the age of the FCs,
451 against which the $^{40}\text{Ar}/^{39}\text{Ar}$ dates are determined, has precluded a high accuracy (<0.2 %) age
452 estimate for the P/E boundary using this method. Together with the uncertainty for the duration
453 of the Paleocene Epoch from floating cyclostratigraphic timescales [*Kuiper et al.*, 2008;
454 *Westerhold et al.*, 2008; *Hilgen et al.*, 2010]) this can therefore account for the difference

455 between our age estimate and those recently derived utilizing $^{40}\text{Ar}/^{39}\text{Ar}$ dates [e.g. *Westerhold*
456 *et al.*, 2008; 2009].

457 Recently, *Jaramillo et al.* [2010] obtained a $^{238}\text{U}/^{206}\text{Pb}$ date of 56.09 ± 0.13 Ma (total uncertainty)
458 on zircons from a felsic pyroclastic tuff from a coastal plain Late Paleocene – Early Eocene
459 section in Venezuela (Riecito Mache section). This pyroclastic tuff is at a level that records a
460 negative CIE that is inferred to represent the PETM, and therefore inferentially constrains the P/E
461 boundary to ~ 56.3 Ma [*Jaramillo et al.*, 2010]. This date is ~ 400 - 500 kyr older than our age for
462 the P/E boundary. The zircons utilized to derive this date were extracted from a sample described
463 as tuffaceous sandstone [*Jaramillo et al.*, 2010; their Figure S3]. It is therefore possible that
464 fluvial reworking of detrital zircons from an eruption ~ 56.1 Ma could account for the discrepancy
465 between the Spitsbergen and Venezuelan P/E boundary ages. In addition, the identification of the
466 PETM CIE at the Riecito Mache section is complicated by $\delta^{13}\text{C}_{\text{TOC}}$ records with a high degree of
467 scatter, and therefore an alternative explanation is that the dated tuffaceous sandstone was not
468 deposited within the PETM CIE.

469 The PETM CIE in Spitsbergen is firmly identified by $\delta^{13}\text{C}_{\text{TOC}}$ records together with the
470 *Apectodinium* acme (Figure 2; e.g. *Crouch et al.* [2001]; *Sluijs and Brinkhuis* [2009]), and
471 dinocyst morphotype *Apectodinium augustum*, which only occurs within the PETM interval [e.g.
472 *Luterbacher et al.*, 2004]. Given the accuracy of the U-Pb (zircon) system by isotope dilution, the
473 context of the dated sample *within* the PETM CIE and the proximity of the dated horizon to the
474 P/E boundary, we consider our age range of 55.728 - 55.964 Ma for the P/E boundary from
475 Spitsbergen to be the most accurate radio-isotopic age estimate. Our age range for the
476 boundary is within error of age option 2 of *Westerhold et al.* [2007; 2008] for the same horizon.
477 The numerical age for the P/E boundary (equivalent to the PETM onset) must fall within one of
478 the age options proposed by *Westerhold et al.* [2007; 2008] in order to maintain the phase

479 relationship of the 405 kyr eccentricity cycle between astronomical solutions and records of the
480 same cycle extracted from ODP Site 1262 [Röhl *et al.*, 2007; Westerhold *et al.*, 2007; 2008].
481 Therefore, our age for the P/E boundary substantiates age option 2 of Westerhold *et al.* [2007,
482 2008] is the correct option, giving a numerical age of ~55.93 Ma for the boundary.

483

484 Insert figure 8 here

485

486 4.2 On the age of the K/Pg boundary

487 Radio-isotopic constraints at the K/Pg boundary (e.g., single crystal $^{40}\text{Ar}/^{39}\text{Ar}$ sanidine dates from
488 the IrZ-Coal bentonite, Hell Creek Formation, Montana, [Swisher *et al.*, 1993]) and immediately
489 overlying the P/E boundary (Spitsbergen, this study) now bracket Paleocene time, constraining
490 its duration. However, at present uncertainty in the numerical age of the monitor standards
491 used in the $^{40}\text{Ar}/^{39}\text{Ar}$ studies that constrain the K/Pg boundary (see Section 1) result in
492 uncertainties on the order of ~600 kyr or greater [Kuiper *et al.*, 2008; Channell *et al.*, 2010;
493 Renne *et al.*, 2010] which precludes the accurate determination of the number of 405 kyr cycles
494 within the Paleocene. Given our high-precision and high-accuracy constraint for the P/E
495 boundary we suggest that the uncertainty of the numerical age of the K/Pg boundary now
496 represents the most substantial source of uncertainty for constraining the duration of the
497 Paleocene. However, an alternative way to derive the age of the K/Pg boundary is to use our P/E
498 boundary age together with the duration of the Paleocene Epoch derived from
499 cyclostratigraphic studies.

500 Such cyclostratigraphic analyses of early Paleogene successions from ODP Legs 198 (Shatsky
501 Rise, NW Pacific Ocean) and 208 (Walvis Ridge, SE Atlantic Ocean), together with ODP sites 1001
502 (Nicaragua Basin), 1051 (Blake Nose) and the Zumaia outcrop section (Basque Basin, Spain), led
503 to the development of an age model for the Paleocene where the K/Pg and P/E boundaries were
504 separated by twenty-four 405 kyr eccentricity cycles giving a duration of 9.720 Myr [*Westerhold*
505 *et al.*, 2008]. However, recent analysis of the Zumaia outcrop section [*Kuiper et al.*, 2008],
506 implies that an additional 405 kyr eccentricity cycle (relative to *Westerhold et al.* [2008]) is
507 present in the Paleocene epoch. A revised analysis of the Fe and magnetic susceptibility records
508 from ODP Site 1263 has also suggested twenty-five 405 kyr eccentricity cycles are present in the
509 Paleocene [*Hilgen et al.*, 2010]. If we assume that the most recent cyclostratigraphic studies for
510 the duration of the Paleocene are accurate (twenty-five 405 kyr cycles [*Kuiper et al.*, 2008;
511 *Hilgen et al.*, 2010]), this would indicate a duration of 10.125 Myr for the Paleocene epoch. This
512 duration combined with our age range of 55.728-55.964 Ma for the P/E boundary predicts an
513 age of ~66 Ma for the K/Pg boundary.

514

515 Insert Figure 9 here

516

517 *4.3 Implications for the PETM trigger mechanism*

518 Our new age for the P/E boundary allows us to investigate the relationship between the PETM
519 and potential forcing mechanisms. It has been proposed that insolation maxima during the peak
520 of both short (~100 kyr) and long (405 kyr) eccentricity cycles may have resulted in warmer
521 water conditions, triggering the dissociation of methane hydrates on the seafloor, and thus

522 generating hyperthermal events such as the PETM [*Cramer et al.*, 2003; *Lourens et al.*, 2005;
523 *Sluijs et al.*, 2007]. However, *Westerhold et al.* [2007] argued that the PETM occurred on the
524 falling limb of a 405 kyr eccentricity cycle, based on records of the this cycle extracted from ODP
525 Site 1262. Here, we plot our age range of 55.728-55.964 Ma for the P/E boundary (equivalent to
526 the PETM CIE onset) against the astronomical solution of *Laskar et al.* [2004] to illustrate the
527 relationship between the PETM onset age and 405 kyr eccentricity forcing (Figure 10). Orbital
528 models have illustrated that the 405 kyr eccentricity phase is stable over the entire Paleogene
529 interval [*Laskar et al.* 2004], which validates our approach, although the relative cycle-to-cycle
530 amplitude is less certain due to the chaotic nature of the solar system. The total uncertainty for
531 the age of the PETM onset from Spitsbergen illustrates that the PETM was not initiated on the
532 peak of a 405 kyr cycle (Figure 10). In addition, it has been argued that the PETM onset age must
533 fall within one of the age options proposed by *Westerhold et al.* [2007; 2008] in order to
534 maintain the phase relationship of the 405 kyr eccentricity cycle between astronomical solutions
535 and records of the same cycle extracted from ODP Site 1262 [*Röhl et al.*, 2007; *Westerhold et al.*,
536 2007; 2008]. Given our age range is within error of astronomical age option 2 (Figure 10), our
537 results are consistent with the hypothesis that the onset of the PETM occurred on the falling
538 limb of a 405 kyr eccentricity cycle [*Westerhold et al.*, 2007]. Conversely, cyclostratigraphic
539 studies of geological datasets have consistently placed ETM2 (equivalent to the Elmo event of
540 *Lourens et al.* [2005]; or event H1 of *Cramer et al.* [2003]), ETM3 (or the X event of *Zachos et al.*
541 [2004]; event K of *Cramer et al.* [2003]) and other potential hyperthermals (negative CIEs of
542 *Cramer et al.* [2003]) either on the maxima of both 100 and 405 kyr cycles [*Lourens et al.*, 2005;
543 *Galeotti et al.*, 2010] or with ETM2 at a 100 kyr eccentricity peak on the rising limb of a 405 kyr
544 eccentricity cycle [*Westerhold et al.*, 2007; *Westerhold and Röhl*, 2009; *Zachos et al.*, 2010],
545 consistent with orbital forcing as a common trigger mechanism. Therefore, the occurrence of

546 the PETM on the falling limb of a 405 kyr eccentricity cycle supports the hypothesis that the
547 event required a different trigger mechanism when compared to other early Eocene
548 hyperthermals [Zachos *et al.*, 2010].

549 It has also been proposed that the PETM may have been triggered by the injection of volcanic
550 sills into organic-rich sediments in the North Atlantic, generating methane and/or carbon
551 dioxide via contact metamorphism, with outgassing through hydrothermal vent systems
552 [Svensen *et al.*, 2004, 2010; Storey *et al.*, 2007]. If correct, it would be expected that the
553 emplacement of these sills occurred immediately prior to the onset of the PETM. Recent
554 estimates for the emplacement of sills on the Vøring Plateau (55.6 ± 0.3 and 56.3 ± 0.4 Ma;
555 Svensen *et al.* [2010]) and for the eruption of mid-ocean ridge basalt-like flows in the North
556 Atlantic (55.5 ± 0.3 Ma; Storey *et al.* [2007]) are within error of our new age for the onset of the
557 PETM. However, given the low uncertainty on our age for the PETM onset, age estimates with
558 equivalent uncertainties are required for igneous units in the North Atlantic, in order to fully test
559 the hypothesis that volcanism was responsible for the release of the isotopically light carbon
560 which gave rise to the PETM.

561

562 **5. Conclusions**

563 Our combined chemo- and bio-stratigraphic analysis enables the PETM to be recognized at two
564 localities in the Central Basin of Spitsbergen, and demonstrates that two coeval bentonite layers
565 occur within the PETM CIE at both localities. By integrating cyclostratigraphic datasets with
566 radio-isotopic dating ($^{238}\text{U}/^{206}\text{Pb}$, zircon) of the PETM CIE, we derive similar numerical ages for
567 the P/E boundary based on two different options for the interpretation of the cyclostratigraphic

568 data. This approach yields a total uncertainty for the P/E boundary (equivalent to the PETM CIE
569 onset age) between 55.728-55.964 Ma, which is within error of astronomical age option 2
570 [Westerhold *et al.*, 2007, 2008]. Combined with models of the duration of the Paleocene
571 spanning twenty-five 405 kyr cycles [Kuiper *et al.*, 2008; Hilgen *et al.*, 2010], our new age range
572 for the boundary predicts that the numerical age of the K/Pg boundary is ~66 Ma. Furthermore,
573 the new age for the P/E boundary (PETM CIE onset age) provides additional constraints on the
574 trigger mechanism for the PETM. Comparing our age range for the PETM CIE onset with the
575 *Laskar et al.* [2004] orbital solution indicates that the event was not initiated on a 405 kyr
576 eccentricity peak. Furthermore, our age range is within error of astronomical age option 2 of
577 *Westerhold et al.* [2007; 2008], consistent with the hypothesis that the onset of the PETM
578 occurred on the falling limb of a 405 kyr eccentricity cycle [Westerhold *et al.*, 2007]. Conversely,
579 other early Eocene hyperthermals have been inferred to occur on eccentricity maxima (or with
580 ETM2 on the rising limb of a 405 kyr cycle) consistent with orbital forcing as a common trigger
581 mechanism. Our results thus suggest that the PETM was triggered by a mechanism different
582 from that proposed for the later Eocene hyperthermals.

583

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599

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839 **Figure captions**

840 **Figure 1:** Study area. **a**, Map of Spitsbergen illustrating study localities (after *Uroza and Steel*
841 [2008]; *Blythe and Kleinspehn* [1998]). **b**, The Paleogene stratigraphy of Spitsbergen illustrating
842 the interval of the Frysjaodden Formation studied at each locality (after *Uroza and Steel* [2008];
843 *Steel et al.* [1985]). **c**, Paleogeographic reconstruction of Spitsbergen (in black) and the Svalbard
844 archipelago in the Eocene (after *Mosar et al.* [2002]).

845

846 **Figure 2:** Lithological, dinocyst and geochemical (organic carbon isotope [$\delta^{13}\text{C}_{\text{TOC}}\text{‰}$]; TOC [%];
847 Log Fe [ppm]) datasets across the P/E boundary from **a**, the Longyearbyen outcrop section
848 [*Harding et al.*, 2011] and **b**, core BH9/05 [Log: *Dypvik et al.*, 2011; $\delta^{13}\text{C}_{\text{TOC}}$: *Cui*, 2010]. Note the
849 Hollendardalen Formation is absent in core BH9/05, due to pinch out south of the Longyearbyen
850 section [e.g. *Dallman et al.*, 1999]. Cycle numbers and CIE phases adhere to those proposed by
851 *Röhl et al.* [2007]. Note that the heights/depths used to define the base and top of recovery
852 phase I are based on analysis of both cyclostratigraphic and $\delta^{13}\text{C}_{\text{TOC}}$ records (as suggested by
853 *Röhl et al.* [2007]), due to the asymptotic shape of CIE recovery interval in Spitsbergen.

854

855 **Figure 3:** Comparison of PETM CIE records from Spitsbergen and selected ODP sites. **a**, Core
856 BH9/05, Spitsbergen, $\delta^{13}\text{C}_{\text{TOC}}$ (‰) record of *Cui* [2010; black], and Log Fe (ppm; this study). **b**,
857 ODP Site 1263 (Leg 208, Walvis Ridge) $\delta^{13}\text{C}_{\text{carbonate}}$ (‰) record from *Zachos et al.* [2005; black],
858 and Ba (area) records from *Röhl et al.* [2007; grey]. **c**, ODP Site 690 (Leg 113, Weddell Sea)
859 $\delta^{13}\text{C}_{\text{carbonate}}$ (‰) record from *Bains et al.* [1999; black] and Ba records from *Röhl et al.* [2007;
860 grey]. Panels **b**, and **c** after *Röhl et al.* [2007]. Cycle numbers and CIE phases adhere to those

861 proposed by *Röhl et al.* [2007]. Note that due to the asymptotic shape of CIE recovery interval in
862 Spitsbergen, we identified the onset and end of recovery phase I using both the $\delta^{13}\text{C}_{\text{TOC}}$ and
863 cyclostratigraphic records of core BH9/05, as suggested by *Röhl et al.* [2007].

864

865 **Figure 4:** BH9/05 time-series in the depth domain. **a** and **c**, Log Mn and Fe wavelet spectra
866 respectively. Black lines indicate 95% significance level. Shaded area indicates the ‘cone of
867 influence’ where edge effects make recognition of cycles less confident [*Torrence and Compo,*
868 1998]. Warm (cold) colors indicate high (low) spectral power. **b**, Log Mn (blue) and Fe (red) time-
869 series. Grey bands represent 2σ error values for the precision of the Niton UK XRF scanner,
870 calculated using the standard deviation derived from repeat analyses of fifteen samples, each
871 measured 10 times. Yellow box indicates stratigraphic thickness of PETM CIE. **d**, and **e**, Multi-
872 taper method power spectra [*Thompson, 1982*] for the intervals from 475-551 m and 135-475 m
873 respectively. Grey bars illustrate the dominant cycles and their stratigraphic thickness. Note the
874 wide bandwidth on panel d is the result of the short stratigraphic thickness of the time-series
875 with respect to the cycle wavelengths being analyzed (which has the effect of smearing out the
876 spectral peaks). Spectra were generated by re-sampling the time-series using a constant sample
877 spacing (0.2 m, panel d; 0.5 m, panel e), using 3 tapers. Red noise models were generated using
878 SSA-MTM toolkit [*Ghil et al., 2002*] to calculate the confidence levels illustrated.

879

880 **Figure 5:** Calibration curve for the Niton UK portable XRF device to wavelength dispersive (WD)
881 XRF.

882

883 **Figure 6:** U-Pb data for sample SB01-1. **a**, conventional U-Pb concordia plot of zircons analysed
884 from sample SB01-1. The grey band reflects the uncertainty in the ^{238}U and ^{235}U decay constants
885 [Jaffey *et al.*, 1971]. **b**, plot of $^{238}\text{U}/^{206}\text{Pb}$ dates for single zircon crystals analyses (same data as in
886 Figure 6a). Dashed ellipses/bars represent analyses of zircon that are considered to be
887 xenocrysts and/or inherited crystals that are disregarded in calculation of final date, whereas as
888 grey filled ellipses/bars represent the analyses used for calculation of the weighted mean final
889 date (see text for discussion).

890

891 **Figure 7:** Filtered records of core BH9/05 in the depth domain. **a**, $\delta^{13}\text{C}_{\text{TOC}}$ (‰) from Cui [2010],
892 illustrating the phases of the PETM CIE from Röhl *et al.* [2007]. **b**, BH9/05 Log Fe (ppm; red) and
893 Mn (ppm; blue) time-series. Cycle numbers adhere to those of Röhl *et al.* [2007], with potential
894 additional cycles marked with an asterisk. **c**, Log Fe (red) and Log Mn (blue) 4.2 m (0.24 ± 0.07
895 cycles/m) Gaussian filter output, representing the precession component of orbital forcing (cycle
896 numbers as in panel b). **e**, Log Fe (red) and Log Mn (blue) 20 m (0.05 ± 0.01 cycles/m) filter,
897 representing the short eccentricity (~ 100 kyr) component of orbital forcing.

898

899 **Figure 8:** The age of the Paleocene/Eocene boundary in Spitsbergen, using cyclostratigraphic
900 Option A. **a**, $\delta^{13}\text{C}_{\text{TOC}}$ (‰) from the Longyearbyen section (black) [Harding *et al.*, 2011] and core
901 BH9/05 (red) [Cui, 2010]. **b**, Longyearbyen TOC (%) [Harding *et al.*, 2011]. **c**, Core BH9/05 Log Fe
902 (ppm, red) and Mn (ppm, blue). **d**, 21 kyr Gaussian filter outputs for TOC (black) Log Fe (red) and
903 Log Mn (blue) respectively, illustrating an ~ 40 kyr duration between the onset of the PETM CIE
904 and the bentonite layer.

905 **Figure 9:** The age of the Paleocene/Eocene boundary in Spitsbergen, using cyclostratigraphic
906 Option B. **a**, $\delta^{13}\text{C}_{\text{TOC}}$ (‰) from core BH9/05 (red) [Cui, 2010], illustrating the phases of the PETM
907 CIE from Röhl *et al.* [2007]. **b**, Core BH9/05 Log Fe (ppm, red) and Mn (ppm, blue). Cycle
908 numbers adhere to those of Röhl *et al.* [2007], with potential additional cycles marked with an
909 asterisk. **d**, 21 kyr Gaussian filter outputs for Log Fe (red) and Log Mn (blue) respectively,
910 illustrating an ~80 kyr duration between the onset of the PETM CIE and the bentonite layer.

911

912 **Figure 10:** The position of the P/E boundary (equivalent to the PETM CIE onset) with respect to
913 orbital forcing. **a**, comparison of P/E boundary ages determined from Spitsbergen with the
914 astronomical age options of Westerhold *et al.* [2007, 2008]. Note that both Spitsbergen age
915 options are within error of astronomical age option 2 (55.93 Ma). **b**, total uncertainty for the age
916 of the P/E boundary from Spitsbergen (grey shaded bar), plotted against the Laskar *et al.* [2004;
917 La2004] orbital solution. Age option 2 of Westerhold *et al.* [2007, 2008] is plotted for
918 comparison.

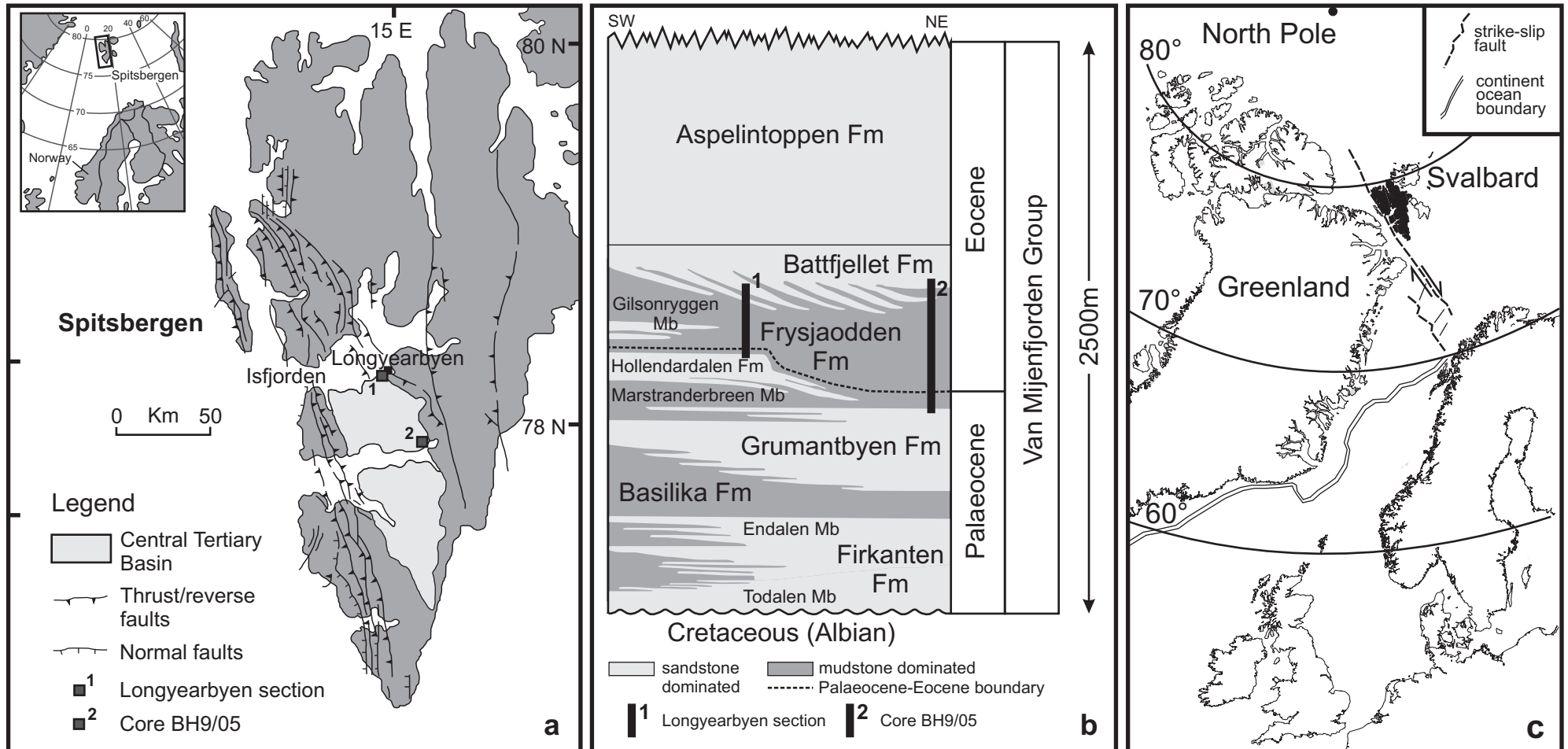


Figure 1: Study area. a, Map of Spitsbergen illustrating study localities (after Uroza and Steel [2008]; Blythe and Kleinspehn [1998]). b, The Paleogene stratigraphy of Spitsbergen illustrating the interval of the Frysjaodden Formation studied at each locality (after Uroza and Steel [2008]; Steel et al. [1985]). c, Paleogeographic reconstruction of Spitsbergen (in black) and the Svalbard archipelago in the Eocene (after Mosar et al. [2002]).

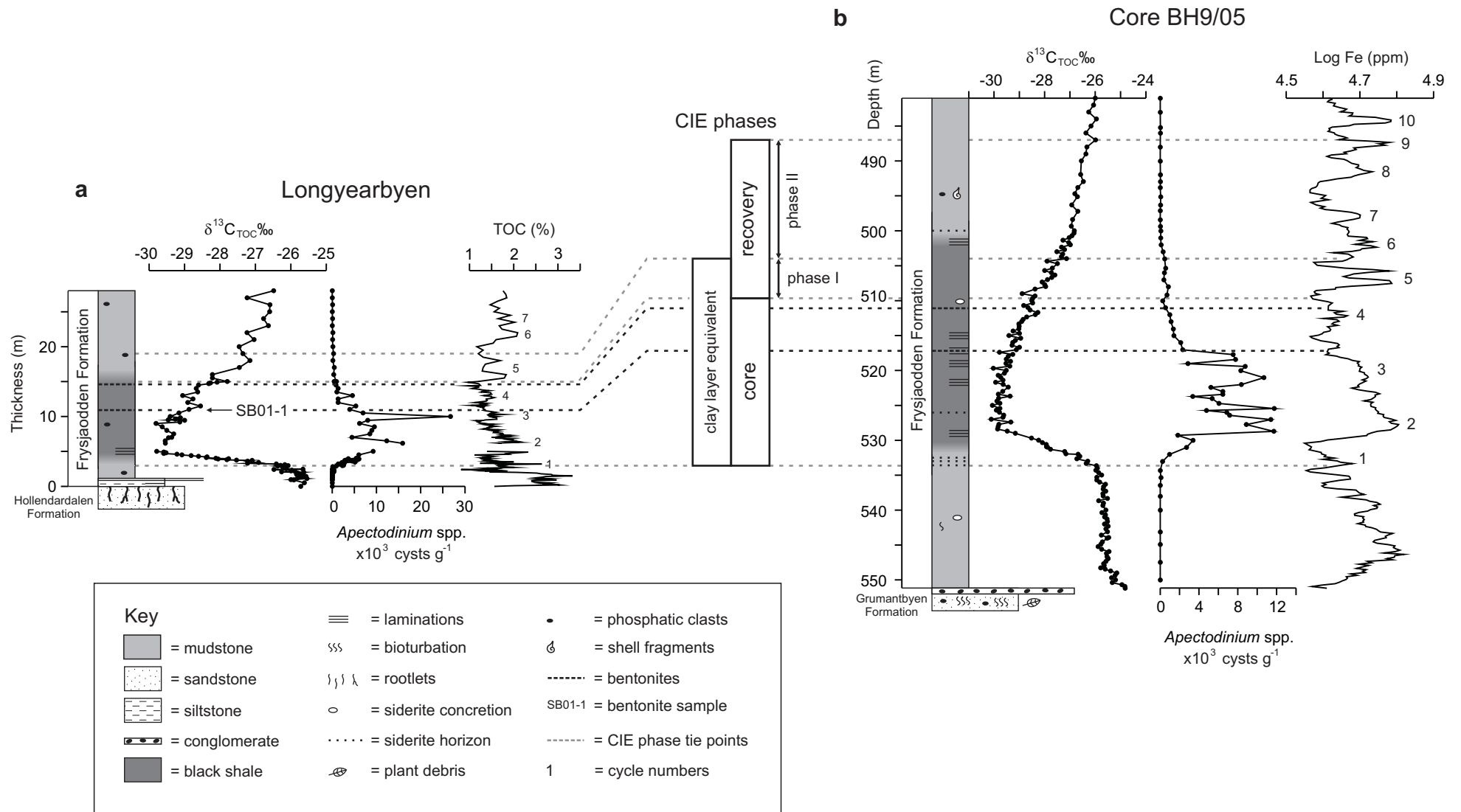


Figure 2: Lithological, dinocyst and geochemical (organic carbon isotope [$\delta^{13}\text{C}_{\text{TOC}}\text{‰}$]; TOC [%]; Log Fe [ppm]) datasets across the P/E boundary from **a**, the Longyearbyen outcrop section [Harding *et al.*, in press] and **b**, core BH9/05 [Log: Dypvik *et al.*, in press; $\delta^{13}\text{C}_{\text{TOC}}$: Cui, 2010]. Note the Hollandardalen Formation is absent in core BH9/05, due to pinch out south of the Longyearbyen section [e.g. Dallman *et al.*, 1999].

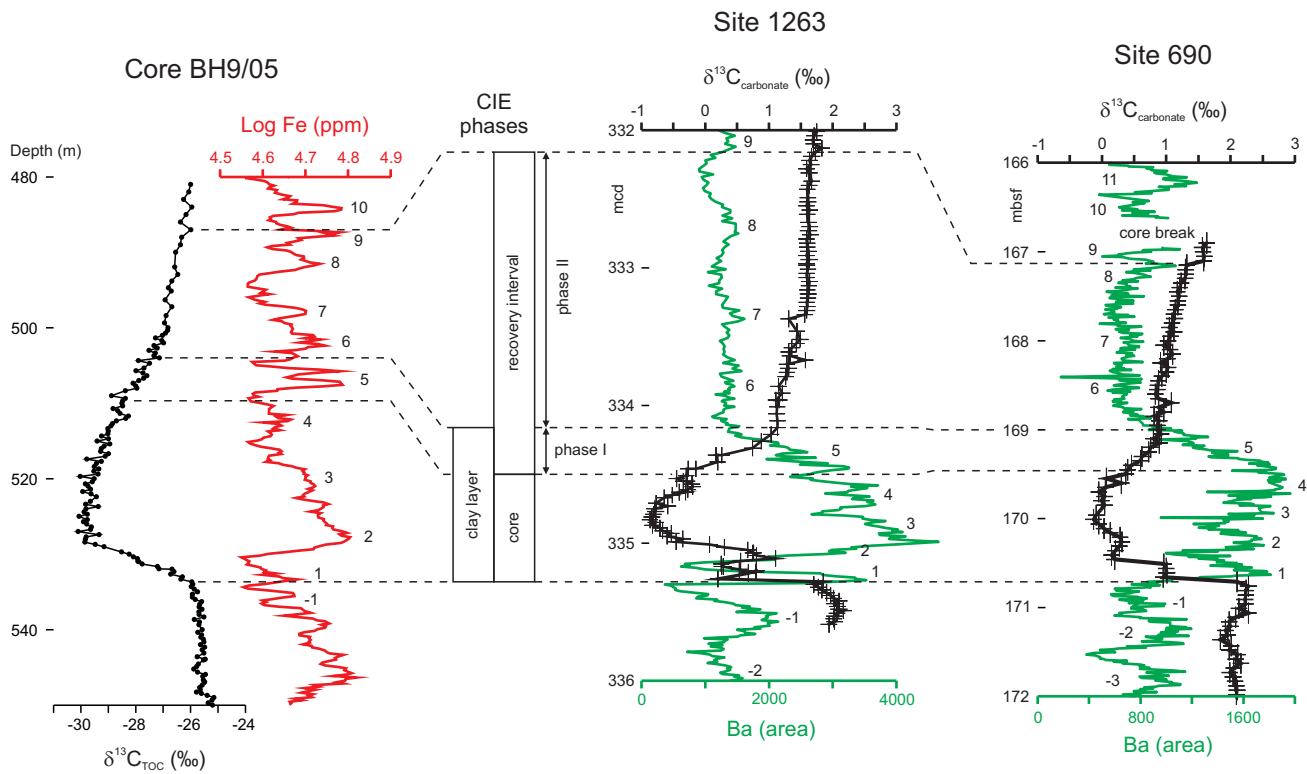


Figure 3: Comparison of PETM CIE records from Spitsbergen and selected ODP sites. **a**, Core BH9/05, Spitsbergen, $\delta^{13}C_{TOC}$ (‰) record of Cui [2010; black], and Log Fe (ppm; this study). **b**, ODP Site 1263 (Leg 208, Walvis Ridge) $\delta^{13}C_{carbonate}$ (‰) record from Zachos *et al.* [2005; black], and Ba (area) records from Röhl *et al.* [2007; grey]. **c**, ODP Site 690 (Leg 113, Weddell Sea) $\delta^{13}C_{carbonate}$ (‰) record from Bains *et al.* [1999; black] and Ba records from Röhl *et al.* [2007; grey]. Panels **b**, and **c** were modified after Röhl *et al.* [2007]. Cycle numbers and CIE phases adhere to those proposed by Röhl *et al.* [2007]. Note that due to the asymptotic shape of CIE recovery interval in Spitsbergen, we identified the onset and end of recovery phase I using both the $\delta^{13}C_{TOC}$ and cyclostratigraphic records of core BH9/05, as suggested by Röhl *et al.* [2007].

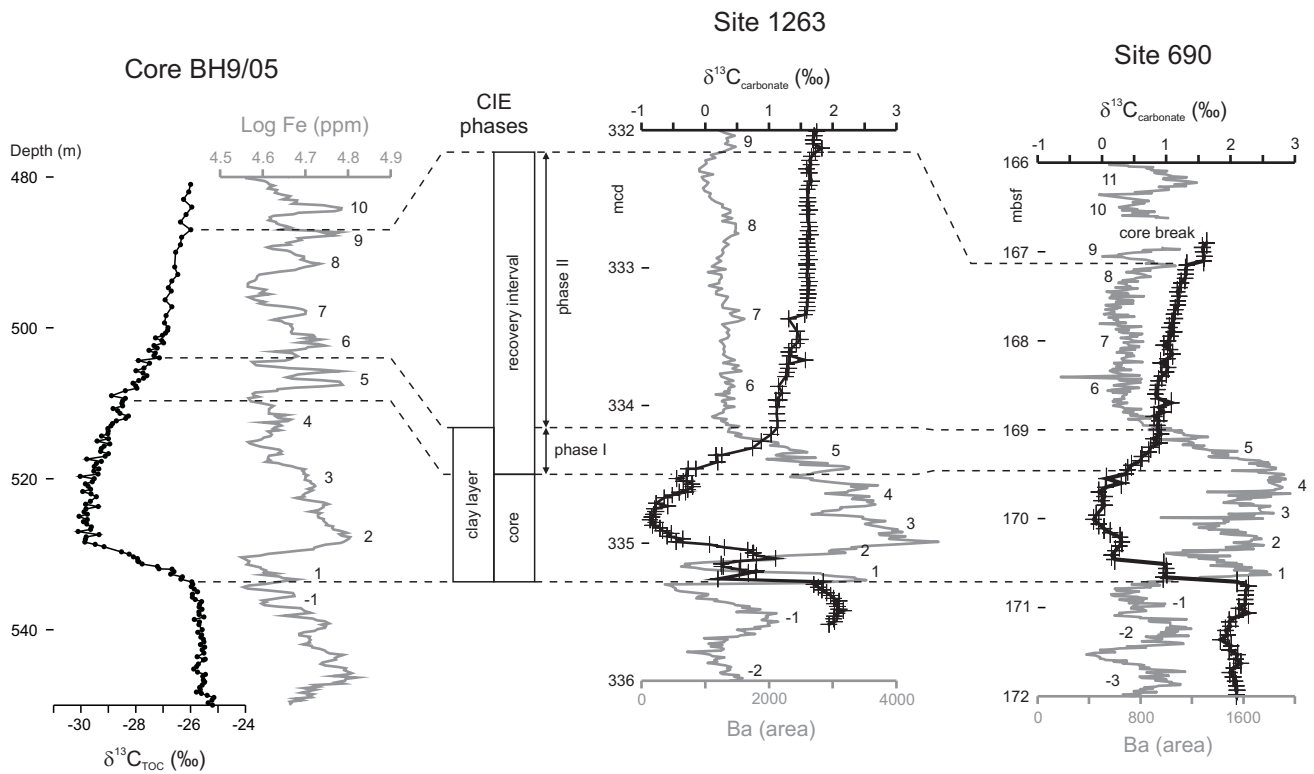
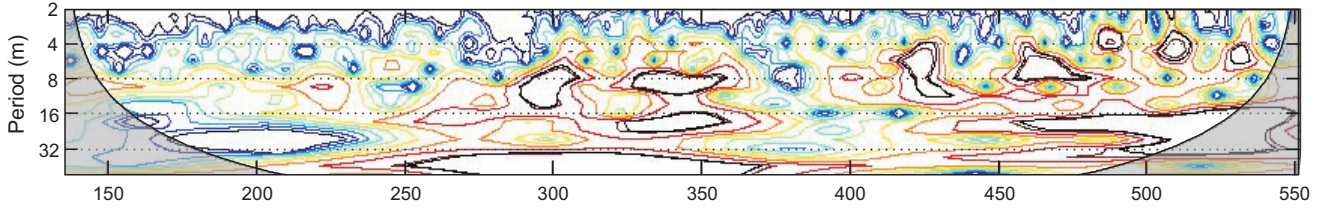
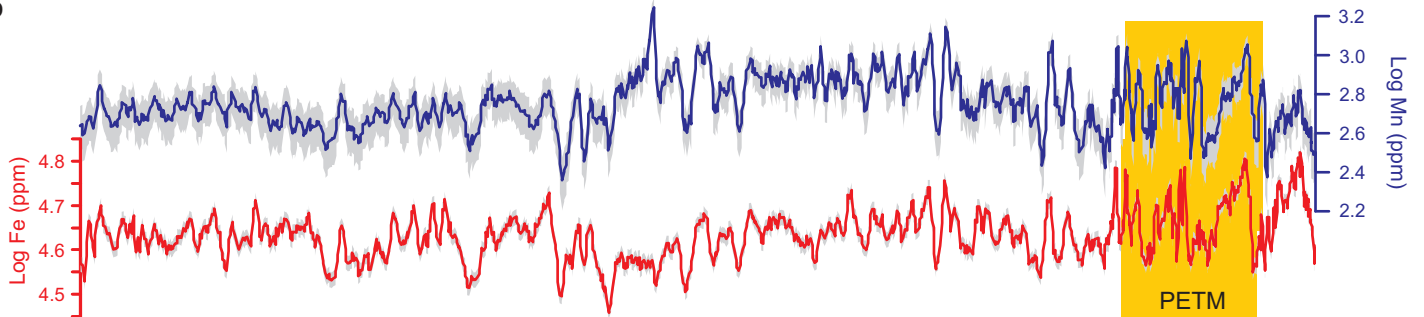


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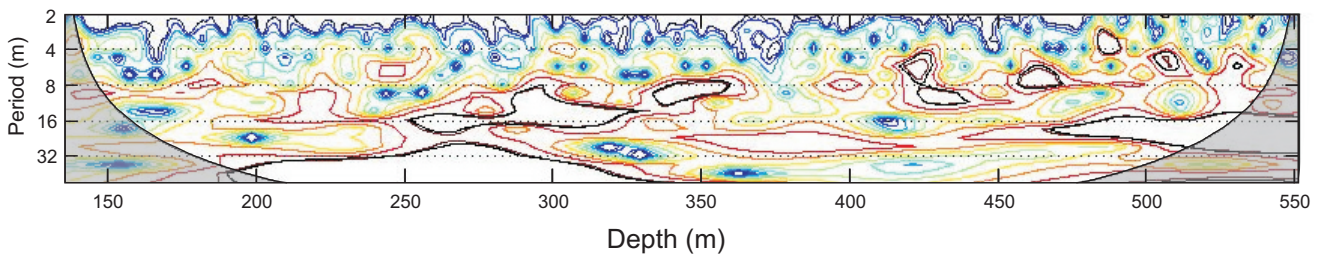
a Log Mn wavelet spectra



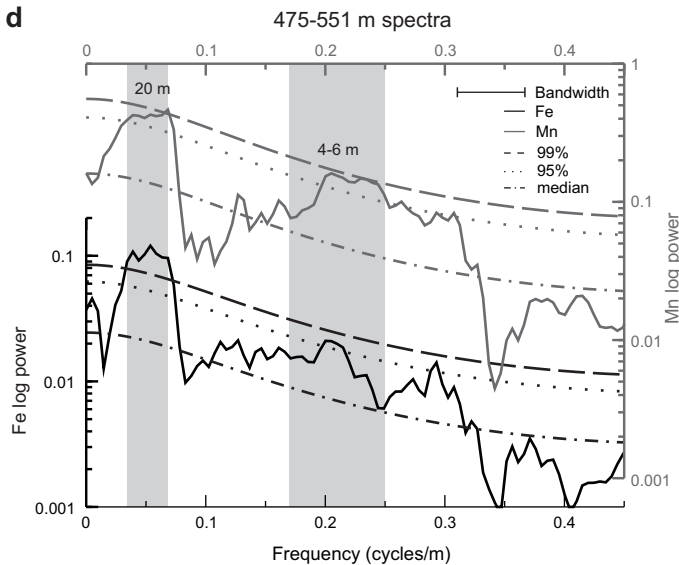
b



c Log Fe wavelet spectra



d



e

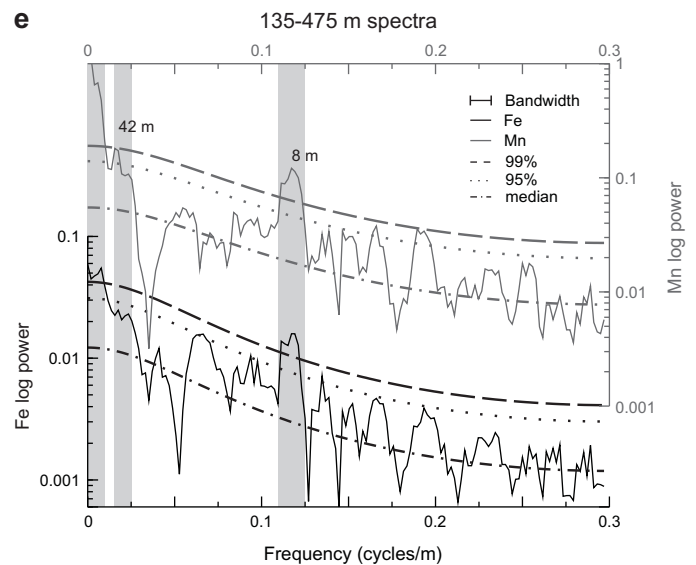
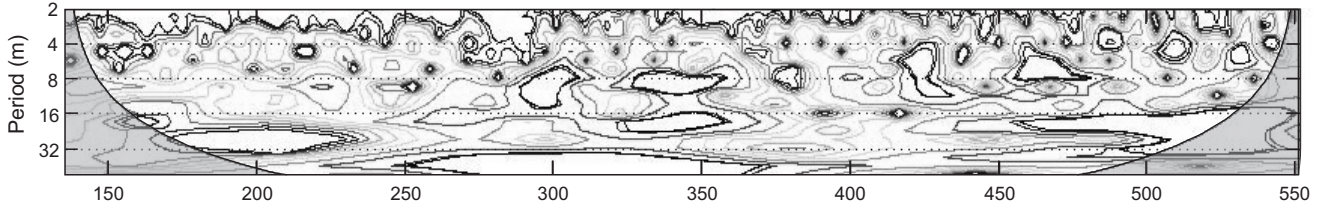
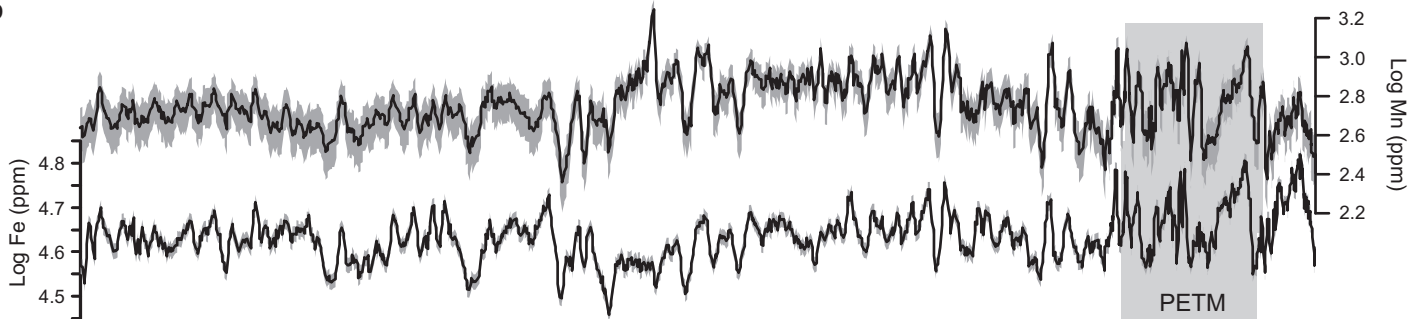


Figure 4: BH9/05 time-series in the depth domain. **a** and **c**, Log Mn and Fe wavelet spectra respectively. Black lines indicate 95% significance level. Shaded area indicates the 'cone of influence' where edge effects make recognition of cycles less confident [Torrence and Compo, 1998]. Warm (cold) colors indicate high (low) spectral power. **b**, Log Mn (blue) and Fe (red) time-series. Grey bands represent 2σ error values for the precision of the Niton UK XRF scanner, calculated using the standard deviation derived from repeat analyses of fifteen samples, each measured 10 times. Yellow box indicates stratigraphic thickness of PETM CIE. **d**, and **e**, Multi-taper method power spectra [Thompson, 1982] for the intervals from 475-551 m and 135-475 m respectively. Grey bars illustrate the dominant cycles and their stratigraphic thickness. Note the wide bandwidth on panel d is the result of the short stratigraphic thickness of the time-series with respect to the cycle wavelengths being analyzed (which has the effect of smearing out the spectral peaks). Spectra were generated by re-sampling the time-series using a constant sample spacing (0.2 m, panel d; 0.5 m, panel e), using 3 tapers. Red noise models were generated using SSA-MTM toolkit [Ghil et al., 2002] to calculate the confidence levels illustrated.

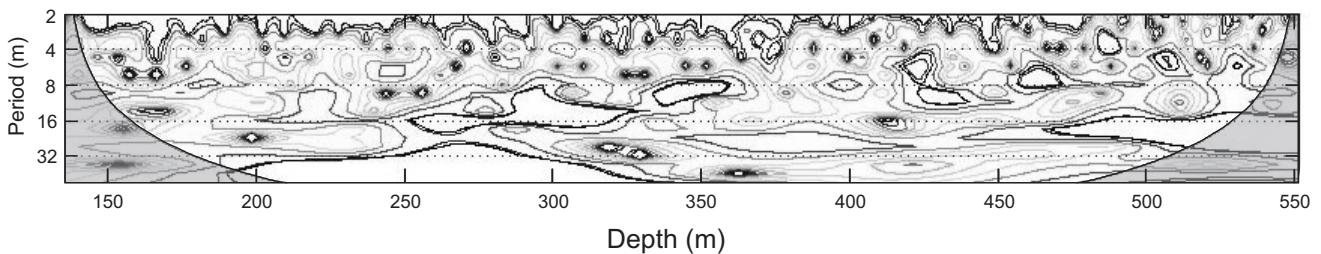
a Log Mn wavelet spectra



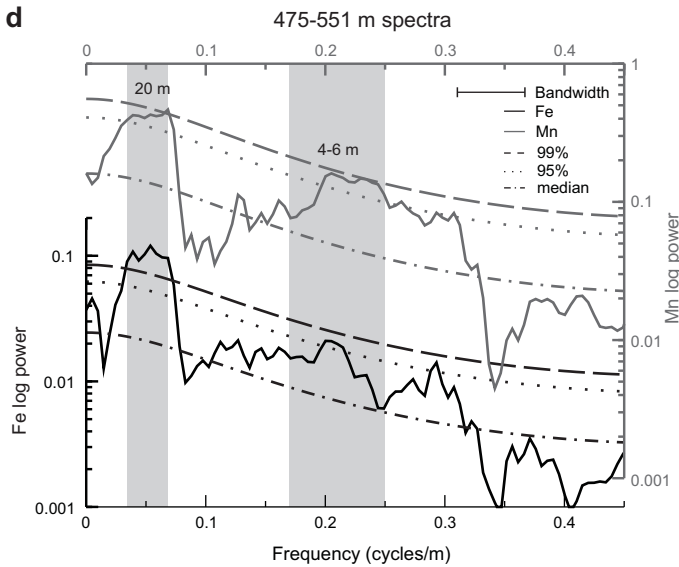
b



c Log Fe wavelet spectra



d



e

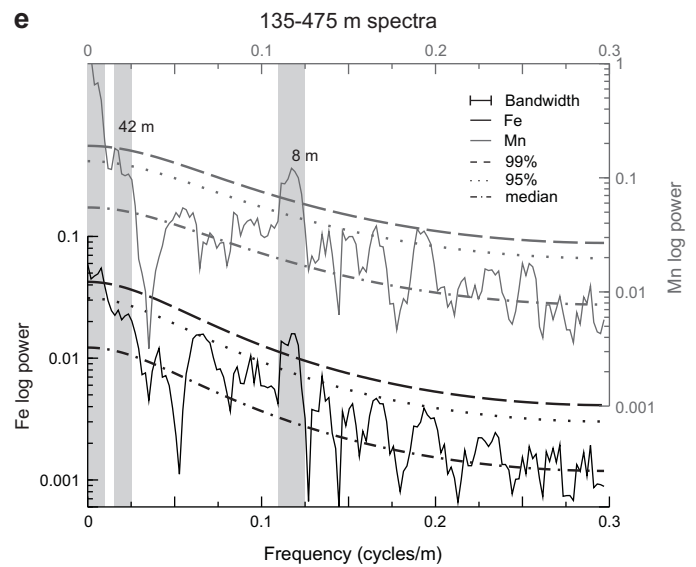


Figure 4: BH9/05 time-series in the depth domain. **a** and **c**, Log Mn and Fe wavelet spectra respectively. Black lines indicate 95% significance level. Shaded area indicates the 'cone of influence' where edge effects make recognition of cycles less confident [Torrence and Compo, 1998]. Warm (cold) colors indicate high (low) spectral power. **b**, Log Mn (blue) and Fe (red) time-series. Grey bands represent 2σ error values for the precision of the Niton UK XRF scanner, calculated using the standard deviation derived from repeat analyses of fifteen samples, each measured 10 times. Yellow box indicates stratigraphic thickness of PETM CIE. **d**, and **e**, Multi-taper method power spectra [Thompson, 1982] for the intervals from 475-551 m and 135-475 m respectively. Grey bars illustrate the dominant cycles and their stratigraphic thickness. Note the wide bandwidth on panel d is the result of the short stratigraphic thickness of the time-series with respect to the cycle wavelengths being analyzed (which has the effect of smearing out the spectral peaks). Spectra were generated by re-sampling the time-series using a constant sample spacing (0.2 m, panel d; 0.5 m, panel e), using 3 tapers. Red noise models were generated using SSA-MTM toolkit [Ghil et al., 2002] to calculate the confidence levels illustrated.

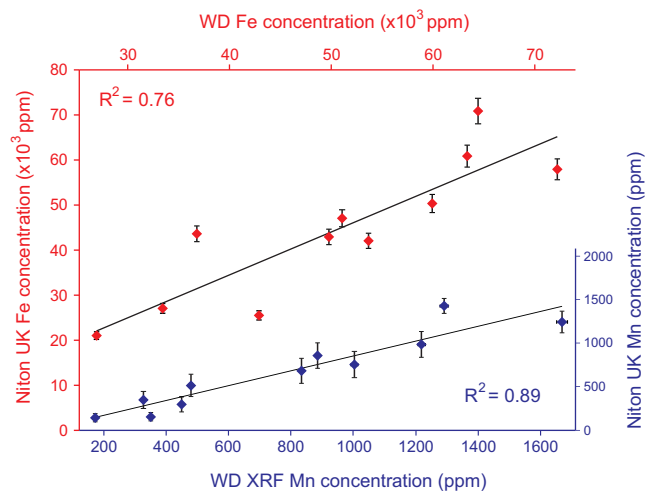


Figure 5: Calibration curve for the Niton UK portable XRF device to wavelength dispersive (WD) XRF.

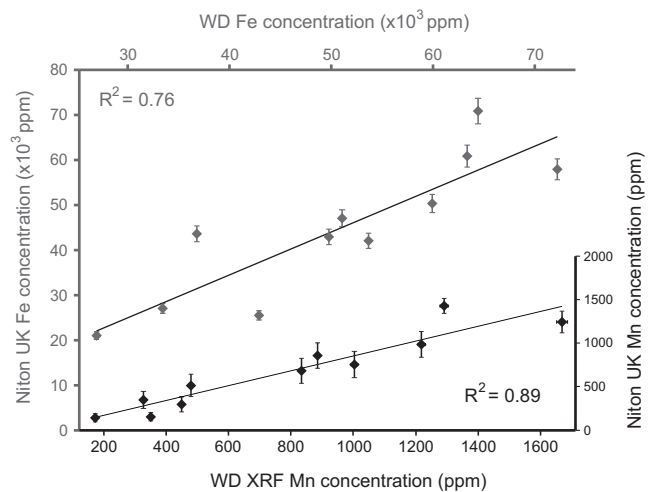


Figure 5: Calibration curve for the Niton UK portable XRF device to wavelength dispersive (WD) XRF.

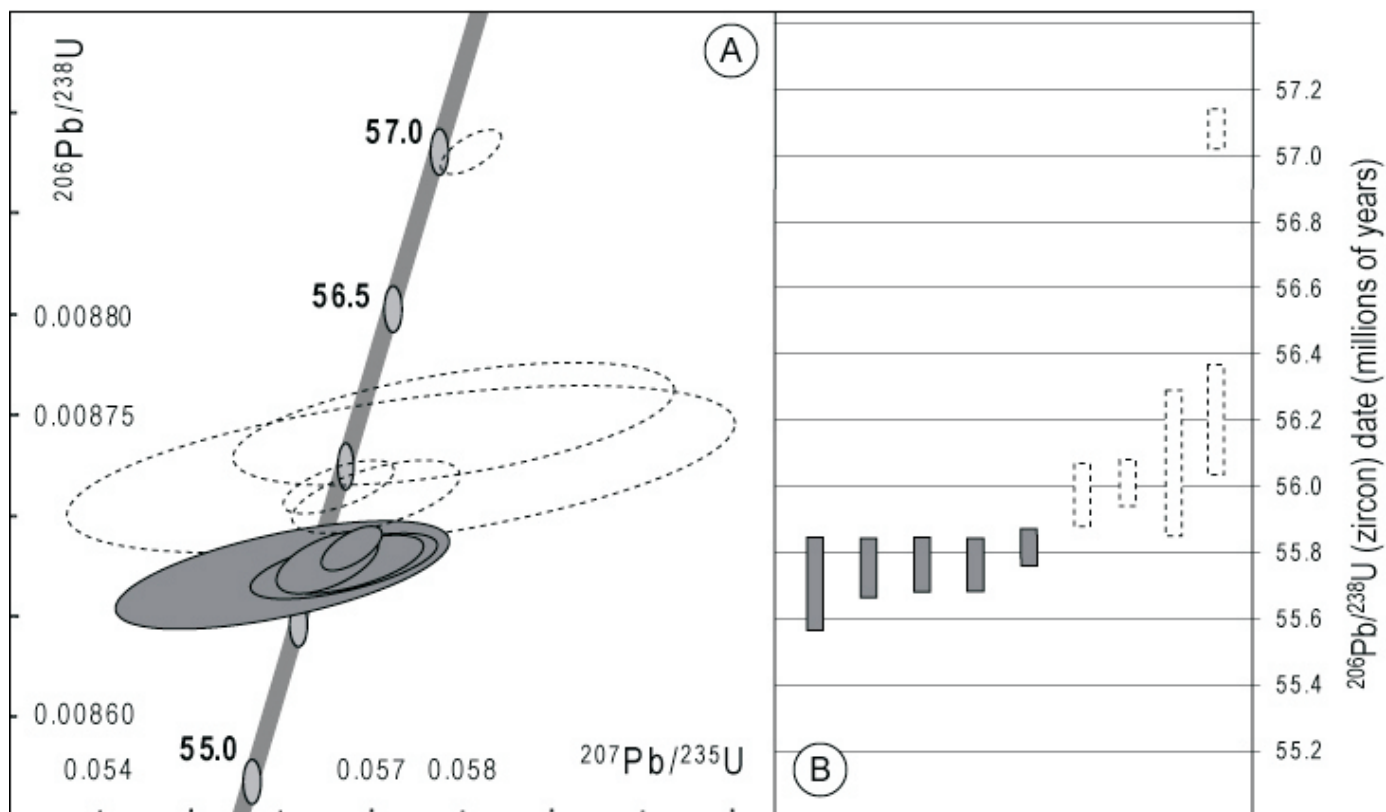


Figure 6: U-Pb data for sample SB01-1. a, conventional U-Pb concordia plot of zircons analysed from sample SB01-1. The grey band reflects the uncertainty in the ^{238}U and ^{235}U decay constants [Jaffey et al., 1971]. b, plot of $^{238}\text{U}/^{206}\text{Pb}$ dates for single zircon crystals analyses (same data as in Figure 6a). Dashed ellipses/bars represent analyses of zircon that are considered to be xenocrysts and/or inherited crystals that are disregarded in calculation of final date, whereas as grey filled ellipses/bars represent the analyses used for calculation of the weighted mean final date (see text for discussion).

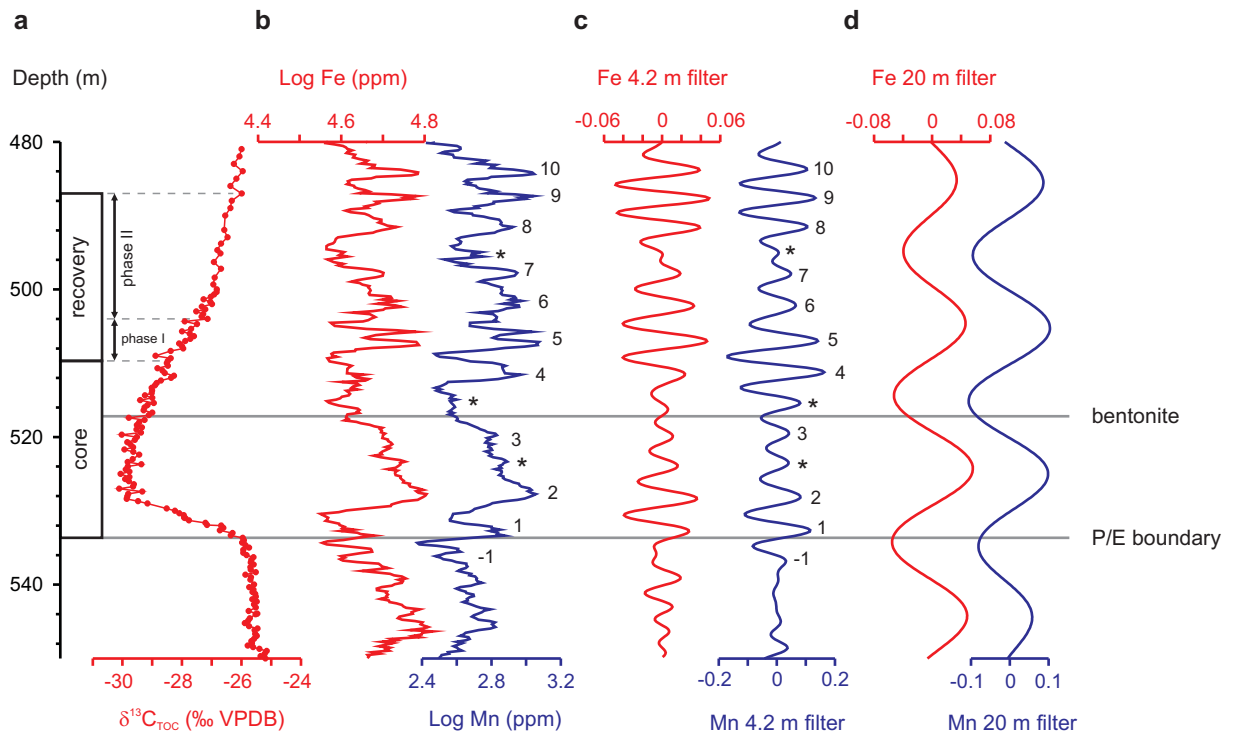


Figure 7: Filtered records of core BH9/05 in the depth domain. **a**, $\delta^{13}\text{C}_{\text{TOC}}$ (‰) from Cui [2010], illustrating the phases of the PETM CIE from Röhl *et al.* [2007]. **b**, BH9/05 Log Fe (ppm; red) and Mn (ppm; blue) time-series. Cycle numbers adhere to those of Röhl *et al.* [2007], with potential additional cycles marked with an asterisk. **c**, Log Fe (red) and Log Mn (blue) 4.2 m (0.24 ± 0.07 cycles/m) Gaussian filter output, representing the precession component of orbital forcing (cycle numbers as in panel b). **d**, Log Fe (red) and Log Mn (blue) 20 m (0.05 ± 0.01 cycles/m) filter, representing the short eccentricity (~ 100 kyr) component of orbital forcing.

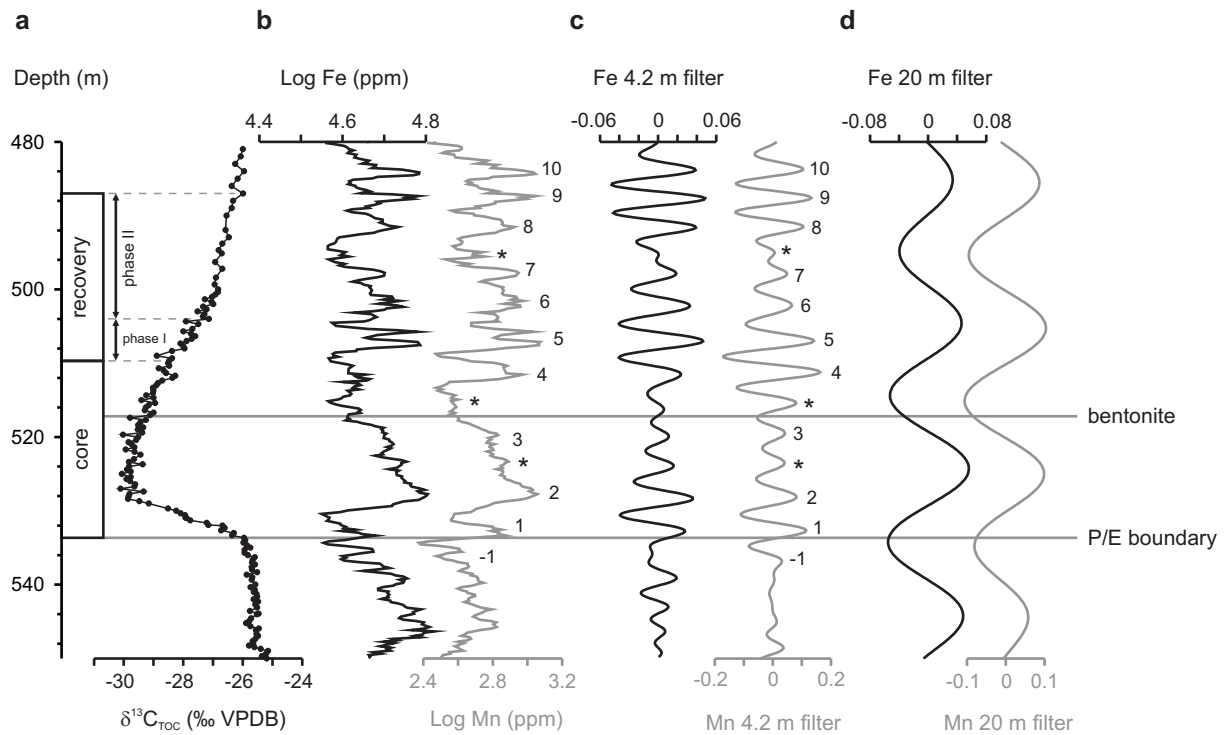


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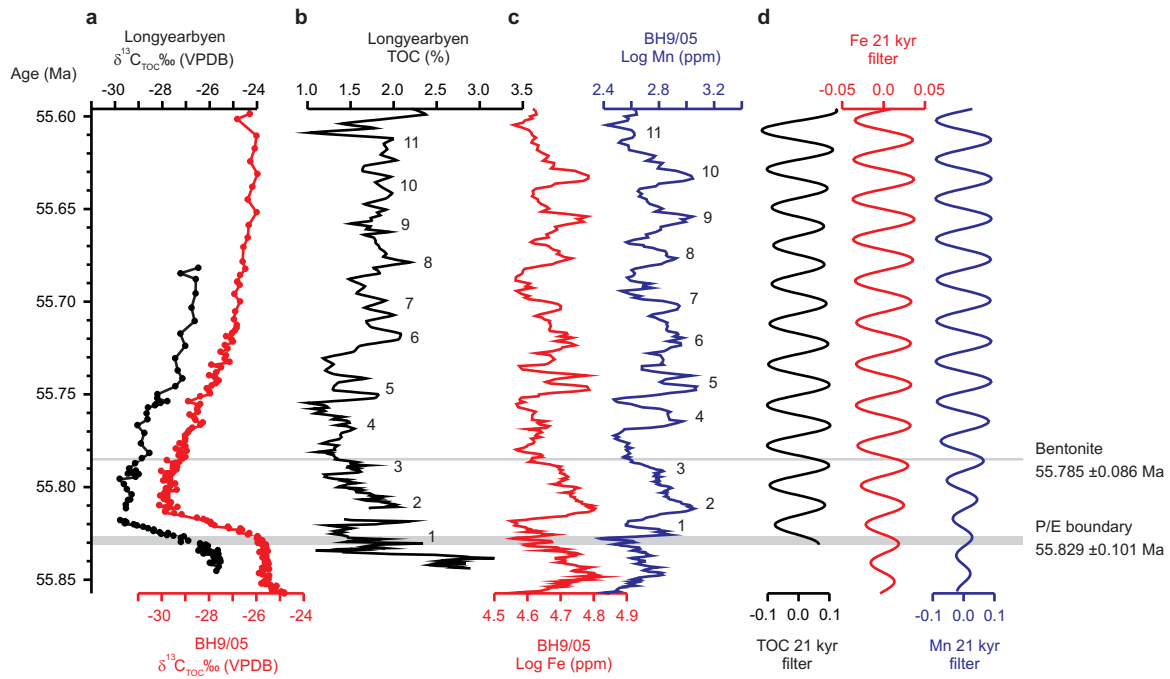


Figure 8: The age of the Paleocene/Eocene boundary in Spitsbergen, using cyclostratigraphic Option A. **a**, $\delta^{13}\text{C}_{\text{TOC}}$ (‰) from the Longyearbyen section (black) [Harding *et al.*, 2011] and core BH9/05 (red) [Cui, 2010]. **b**, Longyearbyen TOC (%) [Harding *et al.*, 2011]. **c**, Core BH9/05 Log Fe (ppm, red) and Mn (ppm, blue). **d**, 21 kyr Gaussian filter outputs for TOC (black) Log Fe (red) and Log Mn (blue) respectively, illustrating an ~40 kyr duration between the onset of the PETM CIE and the bentonite layer.

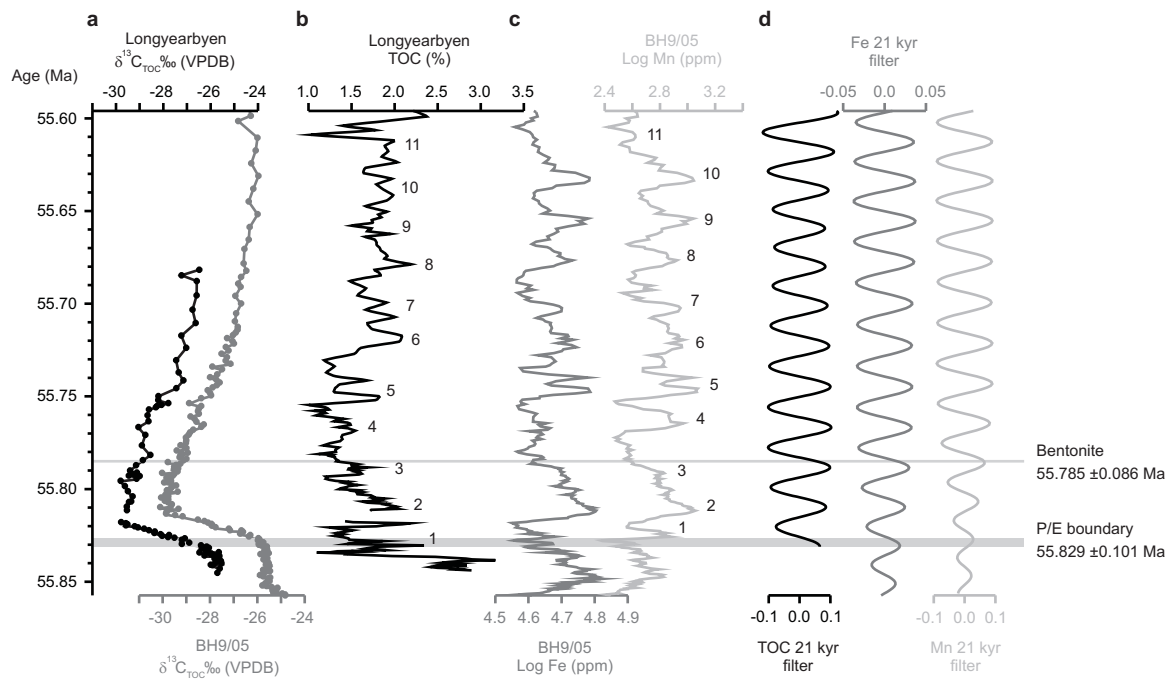


Figure 8: The age of the Paleocene/Eocene boundary in Spitsbergen, using cyclostratigraphic Option A. **a**, $\delta^{13}\text{C}_{\text{TOC}} (\text{‰})$ from the Longyearbyen section (black) [Harding *et al.*, 2011] and core BH9/05 (red) [Cui, 2010]. **b**, Longyearbyen TOC (%) [Harding *et al.*, 2011]. **c**, Core BH9/05 Log Fe (ppm, red) and Mn (ppm, blue). **d**, 21 kyr Gaussian filter outputs for TOC (black) Log Fe (red) and Log Mn (blue) respectively, illustrating an ~40 kyr duration between the onset of the PETM CIE and the bentonite layer.

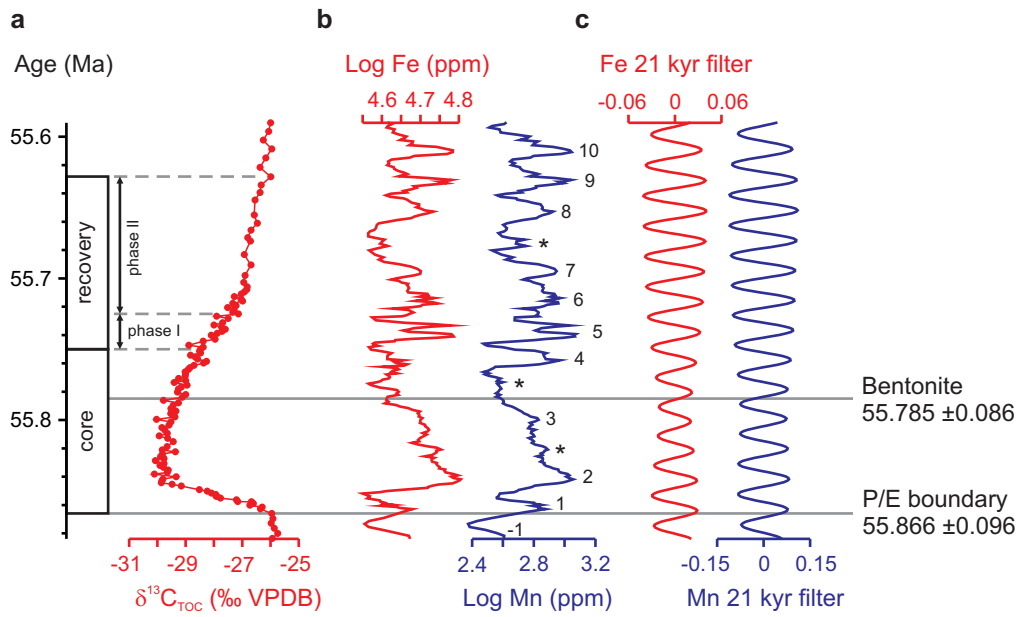


Figure 9: The age of the Paleocene/Eocene boundary in Spitsbergen, using cyclostratigraphic option B. **a**, $\delta^{13}\text{C}_{\text{TOC}}$ (‰) from core BH9/05 (red) [Cui, 2010], illustrating the phases of the PETM CIE from Röhl *et al.* [2007]. **b**, Core BH9/05 Log Fe (ppm, red) and Mn (ppm, blue). Cycle numbers adhere to those of Röhl *et al.* [2007], with potential additional cycles marked with an asterisk. **d**, 21 kyr Gaussian filter outputs for Log Fe (red) and Log Mn (blue) respectively, illustrating an ~80 kyr duration between the onset of the PETM CIE and the bentonite layer

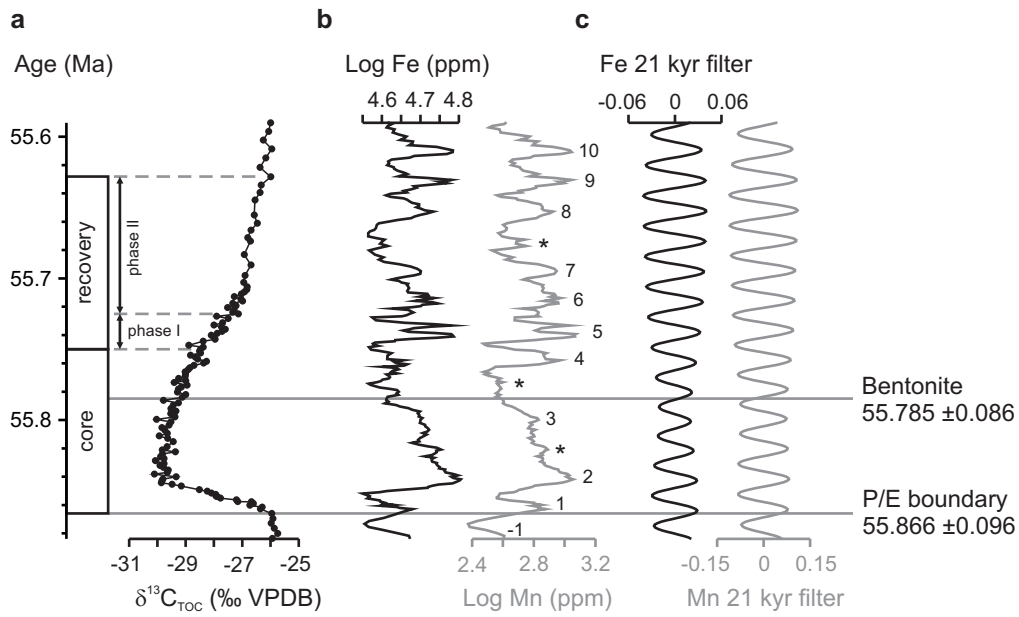


Figure 9: The age of the Paleocene/Eocene boundary in Spitsbergen, using cyclostratigraphic Option B. **a**, $\delta^{13}\text{C}_{\text{TOC}}$ (‰) from core BH9/05 (red) [Cui, 2010], illustrating the phases of the PETM CIE from Röhl *et al.* [2007]. **b**, Core BH9/05 Log Fe (ppm, red) and Mn (ppm, blue). Cycle numbers adhere to those of Röhl *et al.* [2007], with potential additional cycles marked with an asterisk. **d**, 21 kyr Gaussian filter outputs for Log Fe (red) and Log Mn (blue) respectively, illustrating an ~80 kyr duration between the onset of the PETM CIE and the bentonite layer

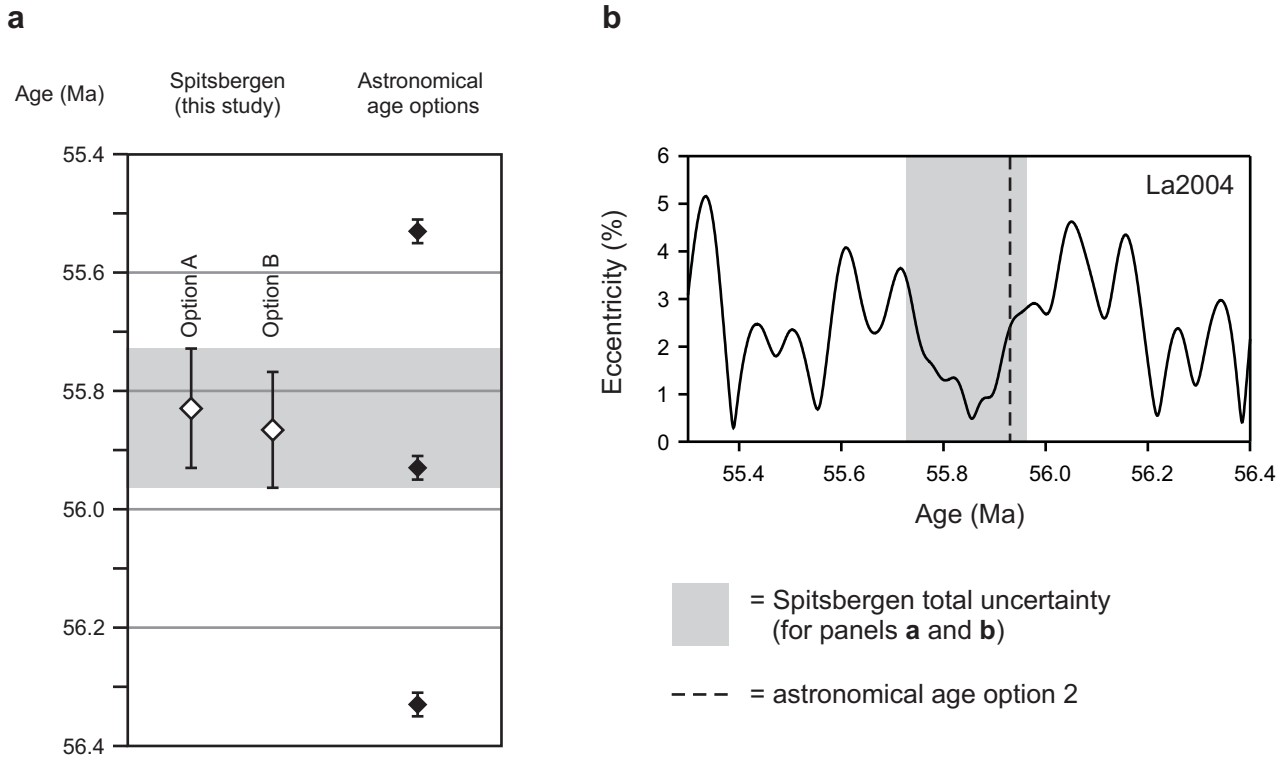


Figure 10: The position of the P/E boundary (equivalent to the PETM CIE onset) with respect to orbital forcing. **a**, comparison of P/E boundary ages determined from Spitsbergen with the astronomical age options of *Westerhold et al.* [2007, 2008]. Note that both Spitsbergen age options are within error of astronomical age option 2 (55.93 Ma). **b**, total uncertainty for the age of the P/E boundary from Spitsbergen (grey shaded bar), plotted against the *Laskar et al.* [2004; La2004] orbital solution. Age option 2 of *Westerhold et al.* [2007, 2008] is plotted for comparison.