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1 A new high-resolution chronology for the late
2 Maastrichtian warming event: Establishing robust temporal
3 links with the onset of Deccan volcanism

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16 **ABSTRACT**

17 The late Maastrichtian warming event was defined by a global temperature
18 increase of ~2.5–5 °C, which occurred ~150–300 k.y. before the K/Pg
19 (Cretaceous/Paleogene) mass extinction. This transient warming event has traditionally
20 been associated with a major pulse of Deccan Trap volcanism, however, large
21 uncertainties associated with radiogenic dating methods have long hampered a definitive
22 correlation. Here we present a new high-resolution, single-species, benthic stable isotope

23 record from the South Atlantic, calibrated to an updated orbitally-tuned age model, to
24 provide a revised chronology of the event, which we then correlate to the latest
25 radiogenic dates of the main Deccan Trap eruption phases. Our data reveals that the
26 initiation of deep-sea warming coincides, within uncertainty, with the onset of the main
27 phase of Deccan volcanism, strongly suggesting a causal link. The onset of deep-sea
28 warming is synchronous with a 405-kyr eccentricity minimum, excluding a control by
29 orbital forcing alone, although amplified carbon cycle sensitivity to orbital precession is
30 evident during the greenhouse warming. A more precise understanding of Deccan-
31 induced climate change paves the way for future work focusing on the fundamental role
32 of these precursor climate shifts in the K/Pg mass extinction.

33 **INTRODUCTION**

34 A period of rapid climate change, represented initially by a transient global
35 warming event and followed by a global cooling, occurred during the last few hundred
36 thousand years of the Maastrichtian and may have played an ancillary role in the ultimate
37 demise of many terrestrial and marine biota at the K/Pg (Cretaceous/Paleogene) boundary
38 (e.g., Keller et al., 2016). The so-called “late Maastrichtian warming event” was
39 characterized by a transient global $\sim 2.5\text{--}4$ °C warming in the marine realm based on
40 benthic $\delta^{18}\text{O}$ and organic paleothermometer ($\text{TEX}_{86}^{\text{H}}$) data (e.g., Li and Keller, 1998;
41 Woelders et al., 2017), and ~ 5 °C warming in the terrestrial realm based on pedogenic
42 carbonate $\delta^{18}\text{O}$ and proportion of untoothed leaf margins in woody dicot plants (Nordt et
43 al., 2003; Wilf et al., 2003). Enhanced deep-sea carbonate dissolution, most pronounced
44 in the high latitudes (Henehan et al., 2016), and abrupt decreases in vertical temperature

45 and carbon isotope gradients in the marine water column have also been documented (Li
46 and Keller, 1998).

47 This transient warming event has previously been linked to a major pulse of
48 Deccan Trap volcanism, centered in modern day western India, however, until recently
49 the large uncertainties associated with radiogenic dating have hampered a robust
50 correlation (e.g., Chenet et al., 2007). In recent years improvements in precision of
51 radiogenic dating methods have allowed for a more robust correlation between pre-K/Pg
52 climate change and volcanism (e.g., Renne et al., 2015; Schoene et al., 2015). To
53 complement advances in dating of the volcanic sequences, here we present the highest
54 resolution (1.5–4 k.y.), complete single-species benthic stable isotope record produced to
55 date, calibrated to an updated orbitally-tuned age model, for the final million years of the
56 Maastrichtian and first 500 k.y. of the Danian. This allows us to much more accurately
57 correlate the major climatic shifts of the terminal Maastrichtian with Deccan volcanism,
58 facilitating future work investigating the link between Deccan-induced climate change
59 and the K/Pg mass extinction.

60 **MATERIALS AND METHODS**

61 A stratigraphically continuous late Maastrichtian–early Danian sedimentary
62 section was recovered at Ocean Drilling Program (ODP) Site 1262 (Walvis Ridge, South
63 Atlantic; 27°11.15'S, 1°34.62'E; water depth 4759 m, Maastrichtian water depth ~3000
64 m, (Shipboard Scientific Party, 2004)), where the late Maastrichtian is represented by an
65 expanded section of foraminifera-bearing, carbonate-rich nannofossil ooze with a mean
66 sedimentation rate of 1.5–2 cm/kyr. We have constructed an updated orbitally-tuned age
67 model for this site based on recognition of the stable 405-kyr eccentricity cycle in our

68 high-resolution benthic carbon isotope ($\delta^{13}\text{C}_{\text{benthic}}$) data set, correlated to the La2010b
69 solution of Laskar et al. (2011) and anchored to an astronomical K/Pg boundary age of
70 66.02 Ma (Dinarès-Turell et al., 2014). The key tie points used to create this age model
71 are listed in Table DR2 in the Data Repository. All existing published data presented
72 herein has also been migrated over to the same age model for comparison (Figs. 1, 2;
73 detailed methods provided in the Data Repository). We generated $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data
74 using the epifaunal benthic foraminifera species *Nuttallides truempyi* on an IsoPrime 100
75 Gas Source Isotope Ratio Mass Spectrometer in dual inlet mode equipped with a
76 Multiprep device at the NERC Isotope Geosciences Facility (British Geological Survey).
77 The internal standard, KCM, calibrated against the international standard NBS-19, was
78 used to place data on the VPDB scale, with average sample analytical precision (1σ) of
79 0.03‰ for $\delta^{13}\text{C}$ and 0.05‰ for $\delta^{18}\text{O}$. The complete benthic stable isotope data set is
80 available online in the PANGAEA database
81 (doi.pangaea.de/10.1594/PANGAEA.881019). Bottom water temperatures were
82 calculated from $\delta^{18}\text{O}_{\text{benthic}}$ data by converting *N. truempyi* data to *Cibicidoides* values,
83 then using Equation 1 of Bemis et al. (1998). Stable isotope data was graphically
84 detrended in KaleidaGraph 4.0 using a 15% running mean, to remove long-term trends,
85 then band pass filtering was conducted in AnalySeries 2.0 (Paillard et al., 1996) for 405-
86 kyr eccentricity at 0.002467 \pm 0.000700 cycles/kyr and 100-kyr eccentricity at 0.010
87 \pm 0.003 cycles/kyr.

88 **RESULTS**

89 The new stable isotope data shows relatively stable and cool temperatures
90 persisted in the deep South Atlantic Ocean from 67.1 to 66.8 Ma, followed by the onset

91 of a longer term gradual warming (1 °C) and decline in $\delta^{13}\text{C}_{\text{benthic}}$ values from 66.75 to
92 66.5 Ma (Fig. 1). The late Maastrichtian warming event initiated at ~66.34 Ma, just over
93 300 k.y. before the K/Pg boundary, with peak warming of ~+4 °C ($\delta^{18}\text{O}_{\text{benthic}}$ excursion of
94 ~-0.8‰) attained between ~66.27–66.18 Ma (Fig. 1). A more gradual, step-wise cooling
95 to pre-excursion temperatures then took place over the next 200 k.y., terminating at the
96 K/Pg boundary (Fig. 1). Conversely, the $\delta^{13}\text{C}_{\text{benthic}}$ record appears to show a muted
97 response compared to the $\delta^{18}\text{O}_{\text{benthic}}$ record during the warming event, with only a minor
98 negative excursion of ~-0.5‰ noted between 66.3 and 66.2 Ma (Fig. 1). The magnitude
99 and character of the excursions in $\delta^{13}\text{C}_{\text{benthic}}$ and $\delta^{18}\text{O}_{\text{benthic}}$ data at Site 1262 are similar to
100 those reported in lower resolution data from Deep Sea Drilling Project (DSDP) Site 525
101 (Li and Keller, 1998; Fig. DR3), located at a shallower paleo-depth of 1–1.5 km on
102 Walvis Ridge, suggesting a similar magnitude of warming in deep and intermediate
103 waters of the South Atlantic. Confirming that these characteristics are global, deep
104 Pacific stable isotope data from ODP Site 1209 also show a coeval but somewhat smaller
105 warming pulse, and a similar muted response in $\delta^{13}\text{C}_{\text{benthic}}$ values to those observed in the
106 Atlantic (Fig. 2; Westerhold et al., 2011). The minor offset of Pacific $\delta^{13}\text{C}_{\text{benthic}}$ values by
107 up to -0.4‰ relative to the South Atlantic, suggests an older water mass was bathing the
108 equatorial Pacific site, consistent with previously reported Paleocene–Eocene trends
109 (Littler et al., 2014; Fig. 2). The onset of the warming event in the Atlantic corresponds to
110 a 405-kyr eccentricity minimum, with the peak of the event occurring during a 100 k.y.
111 eccentricity maximum but prior to a 405-kyr eccentricity maximum. The $\delta^{18}\text{O}_{\text{benthic}}$ leads
112 $\delta^{13}\text{C}_{\text{benthic}}$ (i.e., climate leads carbon cycle) by ~30–40 k.y. within the 405-kyr band,
113 consistent with Late Paleocene–Early Eocene trends recorded further upsection at this

114 site (Littler et al., 2014). Interestingly, the $\delta^{18}\text{O}_{\text{benthic}}$ and $\delta^{13}\text{C}_{\text{benthic}}$ data become antiphase
115 at the 100-kyr frequency during the warming event, but are in phase with carbon lagging
116 oxygen by ~10 k.y. earlier in the Maastrichtian and by ~5 k.y. during the earliest Danian
117 (Fig. 1).

118 **DISCUSSION**

119 The new high-resolution, benthic stable isotope data placed onto our updated
120 orbitally-tuned age model demonstrates that the late Maastrichtian warming event closely
121 coincides with the onset of the main phase of Deccan volcanism, irrespective of
122 radiogenic dating technique used, strongly suggesting a causal link (Fig. 1). Furthermore,
123 both the relatively long duration of the warming event and the initiation of the warming
124 during a minimum in the 405-kyr eccentricity cycle suggest a control by orbital forcing
125 alone is unlikely, and that Deccan volcanogenic CO_2 emissions were likely to be the
126 primary climate driver over 100-kyr timescales. Based on the distribution of red boles
127 (weathering horizons) within the Deccan basalts, volcanism of the pre-K/Pg Kalsubai
128 sub-group was characterized by more frequent eruptions of a smaller magnitude, likely
129 leading to a larger cumulative atmospheric $p\text{CO}_2$ increase than post-K/Pg eruptions
130 (Renne et al., 2015; Schoene et al., 2015). By contrast, Danian eruptions had longer
131 hiatuses between large eruptive events, allowing for partial CO_2 sequestration by silicate
132 weathering or organic burial.

133 Despite strong evidence for climatic warming and some evidence for elevated
134 atmospheric $p\text{CO}_2$ (Barclay and Wing, 2016; Nordt et al., 2002, 2003; Fig. 1),
135 characteristic of many hyperthermals of the early Paleogene such as the Paleocene
136 Eocene Thermal Maximum (PETM; e.g., McInerney and Wing, 2011), the C isotope

137 records and lack of evidence for significant ocean acidification at Site 1262 (e.g.,
138 reduction in %CaCO₃ or increase in Fe concentration) suggest a relatively minor C-cycle
139 perturbation (Figs. 1; 2). Given the comparatively heavy $\delta^{13}\text{C}$ signature (-7%) of
140 volcanogenic CO₂, voluminous Deccan emissions may not have created a major
141 perturbation to the isotope composition of the global $\delta^{13}\text{C}$ pool. The absence of a major
142 negative carbon cycle perturbation suggests that sources of isotopically-light carbon (e.g.,
143 biogenic methane or the oxidation of organic matter), were not destabilized and released
144 in significant quantities during the event. This differential response between the
145 $\delta^{18}\text{O}_{\text{benthic}}$ and $\delta^{13}\text{C}_{\text{benthic}}$ records, and the lack of evidence for significant global deep-
146 ocean acidification (Fig. 1), may be due to rates of volcanogenic CO₂ emission and
147 consequent background–peak warming, which occurred rather slowly over $\sim 70\text{--}80$ k.y.
148 during the late Maastrichtian event, but was much more rapid, on the order of $10\text{--}20$ k.y.,
149 during Paleogene hyperthermals (e.g., McInerney and Wing, 2011; Zeebe et al., 2017).
150 However, evidence for enhanced deep-sea dissolution during this event has been
151 described from the high-latitudes in %CaCO₃ records from ODP Site 690 (Henehan et al.,
152 2016) and in orbitally-tuned Fe intensity and magnetic susceptibility data from IODP Site
153 U1403 on the Newfoundland margin (Batenburg et al., 2017). These deep-sea sites may
154 have been particularly sensitive to smaller carbon cycle perturbations during this time,
155 with Site 690 located in the principle region of deep water formation in the Southern
156 Ocean and with Site U1403, situated at a paleodepth of ~ 4 km, being more sensitive to
157 smaller fluctuations in the Maastrichtian Calcite Compensation Depth than the shallower
158 Site 1262 (Henehan et al., 2016). Clearly, more high-resolution $p\text{CO}_2$ proxy studies are
159 urgently required to more confidently assess Deccan-induced perturbations to the global

160 carbon cycle. The lag between the climate and carbon cycle response within the 405-kyr
161 band (Fig. 1), as seen throughout the Paleocene–Eocene (Littler et al., 2014), may suggest
162 that small quantities of light carbon were released as a positive feedback to orbitally-
163 driven warming. The observed antiphase behavior between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ within the 100
164 k.y. band during the warming event, but not before or after (Fig. 1), may result from the
165 pulsed release of small amounts of isotopically-light carbon superimposed on the longer
166 (300 k.y.) scale warming imparted by the Deccan eruptions. Additionally, amplified
167 precession scale (~21 k.y.) variability visible in the dissolution proxies (Fe and %CaCO₃)
168 and $\delta^{13}\text{C}$ records during the event, also suggest increased carbon-cycle sensitivity,
169 perhaps due to generally elevated CO₂ levels from Deccan activity (Fig. 1).

170 The limited available planktic stable isotope data (e.g., ODP Site 690) suggests
171 significant warming, on the order of ~2.5 °C, occurred in the southern high latitudes
172 during the event (Fig. 2; Stott and Kennett, 1990). Organic paleothermometer TEX₈₆^H data
173 from the Neuquén Basin, Argentina, also suggests significant warming of surface waters
174 of ~3 °C in continental shelf settings at mid-latitudes (Fig. 1; Woelders et al., 2017).
175 Recently, a negative bulk $\delta^{18}\text{O}$ excursion of 1‰ has also been resolved from the
176 Newfoundland margin, suggesting a pronounced surface water warming also occurred in
177 the mid-northern latitudes during this time, although bulk $\delta^{18}\text{O}$ values cannot reliably be
178 converted into absolute surface water temperatures (Batenburg et al., 2017). By contrast,
179 there appears to have been very little change in surface water temperatures at lower
180 latitudes, although this interpretation is tentative based on the availability of only one fine
181 fraction data set from DSDP Site 577 (Fig. 2). A much more significant bottom water
182 warming at mid–low latitudes created a dramatic reduction in the surface-deep

183 temperature gradient and reduced thermal stratification of the water column (Li and
184 Keller, 1998; Fig. 2). Taken together, this data suggests a possible polar amplification of
185 surface water warming during the late Maastrichtian warming event, but clearly, more
186 single-species planktic isotope records over a greater latitudinal coverage are required to
187 fully evaluate latitudinal variations in surface temperature during this event.

188 **CONCLUSIONS**

189 Our revised chronology for the late Maastrichtian warming event, combined with
190 the latest radiogenic dates for Deccan volcanism, point to the synchronous onset of the
191 main phase of Deccan volcanism with the late Maastrichtian warming event ~300 k.y.
192 before the K/Pg boundary. The onset of the warming is unlikely to have been orbitally
193 controlled, further supporting volcanic CO₂ as the trigger. Increased carbon cycle
194 sensitivity to orbital precession is evident during the greenhouse event suggesting system
195 sensitivity to background temperature conditions. Now that the environmental effects of
196 Deccan volcanism have been more confidently established, future work should focus on
197 evaluating the role of these precursor climatic changes in the K/Pg mass extinction.

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315 **FIGURE CAPTIONS**

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317 Figure 1. Correlation of environmental proxies to Deccan volcanism and the La2010b
318 orbital solution. A. Recalibrated atmospheric $p\text{CO}_2$ estimates based on pedogenic

319 carbonate (purple triangles; raw data from Nordt et al., 2002; red triangles; raw data from
320 Nordt et al., 2003, both recalibrated in this study) and stomatal indices (orange circles;
321 Beerling et al., 2002, recalibrated by Barclay and Wing, 2016; green circles;
322 Steinthorsdottir et al., 2016). B. New benthic $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data from Site 1262 and
323 filters at the 405-kyr and 100-kyr bands (this study), correlated to the La2010b solution
324 (Laskar et al., 2011), $\text{TEX}_{86}^{\text{H}}$ data (Woelders et al., 2017) and Site 1262 Fe and % CaCO_3
325 data (Kroon et al., 2007). Error bars on $\text{TEX}_{86}^{\text{H}}$ data represent analytical uncertainty (dark
326 green) and calibration error of absolute temperatures (pale green). Magnetozones are
327 from Bowles (2006) and nannozones from Shipboard Scientific Party (2004), with high-
328 resolution K/Pg biozones from Bernaola and Monechi (2007). C. Timing of Deccan
329 volcanism, with formation volumes calculated by the equal area method (gray), variable
330 area method (red), and red bole distribution illustrated as a black line, using Ar-Ar ages
331 in Renne et al. (2015). U-Pb age data from Schoene et al. (2015) also shown. See Data
332 Repository for detailed methods.

333

334 Figure 2. Stable isotope data across the late Maastrichtian event. A. Benthic $\delta^{13}\text{C}$ and
335 $\delta^{18}\text{O}$ data for Site 1262 (this study) plotted against benthic data from Site 1209
336 (equatorial Pacific; Westerhold et al., 2011) for comparison. B. Planktic $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
337 data from Site 577, equatorial Pacific (Zachos et al., 1985), Site 525, South Atlantic (Li
338 and Keller, 1998) and Site 690, Southern Ocean (Stott and Kennett, 1990). Planktic and
339 bulk $\delta^{18}\text{O}$ data has been normalized to a baseline of 0‰ for pre-event conditions to
340 compare the magnitude of the warming event by latitude. C. Shallow-to-deep $\delta^{13}\text{C}$ and
341 temperature gradients at Site 525 (Li and Keller, 1998).

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343 1GSA Data Repository item 2018xxx, xxxxxxxx, is available online at

344 <http://www.geosociety.org/datarepository/2018/> or on request from

345 editing@geosociety.org.