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

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ABSTRACT

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

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

INTRODUCTION

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

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

MATERIALS AND METHODS

A stratigraphically continuous late Maastrichtian–early Danian sedimentary section was recovered at Ocean Drilling Program (ODP) Site 1262 (Walvis Ridge, South Atlantic; 27°11.15′S, 1°34.62′E; water depth 4759 m, Maastrichtian water depth ~3000 m, (Shipboard Scientific Party, 2004)), where the late Maastrichtian is represented by an expanded section of foraminifera-bearing, carbonate-rich nannofossil ooze with a mean sedimentation rate of 1.5–2 cm/kyr. We have constructed an updated orbitally-tuned age model for this site based on recognition of the stable 405-kyr eccentricity cycle in our high-resolution benthic carbon isotope ($\delta^{13}C_{benthic}$) data set, correlated to the La2010b solution of Laskar et al. (2011) and anchored to an astronomical K/Pg boundary age of 66.02 Ma (Dinarès-Turell et al., 2014). The key tie points used to create this age model are listed in Table DR2 in the Data Repository. All existing published data presented herein has also been migrated over to the same age model for comparison (Figs. 1, 2; detailed methods provided in the Data Repository). We generated $\delta^{13}C$ and $\delta^{18}O$ data using the epifaunal benthic foraminifera species *Nuttallides truempyi* on an IsoPrime 100 Gas Source Isotope Ratio Mass Spectrometer in dual inlet mode equipped with a Multiprep device at the NERC Isotope Geosciences Facility (British Geological Survey). The internal standard, KCM, calibrated against the international standard NBS-19, was used to place data on the VPDB scale, with average sample analytical precision (1σ) of 0.03‰ for $\delta^{13}C$ and 0.05‰ for $\delta^{18}O$. The complete benthic stable isotope data set is available online in the PANGAEA database (doi.pangaea.de/10.1594/PANGAEA.881019). Bottom water temperatures were calculated from $\delta^{18}O_{benthic}$ data by converting *N. truempyi* data to *Cibicidoides* values, then using Equation 1 of Bemis et al. (1998). Stable isotope data was graphically detrended in KaleidaGraph 4.0 using a 15% running mean, to remove long-term trends, then band pass filtering was conducted in AnalySeries 2.0 (Paillard et al., 1996) for 405-kyr eccentricity at 0.002467 +/– 0.000700 cycles/kyr and 100-kyr eccentricity at 0.010 +/– 0.003 cycles/kyr.

RESULTS

The new stable isotope data shows relatively stable and cool temperatures persisted in the deep South Atlantic Ocean from 67.1 to 66.8 Ma, followed by the onset of a longer term gradual warming (1 °C) and decline in $\delta^{13}C_{benthic}$ values from 66.75 to 66.5 Ma (Fig. 1). The late Maastrichtian warming event initiated at ~66.34 Ma, just over 300 k.y. before the K/Pg boundary, with peak warming of ~+4 °C ($\delta^{18}O_{benthic}$ excursion of ~0.8‰) attained between ~66.27–66.18 Ma (Fig. 1). A more gradual, step-wise cooling to pre-excursion temperatures then took place over the next 200 k.y., terminating at the K/Pg boundary (Fig. 1). Conversely, the $\delta^{13}C_{benthic}$ record appears to show a muted response compared to the $\delta^{18}O_{benthic}$ record during the warming event, with only a minor negative excursion of ~0.5‰ noted between 66.3 and 66.2 Ma (Fig. 1). The magnitude and character of the excursions in $\delta^{13}C_{benthic}$ and $\delta^{18}O_{benthic}$ data at Site 1262 are similar to those reported in lower resolution data from Deep Sea Drilling Project (DSDP) Site 525 (Li and Keller, 1998; Fig. DR3), located at a shallower paleo-depth of 1–1.5 km on Walvis Ridge, suggesting a similar magnitude of warming in deep and intermediate waters of the South Atlantic. Confirming that these characteristics are global, deep Pacific stable isotope data from ODP Site 1209 also show a coeval but somewhat smaller warming pulse, and a similar muted response in $\delta^{13}C_{benthic}$ values to those observed in the Atlantic (Fig. 2; Westerhold et al., 2011). The minor offset of Pacific $\delta^{13}C_{benthic}$ values by up to –0.4‰ relative to the South Atlantic, suggests an older water mass was bathing the equatorial Pacific site, consistent with previously reported Paleocene–Eocene trends (Littler et al., 2014; Fig. 2). The onset of the warming event in the Atlantic corresponds to a 405-kyr eccentricity minimum, with the peak of the event occurring during a 100 k.y. eccentricity maximum but prior to a 405-kyr eccentricity maximum. The $\delta^{18}O_{benthic}$ leads $\delta^{13}C_{benthic}$ (i.e., climate leads carbon cycle) by ~30–40 k.y. within the 405-kyr band, consistent with Late Paleocene–Early Eocene trends recorded further upsection at this

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

DISCUSSION

The new high-resolution, benthic stable isotope data placed onto our updated orbitally-tuned age model demonstrates that the late Maastrichtian warming event closely coincides with the onset of the main phase of Deccan volcanism, irrespective of radiogenic dating technique used, strongly suggesting a causal link (Fig. 1). Furthermore, both the relatively long duration of the warming event and the initiation of the warming during a minimum in the 405-kyr eccentricity cycle suggest a control by orbital forcing alone is unlikely, and that Deccan volcanogenic CO_2 emissions were likely to be the primary climate driver over 100-kyr timescales. Based on the distribution of red boles (weathering horizons) within the Deccan basalts, volcanism of the pre-K/Pg Kalsubai sub-group was characterized by more frequent eruptions of a smaller magnitude, likely leading to a larger cumulative atmospheric pCO_2 increase than post-K/Pg eruptions (Renne et al., 2015; Schoene et al., 2015). By contrast, Danian eruptions had longer hiatuses between large eruptive events, allowing for partial CO_2 sequestration by silicate weathering or organic burial.

Despite strong evidence for climatic warming and some evidence for elevated atmospheric pCO_2 (Barclay and Wing, 2016; Nordt et al., 2002, 2003; Fig. 1), characteristic of many hyperthermals of the early Paleogene such as the Paleocene Eocene Thermal Maximum (PETM; e.g., McInerney and Wing, 2011), the C isotope

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records and lack of evidence for significant ocean acidification at Site 1262 (e.g., reduction in %$CaCO_3$ or increase in Fe concentration) suggest a relatively minor C-cycle perturbation (Figs. 1; 2). Given the comparatively heavy $\delta^{13}C$ signature (–7‰) of volcanogenic CO_2, voluminous Deccan emissions may not have created a major perturbation to the isotope composition of the global $\delta^{13}C$ pool. The absence of a major negative carbon cycle perturbation suggests that sources of isotopically-light carbon (e.g., biogenic methane or the oxidation of organic matter), were not destabilized and released in significant quantities during the event. This differential response between the $\delta^{18}O_{benthic}$ and $\delta^{13}C_{benthic}$ records, and the lack of evidence for significant global deep-ocean acidification (Fig. 1), may be due to rates of volcanogenic CO_2 emission and consequent background–peak warming, which occurred rather slowly over ~70–80 k.y. during the late Maastrichtian event, but was much more rapid, on the order of 10–20 k.y., during Paleogene hyperthermals (e.g., McInerney and Wing, 2011; Zeebe et al., 2017). However, evidence for enhanced deep-sea dissolution during this event has been described from the high-latitudes in %$CaCO_3$ records from ODP Site 690 (Henehan et al., 2016) and in orbitally-tuned Fe intensity and magnetic susceptibility data from IODP Site U1403 on the Newfoundland margin (Batenburg et al., 2017). These deep-sea sites may have been particularly sensitive to smaller carbon cycle perturbations during this time, with Site 690 located in the principle region of deep water formation in the Southern Ocean and with Site U1403, situated at a paleodepth of ~4 km, being more sensitive to smaller fluctuations in the Maastrichtian Calcite Compensation Depth than the shallower Site 1262 (Henehan et al., 2016). Clearly, more high-resolution pCO_2 proxy studies are urgently required to more confidently assess Deccan-induced perturbations to the global carbon cycle. The lag between the climate and carbon cycle response within the 405-kyr band (Fig. 1), as seen throughout the Paleocene–Eocene (Littler et al., 2014), may suggest that small quantities of light carbon were released as a positive feedback to orbitally-driven warming. The observed antiphase behavior between $\delta^{13}C$ and $\delta^{18}O$ within the 100 k.y. band during the warming event, but not before or after (Fig. 1), may result from the pulsed release of small amounts of isotopically-light carbon superimposed on the longer (300 k.y.) scale warming imparted by the Deccan eruptions. Additionally, amplified precession scale (~21 k.y.) variability visible in the dissolution proxies (Fe and %$CaCO_3$) and $\delta^{13}C$ records during the event, also suggest increased carbon-cycle sensitivity, perhaps due to generally elevated CO_2 levels from Deccan activity (Fig. 1).

The limited available planktic stable isotope data (e.g., ODP Site 690) suggests significant warming, on the order of ~2.5 °C, occurred in the southern high latitudes during the event (Fig. 2; Stott and Kennett, 1990). Organic paleothermometer TEX_{86}^{H} data from the Neuquén Basin, Argentina, also suggests significant warming of surface waters of ~3 °C in continental shelf settings at mid-latitudes (Fig. 1; Woelders et al., 2017). Recently, a negative bulk $\delta^{18}O$ excursion of 1‰ has also been resolved from the Newfoundland margin, suggesting a pronounced surface water warming also occurred in the mid-northern latitudes during this time, although bulk $\delta^{18}O$ values cannot reliably be converted into absolute surface water temperatures (Batenburg et al., 2017). By contrast, there appears to have been very little change in surface water temperatures at lower latitudes, although this interpretation is tentative based on the availability of only one fine fraction data set from DSDP Site 577 (Fig. 2). A much more significant bottom water warming at mid–low latitudes created a dramatic reduction in the surface-deep temperature gradient and reduced thermal stratification of the water column (Li and Keller, 1998; Fig. 2). Taken together, this data suggests a possible polar amplification of surface water warming during the late Maastrichtian warming event, but clearly, more single-species planktic isotope records over a greater latitudinal coverage are required to fully evaluate latitudinal variations in surface temperature during this event.

CONCLUSIONS

Our revised chronology for the late Maastrichtian warming event, combined with the latest radiogenic dates for Deccan volcanism, point to the synchronous onset of the main phase of Deccan volcanism with the late Maastrichtian warming event ~300 k.y. before the K/Pg boundary. The onset of the warming is unlikely to have been orbitally controlled, further supporting volcanic CO_2 as the trigger. Increased carbon cycle sensitivity to orbital precession is evident during the greenhouse event suggesting system sensitivity to background temperature conditions. Now that the environmental effects of Deccan volcanism have been more confidently established, future work should focus on evaluating the role of these precursor climatic changes in the K/Pg mass extinction.

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FIGURE CAPTIONS

Figure 1. Correlation of environmental proxies to Deccan volcanism and the La2010b orbital solution. A. Recalibrated atmospheric $p\mathrm{CO_2}$ estimates based on pedogenic

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

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

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