GSA Data Repository 2018076

Deccan volcanism caused coupled pCO_2 and terrestrial temperature rises,

and pre-impact extinctions in North China

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1 Geological Background

2 <u>Stratigraphy</u>

3	The Songliao Basin is approximately 820 km long in a north-south direction and
4	approximately 350 km wide in an east-west direction, and covers ~260,000 km ² in NE
5	China (Fig. 1). Paleomagnetic data indicate that Songliao Basin was located at mid-
6	latitudes in the Cretaceous similar to where it is now (Wang et al., 2013a; Wang et al.,
7	2013b) (Fig. DR1).
8	The basin is filled predominantly with volcaniclastic, alluvial fan, fluvial and
9	lacustrine sediments of the Late Jurassic, Cretaceous and Paleogene ages (Wang et al.,
10	2013a; Wang et al., 2013b). From the bottom to the top, the Mesozoic sedimentary
11	cover within the basin are the Upper Jurassic Huoshiling Formation (J3h); the Lower
12	Cretaceous Shahezi (K1sh), Yingcheng (K1y), Denglouku (K1d), and Quantou (K1q)
13	formations; the Upper Cretaceous Qinshankou (K2qn), Yaojia (K2y), Nenjiang (K2n),
14	Sifangtai (K2s), and Mingshui (K2m) formations (Wang et al., 2013a).
15	The Late Cretaceous stratigraphy was recovered in a borehole named SK-In
16	(north core) (44°12′44.22″N, 124°15′56.78″E; Fig. 1 and DR1) in the central part of
17	Songliao Basin by the "Cretaceous Continental Scientific Drilling Program of China"
18	(Wang et al., 2013a; Wang et al., 2013b). A high-temporal-resolution age model (Fig.
19	DR2) was established for the SK-In borehole using a geomagnetic polarity sequence,
20	U-Pb zircon ages, Milankovitch cycles, and biostratigraphic data (He et al., 2012;
21	Deng et al., 2013; Wan et al., 2013; Wu et al., 2014; Wang et al., 2016).

22	Diverse lines of evidences place the K-Pg boundary in the top part of the
23	Mingshui Formation (Li et al., 2011; Deng et al., 2013; Wan et al., 2013). According
24	to the magnetostratigraphy, the chron C29r was recorded at the depth interval of
25	317.03-342.1 m in the north borehole (Deng et al., 2013), which corresponds to the
26	top part of the Mingshui Formation. In addition, biostratigraphic studies also indicate
27	major micropaleontologic changes in the top part of the Mingshui Formation (Li et al.,
28	2011; Wan et al., 2013). The Sifangtai and Mingshui formations are composed of
29	gray-green, gray, black and brown-red shale and gray-green sandstone, and consists of
30	alluvial plain - shore to shallow lake - alluvial plain deposits across most of the basin
31	(Wang et al., 2013a). They record a semi-humid, temperate environment developed
32	during the post-rift phase of the basin (Chamberlain et al., 2013; Wang et al., 2013a).
33	
33 34	Age model
	<u>Age model</u> The chronology of SK-In borehole has been well established using a
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34 35 36 37	The chronology of SK-In borehole has been well established using a combination of biostratigraphy (Wan et al., 2013), magnetostratigraphy (Deng et al., 2013), cyclostratigraphy (Wu et al., 2014) and radiometric ages (He et al., 2012;
3435363738	The chronology of SK-In borehole has been well established using a combination of biostratigraphy (Wan et al., 2013), magnetostratigraphy (Deng et al., 2013), cyclostratigraphy (Wu et al., 2014) and radiometric ages (He et al., 2012; Wang et al., 2016) (Fig. DR2). Eleven magnetozones with five reversed, five normal
 34 35 36 37 38 39 	The chronology of SK-In borehole has been well established using a combination of biostratigraphy (Wan et al., 2013), magnetostratigraphy (Deng et al., 2013), cyclostratigraphy (Wu et al., 2014) and radiometric ages (He et al., 2012; Wang et al., 2016) (Fig. DR2). Eleven magnetozones with five reversed, five normal and one mixed polarities were identified in SK-In (Deng et al., 2013). The lowermost
 34 35 36 37 38 39 40 	The chronology of SK-In borehole has been well established using a combination of biostratigraphy (Wan et al., 2013), magnetostratigraphy (Deng et al., 2013), cyclostratigraphy (Wu et al., 2014) and radiometric ages (He et al., 2012; Wang et al., 2016) (Fig. DR2). Eleven magnetozones with five reversed, five normal and one mixed polarities were identified in SK-In (Deng et al., 2013). The lowermost geomagnetic reversal is interpreted as the C34n/C33r boundary based on a SIMS U-

44	magnetozones are present: the lower part of C29r (317.0-342.1m), C30n-C31n (342.1-
45	530.78m), C31r (530.78-700.88 m), and C32n (700.88-852.6m), C32r.1r (852.6-
46	887.8m), C32r.1n (887.8-895.8m), C32r.2r (895.8-910.2m), C33n (910.2-1020.4m).
47	The 405 kyr eccentricity cycles were recognized using thorium (Th) data from
48	the Sifangtai and Mingshui formations (Wu et al., 2014). The C30n/C29r boundary is
49	very close to a minimum in the 405-kyr eccentricity cycle and about 300-400 ky older
50	than the K-Pg boundary (Husson et al., 2011; Batenburg et al., 2014; Clyde et al.,
51	2016). In the Mingshui Formation, the C30n/C29r boundary (66.398 Ma) (Gradstein
52	et al., 2012) was set as the initial age control point and the maximum of the first 405
53	kyr eccentricity cycle above C30n/C29r boundary was set as the starting point. Then
54	the maxima of the filtered 405 kyr sedimentary cycles were tuned to the maxima of
55	the target 405 kyr eccentricity curve filtered from La2010d to establish an
56	astronomical time scale (ATS) (Wu et al., 2014).
57	It is important to note that although the upper boundary for C29r is not clearly
58	
	represented in the core, with C29r being overlaid by a "mixed polarity" interval, this
59	represented in the core, with C29r being overlaid by a "mixed polarity" interval, this does not have any influences on the age model. The location of the upper boundary
59 60	
	does not have any influences on the age model. The location of the upper boundary
60	does not have any influences on the age model. The location of the upper boundary for C29r was not used to determine the age model. The age model was established
60 61	does not have any influences on the age model. The location of the upper boundary for C29r was not used to determine the age model. The age model was established based on the 405 kyr eccentricity cycles recognized using thorium (Th) data from the
60 61 62	does not have any influences on the age model. The location of the upper boundary for C29r was not used to determine the age model. The age model was established based on the 405 kyr eccentricity cycles recognized using thorium (Th) data from the Sifangtai and Mingshui formations and location of the C30n/C29r boundary, which

66	Ma and 66.04 Ma, respectively) (Gradstein et al., 2012) and results from marine strata
67	(Husson et al., 2011; Batenburg et al., 2014). Recently, the CA-ID-TIMS U-Pb zircon
68	ages of Deccan Traps have suggested that the age of the C30n/C29r boundary is very
69	close to the base of the main Deccan phase at 66.288 ±0.027 Ma and the age of K-Pg
70	boundary is 65.968 \pm 0.085 Ma (Schoene et al., 2015). The high-precision ${}^{40}\text{Ar}/{}^{39}\text{Ar}$
71	data suggests the age of the C30n/C29r boundary is 66.38 ± 0.05 Ma and the age of
72	K-Pg boundary is 66.043 ± 0.086 Ma (Renne et al., 2013; Renne et al., 2015). The U-
73	Pb ages from CA-ID-TIMS analysis suggests the C30n/C29r boundary is 66.436 \pm
74	0.039 Ma and the age of K-Pg boundary is 66.021 \pm 0.081 Ma (Clyde et al., 2016).
75	Therefore, the age model (ATS) of SK-In is reasonable and valid, and the age of each
76	sample can be calculated (see supplementary Table DR4 "Depth and ATS ages in the
77	SK-In borehole" in ref 5). In this study, the ages of paleosol carbonates were set at the
78	burial depth of the paleosol surfaces, not the depths of the carbonate nodules
79	themselves.
80	Although an iridium anomaly has not been located in SK-In, there are several
81	locations proposed for the K-Pg boundary (Li et al., 2011; Deng et al., 2013; Wan et
82	al., 2013). Based on a major palynofloral change, Li et al. (2011) suggested that the
83	K-Pg boundary should be located above 360.6 m. Based on a magnetostratigraphic
84	study, Deng et al. (2013) suggested that the K-Pg boundary should be located between
85	342.1-317.0 m. Based on the compiled data of charophytes, palynology, and
86	magnetostratigraphy, Wan et al. (2013) suggested that the K-Pg boundary should be
87	located at 328 m.

88	In this study, the K-Pg boundary was determined based on the ATS with
89	resolution better than 0.1 Ma (Wu et al., 2014). As we mentioned above, the
90	C30n/C29r boundary is about 300-340 ky older than the K-Pg boundary (Husson et
91	al., 2011; Batenburg et al., 2014). With the C30n/C29r boundary located at 342.1m \pm
92	1.4 m in depth (Deng et al., 2013), the location of the K-Pg boundary is 318 ± 1.2 m
93	in depth (Wu et al., 2014).
94	According to Wu et al. (2014), the sediment accumulation rate was ~0.1 m/ky. In
95	previous paleontological studies, the samples for ostracode extraction were taken at
96	~1 m (10 ky) intervals (Qu, 2014), the samples for spores/pollen extraction were
97	taken at ~15-25 m (150-250 ky) intervals where mudstones and siltstones dominate
98	and ~5-10 m (50-100 ky) intervals in the varicoloured segments (Li et al., 2011), and
99	the samples for charophyte extraction were taken at ~1 m (10 ky) intervals (Li, 2013).
100	Materials and Methods
101	
	Sample collection
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103 104 105	In the Sifangtai and Mingshui formations, many distinctive calcareous paleosols, or "calcisols" according to the Mack et al. (1993) soil classification, were identified and consist of carbonate nodules, slickensides, mottled colors, and fossil root traces (Huang et al., 2013; Gao et al., 2015) (Fig. DR2). They are interbedded with fluvial,
103 104 105 106	In the Sifangtai and Mingshui formations, many distinctive calcareous paleosols, or "calcisols" according to the Mack et al. (1993) soil classification, were identified and consist of carbonate nodules, slickensides, mottled colors, and fossil root traces (Huang et al., 2013; Gao et al., 2015) (Fig. DR2). They are interbedded with fluvial, alluvial, and lacustrine sediments. Due to the dehydration and recrystallization of iron

110	Paleosols generally form within 2,000-30,000 years from sediment or rock
111	exposed at the earth surface (Kraus, 1999). The morphology of the paleosol nodules
112	(Gile et al., 1966) in SK-In indicates they belong to stage I-II: "few filaments or faint
113	coatings/few to common nodules", which form in 100s to 1000s of years according to
114	U-series isochron dating of Quaternary examples (Candy et al., 2005). These paleosol
115	carbonates therefore provide a relatively continuous climate record at the time of their
116	formation with temporal resolution better than tens of millennia.
117	In this study, 51 paleosol carbonates were collected from 44 paleosol Bk
118	horizons of SK-In (Table DR4 and Table DR5). The diameters of the samples range
119	from 1.0 to 3.0 cm. The depths of carbonate nodules (soil depth) below the paleosol
120	surfaces (cm) and the burial depths of paleosols (m) were recorded. In practice, the
121	resolution of burial depth is at a meter scale. Almost all the samples were collected
122	from \geq 30 cm below the paleosol surface, thus minimizing effects from diurnal
123	heating and evaporation (Quade et al., 2013).
124	
125	Sample preparation
126	A total of 40-50 mg of carbonate powder was drilled from a polished surface of
127	each paleosol nodule by a micro-drill or milled by mortar and pestle. Drill depth was

no deeper than 2 mm to avoid drilling secondary carbonate. Carbonate powder from

- 129 different drill holes was homogenized. Drilling using a micro mill or equivalent
- 130 system can partially convert aragonite to calcite and may also alter the Δ_{47} (Staudigel
- 131 and Swart, 2016). However, in this study, all the paleosol carbonates are calcite and

132 drilling rotation speed was set <1,500 rpm to minimize frictional heating and Δ_{47} 133 alteration.

134

135 <u>Sample preservation style</u>

136	Under optical and cathodoluminescence (CL) microscope all the samples were
137	found to be dominated by dense micrite (except for sample "SK-31") with sparry
138	calcite constrained to the cracks (Fig. DR3). This fine-grained, homogenous texture
139	indicates that samples are very likely unaltered. In addition, our $\delta^{18}O$ and $\delta^{13}C$ values
140	are similar to published data indicating no significant alteration (Fig. DR4). An
141	exception is sample "SK-31", a sandstone with sparry calcite cement (Fig. DR3), that
142	is unlikely to have recorded the original climatic signal.
143	In addition to obvious diagentic alteration solid-state reordering of C-O bonds
144	may occur without significant changes of the bulk isotopes and textures of the
145	carbonate (Henkes et al., 2014). The Mingshui Formation is the uppermost strata in
146	Mesozoic and the depth of Cenozoic strata is less than 1 km in this region (Wang et
147	al., 2013a). Therefore, in this study, all of the samples have experienced a short
148	history of burial at a shallow depth (<76 myr and <1 km), which is below the burial
149	limit (100 °C for 10 ⁶ -10 ⁸ year) for solid-state C-O bond reordering (Henkes et al.,
150	2014). There is no apparent relationship between Δ_{47} temperatures and burial depths
151	or soil depth (below the soil surface) for the soil nodules analyzed, and also a lack of
152	correlation of δ^{18} O value and soil depth (Fig. DR4). In addition, an expected
153	(although weak) negative relationship between $\delta^{13}C$ value and soil depth is observed

154	(Fig. DR4). The correlation between the $\delta^{18}O_{water}$ and Δ_{47} temperatures also does not
155	show signs of closed-system alteration (Fig. DR5). This suggests that our results
156	reflect primary conditions and that the samples have, at most, only been slightly
157	influenced by burial diagenesis or solid-state C-O bond reordering (Passey and
158	Henkes, 2012; Henkes et al., 2014).
159	Notably, our Δ_{47} temperatures in Songliao Basin are similar to Δ_{47} temperatures
160	of fossil bivalves (Tobin et al., 2014) and paleosol carbonates (Snell et al., 2014) (Fig.
161	DR6) from similar paleolatitudes across the K-Pg boundary interval in North
162	America, which further support the reliability of our results.
163	
164	Clumped isotope analyses
165	Clumped isotope thermometry of carbonates provides a means of reconstructing
166	the growth temperatures of carbonate minerals by evaluating the extent to which ^{13}C
167	and ¹⁸ O are chemically bound to one another (clumped) within the same carbonate ion
168	group. The technique is based on a homogeneous isotope exchange equilibrium and
169	thus constrains temperature independent of the isotopic composition of waters from
170	which carbonates grew (Eiler, 2011).
171	The clumped isotope analyses were conducted at Johns Hopkins University in
172	2013 and 2014 (the lab has now moved to University of Michigan, Ann Arbor)
173	following the methods described in Passey et al. (2010). The CO_2 was liberated from
174	10-15 mg carbonate powder in an acid bath containing 105% H_3PO_4 at 90 °C for 10
175	min, then purified and introduced to a Thermo Scientific MAT 253 mass spectrometer

176	using an automated system. We report Δ_{47} values relative to the "absolute reference
177	frame (ARF)" by periodically analyzing aliquots of enriched/depleted CO ₂ that were
178	isotopically equilibrated at 30°C or heated to 1000°C (Dennis et al., 2011). We also
179	analyzed carbonate standards, HAF Carrara, NBS-19, or 102-GC-AZ01, alongside
180	samples to monitor system stability and precision. In the first session, the long-term
181	averages are HAF Carrara (n = 10) Δ_{47} = 0.398 ± 0.020‰ and 102-GC-AZ01 (n = 10)
182	$\Delta_{47} = 0.698 \pm 0.014\%$ (ARF, mean $\pm 1\sigma$ standard deviation). In the second session,
183	the long-term averages are HAF Carrara (n = 5) Δ_{47} = 0.398 ± 0.005‰, NBS-19 (n=5)
184	$\Delta_{47} = 0.405 \pm 0.011$ ‰, and 102-GC-AZ01 (n = 9) $\Delta_{47} = 0.695 \pm 0.007$ ‰ (ARF, mean
185	\pm 1 σ standard deviation) (Table DR1). The long term accepted values are HAF
186	Carrara $\Delta_{47} = 0.396\%$, NBS-19 $\Delta_{47} = 0.393\%$, and 102-GC-AZ01 $\Delta_{47} = 0.714\%$. The
187	observed long-term Standard Deviation (SD) of lab standards is 0.013 %. The 17 O
188	correction was applied (Schauer et al., 2016) and the differences are within 0.01‰.
189	The parameters in the original CIDS files were changed. According to Daëron et al.
190	(2016), the R13 (VPDB) was changed from 0.0112372 to 0.011180, the R17
191	(VSMOW) changed from 0.0003799 to 0.00038475, and the λ value changed from
192	0.5164 to 0.528.
193	In 2017, further clumped isotope analyses were conducted at Heidelberg
194	University following the methods described in Kluge et al. (2015). Between 6 to 8 mg
195	of carbonate powder (equivalent to 2-3 mg pure carbonate powder) were reacted for
196	10 minutes in 105% phosphoric acid held at 90 °C. Then CO ₂ gas was purified by
197	passage through a conventional off-line vacuum line with multiple cryogenic traps

198	and a Porapak-Q trap held at -35 °C. The purified CO ₂ gas was analyzed using a MAT
199	253 Plus mass spectrometer from Thermo Fisher Scientific equipped with 10^{13} ohm
200	resistors at masses 47-49 and includes a background monitoring cup. The data are
201	reported relative to the "absolute reference frame (ARF)" by periodically analyzing
202	gas standards that were isotopically equilibrated at 5°C and 90°C or heated to 1000°C
203	(Dennis et al., 2011) and compared with calcite standards, Marble Richter, ETH-1,
204	ETH-2, ETH-3, ETH-4, H-II, and L, alongside samples. The average values (ARF,
205	mean \pm 1 σ standard deviation) for the measurement period is 0.292 \pm 0.015‰ (n = 3)
206	for ETH-1, 0.305 \pm 0.006‰ (n = 3) for ETH-2, 0.712 \pm 0.014‰ (n = 6) for H-II and
207	L, and 0.396 \pm 0.019‰ (n = 3) for Marble Richter. The observed long-term Standard
208	Deviation (SD) of lab standards is 0.013‰. The ¹⁷ O correction was applied as
209	described above (Schauer et al., 2016).
209 210	described above (Schauer et al., 2016). The Δ_{47} temperatures are calculated using the calibration of Passey and Henkes
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210 211	The Δ_{47} temperatures are calculated using the calibration of Passey and Henkes (2012) with an acid temperature correction of 0.082% (Defliese et al., 2015). The
210211212	The Δ_{47} temperatures are calculated using the calibration of Passey and Henkes (2012) with an acid temperature correction of 0.082% (Defliese et al., 2015). The $\delta^{18}O_{water}$ (soil water) are calculated from the Δ_{47} temperatures and $\delta^{18}O$ of paleosol
210211212213	The Δ_{47} temperatures are calculated using the calibration of Passey and Henkes (2012) with an acid temperature correction of 0.082% (Defliese et al., 2015). The $\delta^{18}O_{water}$ (soil water) are calculated from the Δ_{47} temperatures and $\delta^{18}O$ of paleosol carbonates using the calibration of Kim and O'Neil (1997). The $\delta^{13}C$ and $\delta^{18}O$ are
 210 211 212 213 214 	The Δ_{47} temperatures are calculated using the calibration of Passey and Henkes (2012) with an acid temperature correction of 0.082% (Defliese et al., 2015). The $\delta^{18}O_{water}$ (soil water) are calculated from the Δ_{47} temperatures and $\delta^{18}O$ of paleosol carbonates using the calibration of Kim and O'Neil (1997). The $\delta^{13}C$ and $\delta^{18}O$ are reported relative to either the VPDB (mineral) or the VSMOW (water) scales (Table
 210 211 212 213 214 215 	The Δ_{47} temperatures are calculated using the calibration of Passey and Henkes (2012) with an acid temperature correction of 0.082% (Defliese et al., 2015). The $\delta^{18}O_{water}$ (soil water) are calculated from the Δ_{47} temperatures and $\delta^{18}O$ of paleosol carbonates using the calibration of Kim and O'Neil (1997). The $\delta^{13}C$ and $\delta^{18}O$ are reported relative to either the VPDB (mineral) or the VSMOW (water) scales (Table DR1 and DR2). Four samples were analyzed in both labs to evaluate the possible
 210 211 212 213 214 215 216 	The Δ_{47} temperatures are calculated using the calibration of Passey and Henkes (2012) with an acid temperature correction of 0.082% (Defliese et al., 2015). The $\delta^{18}O_{water}$ (soil water) are calculated from the Δ_{47} temperatures and $\delta^{18}O$ of paleosol carbonates using the calibration of Kim and O'Neil (1997). The $\delta^{13}C$ and $\delta^{18}O$ are reported relative to either the VPDB (mineral) or the VSMOW (water) scales (Table DR1 and DR2). Four samples were analyzed in both labs to evaluate the possible differences from the slightly different methods and machines used in Johns Hopkins

221 <u>Calculation of average stable and clumped isotope values</u>

222	Average δ^{13} C and δ^{18} O values are calculated as the mean of n (2-3) replicates
223	with error taken as 1 standard deviation (SD). Average Δ_{47} values are calculated as the
224	mean of n (2-3) replicates with error taken as 1 standard error (SE) (Table DR4). The
225	SE of Δ_{47} equal to SD divided by the square root of n (2-3). When SD of a sample is
226	less than the observed long-term SD of lab standards (0.013‰), 0.013‰ is assigned
227	as the SD of the sample. Then the Δ_{47} temperatures and $\delta^{18}O_{water}$ values are calculated
228	from average Δ_{47} values and average $\delta^{18}O$ values. The 1 SE of Δ_{47} temperatures and
229	$\delta^{18}O_{water}$ values are calculated by Gaussian error propagation. For most samples, the
230	uncertainties are relatively consistent, generally lower than 5 $^{\circ}$ C. The relatively large
231	uncertainties may be due to the heterogeneity of the samples. We did notice a gradual
232	increase in the uncertainties. In this study, the uncertainties of Δ_{47} temperatures are
233	calculated by Gaussian error propagation and the Δ_{47} values are part of the
234	denominator in the equation. According to the equation, the relatively lower Δ_{47}
235	values (higher temperatures) for older (Campanian) samples would lead to a higher
236	uncertainty. Finally, the Δ_{47} temperatures of samples from the same burial depth are
237	averaged and treated equally, using the equation as the inverse variance weighted
238	mean (Table DR4 and Table DR5).
230	

Δ_{47} -Temperature calibrations

Different Δ_{47} -temperature calibrations possess slightly different slopes and 241 intercepts, which produces different results. Four of them are evaluated here (Table 242 DR1 and DR2), these are calibrations from Passey and Henkes (2012), Defliese et al. 243 (2015), Kluge et al. (2015), and Kelson et al. (2017). The acid temperature correction 244 of 0.082‰ was adopted from Defliese et al. (2015). 245 The temperature curves generated by these calibrations show similar trends but 246 with slightly different amplitudes (no more than 5 °C). The calibration of Passey and 247 Henkes (2012) with an acid temperature correction of 0.082% (Defliese et al., 2015) 248 249 was used. The controversies regarding Δ_{47} -temperature calibrations are of minor importance for this study as almost all calibrations produce values that overlap in the 250 investigated temperature interval (Kluge et al., 2015). 251 252 Calculation of paleo-atmospheric CO₂ concentrations 253 The carbon isotopes of paleosol carbonate is mainly derived from two different 254 δ^{13} C sources, the atmospheric CO₂ and the soil-respired CO₂. Therefore, the carbon 255 isotope values of pedogenic carbonates will rise or fall alongside the variations of 256 atmospheric CO₂ concentrations (Breecker and Retallack, 2014). The equations of 257

- 258 paleo-atmospheric CO₂ concentration are:
- 259

260
$$P_a = P_r \times (\delta^{I3}C_s - 1.0044\delta^{I3}C_r - 4.4) / (\delta^{I3}C_a - \delta^{I3}C_s)$$
(1)

261

262
$$\delta^{13}C_s = (\delta^{13}C_c + 1000)/[(11.98 - 0.12T)/1000 + 1] - 1000$$
(2)

$$264 \qquad \qquad \delta^{13}C_a = \delta^{13}C_{ocean} - 7.9 \tag{3}$$

266
$$\delta^{13}C_o = 1.1\delta^{13}C_a - 18.67$$
 (4)

267

$$\delta^{I3}C_r = \delta^{I3}C_o - 1 \tag{5}$$

270
$$P_r = 35.3D_s + 588$$
 (6)

271

272
$$D_s = D_p / [-0.62 / (0.38 / e^{0.17K} - 1)]$$
 (7)

273

where P_a is the atmospheric CO₂ concentration (ppmv), P_r is the soil-respired 274 CO₂ concentration (ppmv), and the $\delta^{13}C_s$, $\delta^{13}C_r$, and $\delta^{13}C_a$ are the stable carbon 275 isotope compositions (‰) of soil CO₂, soil-respired CO₂, and the atmospheric CO₂, 276 respectively. K (km) is the estimated thickness overburden of the samples (burial 277 depth), and D_s/D_p (cm) are the original/buried soil depths carbonate nodules below the 278 paleosol surfaces (Breecker and Retallack, 2014). 279 The $\delta^{I3}C_s$ can be determined from the carbon isotope composition of the 280 pedogenic carbonate ($\delta^{I3}C_c$) and the formation temperature of the pedogenic 281 carbonate (T: Δ_{47} temperature) using the "Eq. (2)". We estimated the $\delta^{13}C_a$ through 282 the average δ^{I3} C values of planktonic foraminifera ($\delta^{I3}C_{ocean}$) (Thibault et al., 2012), 283 and -7.9‰ was assumed as the isotopic equilibrium fractionation value between the 284

- ocean and the atmospheric CO₂ (Passey and Cerling, 2002). The $\delta^{I3}C_r$ can be
- calculated from the organic matter ($\delta^{I3}C_o$) in the paleosol (Breecker and Retallack,
- 287 2014), and the $\delta^{13}C_o$ in turn can be estimated from the $\delta^{13}C_a$. The standard errors of
- the atmospheric CO₂ concentration (P_a) are calculated using the Gaussian error
- propagation (Table DR3). The equations are those of Breecker and Retallack (2014).

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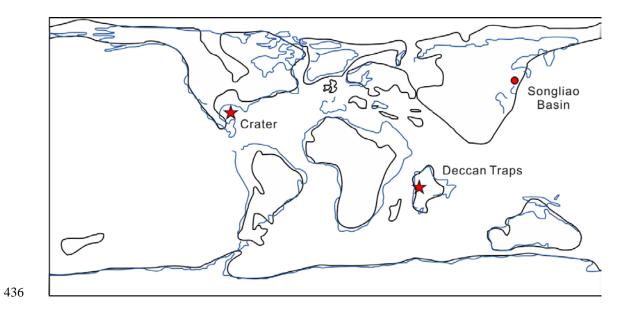
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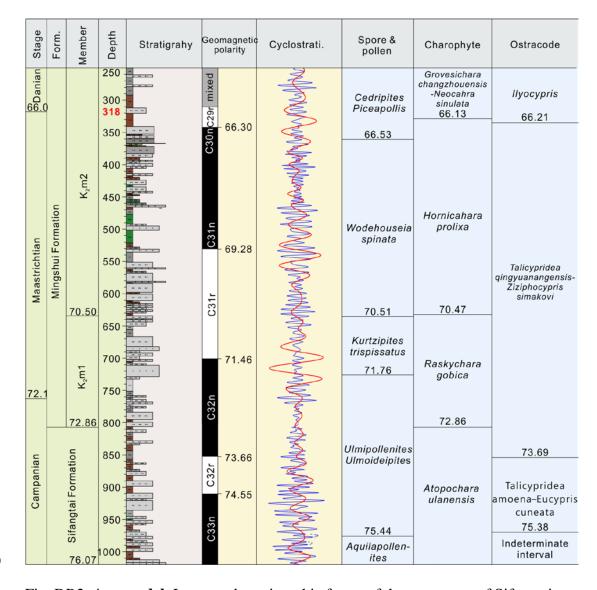
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437 Fig. DR1. Schematic paleogeography map. Paleogeographic map of the K-Pg

- 438 boundary interval showing the locations of the Chicxulub impact crater, the Deccan
- 439 Traps, and the Songliao Basin (Wang et al., 2013a).



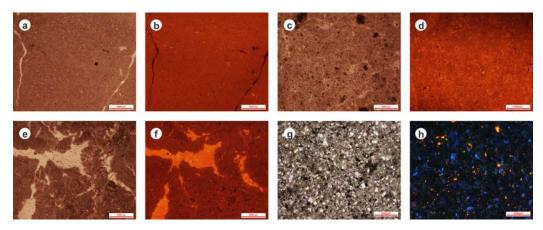
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Fig. DR2. Age model. Integrated stratigraphic frame of the upper part of Sifangtai
Formation and Mingshui Formation of the SK-In based on magnetostratigraphy (Deng

et al., 2013), cyclostratigraphy (Wu et al., 2014), and biostratigraphy (Wan et al.,

444 2013; Qu, 2014). The 405-kyr (red) and 100-kyr (blue) cycles are from Wu et al.

- 445 (2014). The red bold number "318" in the "Depth" column represent the location of
- the K-Pg boundary. "Cyclostrati" represents "Cyclostratigraphy". "Form." represents
- ⁴⁴⁷ "Formation". Modified after Wan et al. (2013) and Wu et al. (2014).



- 449 Fig. DR3. Petrographic images. (a-d) Optical and cathodoluminescence
- 450 petrographic images for dense micrite. (**e-f**) Optical and cathodoluminescence
- 451 petrographic images for dense micrite with fractures containing secondary spar. (g-h)
- 452 Optical and cathodoluminescence petrographic images for the altered sample "SK-
- 453 31"**.**

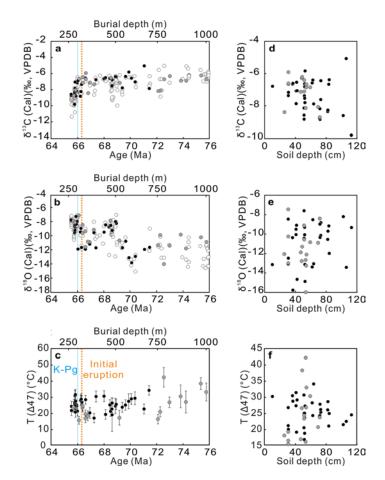
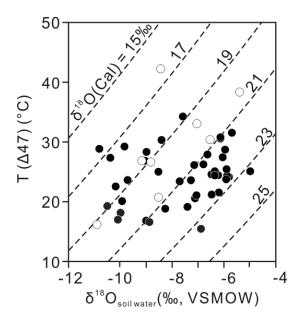


Fig. DR4. The results of stable and clumped isotopes analyses. (a) The δ^{13} C vs 455 age/burial depth. (b) The δ^{18} O vs age/burial depth. (c) The Δ_{47} temperature vs 456 age/burial depth. (d) The δ^{13} C vs soil depth. (e) The δ^{18} O vs soil depth. (f) The Δ_{47} 457 temperature vs soil depth. The black (Johns Hopkins) and grey (Heidelberg) circles 458 represent results of this study, and the white circles represent the previous published 459 data from the Songliao Basin (Huang et al., 2013; Gao et al., 2015). The average 1σ 460 standard error in δ^{13} C and δ^{18} O are < 0.07‰ and < 0.06‰, respectively. The 1σ 461 standard error in the Δ_{47} temperatures are shown as vertical bars. The dotted orange 462 line marks the onset of the main Deccan eruptions at 66.288 ± 0.085 Ma (Schoene et 463 al., 2015) or 66.38 \pm 0.05 Ma (Renne et al., 2015). The dotted blue line marks the K-464 Pg boundary at ~66.00 Ma (Wu et al., 2014) or 66.043 ± 0.086 Ma (Renne et al., 465

- 466 2013) and the Chicxulub impact occurred at 66.038 Ma \pm 0.098 Ma (Renne et al.,
- 467 2013). The bulk and clumped isotope results for all the samples are presented in Table
- 468 DR1, DR2, and DR4.



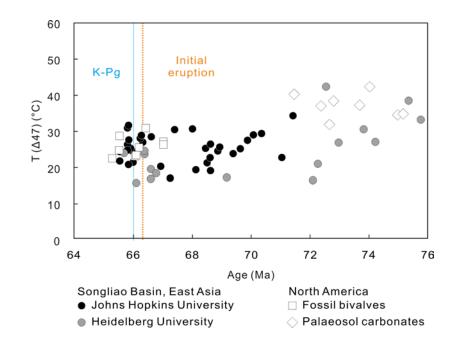
470 Fig. DR5. The δ^{18} O_{water} values (soil water) vs Δ_{47} temperature. Contours of δ^{18} O

471 (Cal) (‰, VSMOW) calculated from the calibration Kim and O'Neil (1997). The

472 black and white circles represent results from Maastrichtian and Campanian,

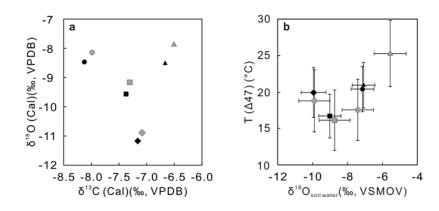
- 473 respectively. There is no statistically correlation between Δ_{47} temperature and
- 474 $\delta^{18}O_{water}$ values in the Maastrichtian, whereas in the Campanian there is a positive

475 relationship.



477 Fig. DR6. A comparison between Δ_{47} temperature from the Songliao Basin and

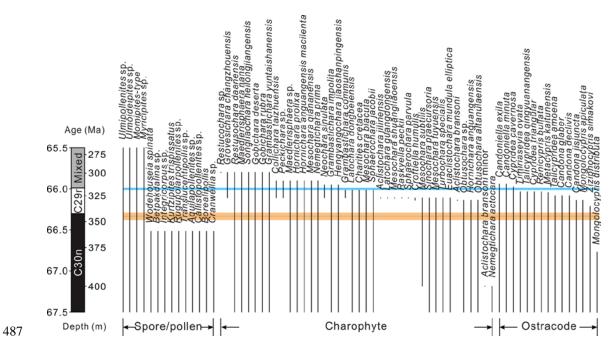
478 **North America.** The black (Johns Hopkins) and gray (Heidelberg) circles represent 479 Δ_{47} temperatures of paleosol carbonates in the Songliao Basin. The white squares and 480 diamonds represent the Δ_{47} temperatures of fossil bivalves (Tobin et al., 2014) and 481 paleosol carbonates (Snell et al., 2014) from similar paleolatitudes in North America 482 (see legends).



483

484 Fig. DR7. A comparison between analyses of same samples from different labs.

- 485 (a) The δ^{13} C vs δ^{18} O. (b) The Δ_{47} temperature vs the δ^{18} O_{water} values. The 1 σ standard
- 486 errors are shown as vertical/horizontal bars.



488 Fig. DR8. Fossil range data from the Songliao Basin across the K-Pg boundary

489 **interval.** The fossil range data from the Songliao Basin is from Scott et al. (2012).

- 490 The dotted orange line marks the onset of the main Deccan eruptions at $66.288 \pm$
- 491 0.085 Ma (Schoene et al., 2015) or 66.38 Ma \pm 0.05 (Renne et al., 2015). The
- 492 magnetozones are derived from Deng et al. (2013) and Wu et al. (2014). The dotted
- 493 blue line marks the K-Pg boundary at ~66.00 Ma (Wu et al., 2014) or 66.043 ± 0.086
- 494 Ma (Renne et al., 2013) and the Chicxulub impact occurred at 66.038 Ma \pm 0.098 Ma

495 (Renne et al., 2013).

Sample ID	Age*	$\mathrm{D}\mathrm{p}^\dagger$	Burial depth	Ds^\dagger	N‡	$\delta^{13}C^{\$}$	$\delta^{18}O^{\$}$	$\Delta47^{\P}$	$T(\Delta 47)^{\parallel}$	$\delta^{18}O_{water}^{**}$
Sample ID	(Ma)	(cm)	(km)	(cm)	(cm)	(‰, VPDB)	(‰, VPDB)	(‰, ARF)	(°C)	(‰, VSMOW)
SK-01	65.52	70	0.269	72	2	-8.75	-7.91	0.694 (0.009)	23.9 (3.2)	-5.8 (0.66)
SK-03	65.52	100	0.269	103	2	-8.59	-7.76	0.702 (0.009)	21.3 (3.2)	-6.2 (0.65)
SK-06	65.78	80	0.297	82	2	-8.35	-9.64	0.688 (0.009)	25.9 (3.3)	-7.1 (0.66)
SK-07	65.78	110	0.297	113	2	-9.80	-8.66	0.693 (0.009)	24.4 (3.3)	-6.5 (0.66)
SK-08	65.79	50	0.298	52	2	-8.57	-9.54	0.675 (0.009)	30.6 (3.5)	-6.1 (0.67)
SK-09	65.81	40	0.300	41	3	-7.85	-9.25	0.673 (0.010)	31.3 (3.9)	-5.7 (0.76)
SK-10	65.81	50	0.300	52	2	-8.12	-8.48	0.705 (0.009)	20.4 (3.1)	-7.1 (0.65)
SK-11	65.82	40	0.301	41	2	-7.07	-8.81	0.684 (0.009)	27.2 (3.3)	-6.0 (0.67)
SK-12	65.88	50	0.307	52	2	-8.82	-7.28	0.691 (0.009)	24.9 (3.3)	-5.0 (0.66)
SK-13	65.92	70	0.311	72	2	-8.17	-8.39	0.693 (0.009)	24.2 (3.2)	-6.2 (0.66)
SK-16	65.98	30	0.316	31	3	-7.16	-7.97	0.703 (0.009)	21.0 (3.1)	-6.5 (0.65)
SK-17	66.60	30	0.366	31	3	-6.57	-11.92	0.682 (0.008)	28.1 (2.8)	-9.0 (0.55)
SK-20	68.61	70	0.478	73	2	-7.60	-9.31	0.688 (0.009)	26.0 (3.3)	-6.8 (0.66)
SK-21	68.61	50	0.478	52	3	-7.52	-9.27	0.710 (0.033)	18.6 (10.6)	-8.3 (2.22)
SK-22	68.62	50	0.479	52	2	-6.80	-9.26	0.695 (0.009)	23.4 (3.2)	-7.3 (0.66)
SK-24	67.24	50	0.403	52	2	-7.37	-9.58	0.716 (0.009)	16.7 (3.0)	-9.0 (0.64)
SK-25	67.39	10	0.411	10	2	-6.78	-11.72	0.676 (0.009)	30.1 (3.4)	-8.4 (0.67)
SK-26	68.87	60	0.498	63	3	-6.39	-8.02	0.693 (0.014)	24.2 (4.9)	-5.9 (1.00)
SK-27	68.93	70	0.503	74	2	-6.43	-8.26	0.690 (0.009)	25.2 (3.3)	-5.9 (0.66)
SK-28	71.05	100	0.668	107	2	-5.06	-11.95	0.699 (0.009)	22.3 (3.2)	-10.2 (0.65)
SK-29	71.43	60	0.699	64	3	-7.87	-11.65	0.666 (0.008)	34.0 (3.0)	-7.6 (0.56)
SK-32	66.22	70	0.336	72	2	-8.83	-9.48	0.683 (0.009)	27.7 (3.4)	-6.6 (0.67)
SK-34	66.26	80	0.339	83	2	-8.25	-8.97	0.681 (0.009)	28.5 (3.4)	-5.9 (0.67)

Table DR4 Results of clumped isotope analyses.

SK-35	66.31	30	0.343	31	2	-7.36	-11.68	0.686 (0.012)	26.6 (4.2)	-9.0 (0.83)
SK-42	68.00	35	0.445	37	2	-6.64	-9.50	0.676 (0.009)	30.3 (3.5)	-6.1 (0.67)
SK-43	68.12	40	0.451	42	2	-6.53	-8.48	0.709 (0.009)	19.0 (3.1)	-7.4 (0.65)
SK-45	68.45	50	0.466	52	2	-6.62	-8.64	0.691 (0.009)	24.9 (3.3)	-6.3 (0.66)
SK-46	68.50	80	0.471	84	2	-6.66	-8.53	0.703 (0.009)	20.9 (3.1)	-7.1 (0.65)
SK-51	69.39	50	0.539	53	2	-7.79	-11.71	0.695 (0.009)	23.4 (3.2)	-9.7 (0.66)
SK-52	69.64	80	0.558	84	2	-6.37	-10.80	0.691 (0.009)	24.8 (3.3)	-8.5 (0.66)
SK-53	69.88	50	0.577	53	2	-5.83	-13.11	0.685 (0.014)	27.1 (4.8)	-10.4 (0.96)
SK-54	70.08	35	0.594	37	2	-6.59	-13.83	0.680 (0.009)	28.6 (3.4)	-10.8 (0.67)
SK-55	70.36	40	0.627	43	3	-7.05	-12.94	0.679 (0.011)	29.0 (4.1)	-9.8 (0.80)
SK-56	66.92	30	0.387	31	2	-7.15	-11.19	0.706 (0.010)	19.9 (3.4)	-9.9 (0.72)
SKnew-01	65.69	70	0.287	72	2	-8.69	-7.93	0.695 (0.009)	23.6 (3.2)	-5.9 (0.66)
SKknew-05	66.11	30	0.327	31	3	-6.60	-7.17	0.721 (0.008)	15.2 (2.5)	-6.9 (0.53)
SKnew-06-01	66.39	50	0.349	52	3	-6.40	-8.50	0.693 (0.009)	24.2 (3.1)	-6.3 (0.62)
SKnew-06-02	66.39	50	0.349	52	3	-7.10	-9.66	0.696 (0.008)	23.2 (2.7)	-7.7 (0.54)
SKnew-07	66.60	30	0.366	31	3	-5.90	-9.40	0.717 (0.008)	16.4 (2.6)	-8.9 (0.56)
SKnew-08	66.60	30	0.366	31	3	-6.64	-11.60	0.708 (0.008)	19.1 (2.6)	-10.5 (0.55)
SKnew-09	66.78	25	0.380	26	3	-8.38	-10.85	0.712 (0.009)	17.9 (3.1)	-10.0 (0.65)
SKnew-12	69.18	45	0.523	47	2	-7.12	-10.71	0.716 (0.014)	16.8 (4.6)	-10.1 (0.97)
SKnew-13	72.10	50	0.753	54	2	-8.13	-11.35	0.718 (0.009)	16.0 (3.0)	-10.9 (0.64)
SKnew-14	72.28	65	0.765	70	2	-8.06	-9.93	0.704 (0.009)	20.5 (3.1)	-8.5 (0.65)
SKnew-15	72.55	50	0.784	54	2	-6.66	-14.00	0.645 (0.015)	42.1 (6.1)	-8.4 (1.10)
SKnew-16	72.98	45	0.814	49	2	-6.27	-11.43	0.687 (0.009)	26.5 (3.3)	-8.8 (0.66)
SKnew-18	73.83	55	0.861	60	2	-6.84	-9.88	0.676 (0.020)	30.2 (7.1)	-6.5 (1.39)

SKnew-20	74.23	50	0.887	54	2	-6.84	-11.81	0.686 (0.019)	26.7 (6.9)	-9.2 (1.36)
SKnew-21	75.36	45	0.968	49	2	-6.20	-10.25	0.655 (0.009)	38.2 (3.7)	-5.4 (0.69)
SKnew-22	75.77	50	1.001	55	2	-6.66	-10.90	0.669 (0.015)	32.9 (5.6)	-7.0 (1.08)

* Age model see Supplementary text.

 † Dp/Ds are the burial/original depths carbonate nodules blew the paleosol surfaces.

[‡] Number of unique analyses of CO₂ from carbonate.

 $^{\$}$ VPDB = Vienna Pee Dee Belemnite. Uncertainties on δ^{13} C and δ^{18} O are < 0.07‰ and 0.06‰ respectively.

 \P ARF = Absolute Reference Frame. With acid correction of 0.082‰. Uncertainty is reported in parentheses. Standard error of $\Delta 47$, SE = SD/SQRT (N). When SD of a sample is less than the

observed long-term SD of lab standards (0.013‰), the long-term value of 0.013‰ is assigned as the SD of the sample.

^{II} Calculated using the Equation (5) in Passey and Henkes (2012). Uncertainty is reported in parentheses.

** VSMOW = Vienna Standard Mean Ocean Water. Calculated using the equation reported in Kim and O'Neil (1997). Uncertainty is reported in parentheses.

Age*	Burial depth	$\frac{\delta^{13}C^{\dagger}}{\delta^{13}C^{\dagger}}$	$\delta^{18}O^{\dagger}$	T(Δ47) [‡]	$\delta^{18}O_{water}$ §	pCO ₂ ¶
(Ma)	(km)	(‰, VPDB)	(‰, VPDB)	(°C)	(‰, VSMOW)	(ppmv)
65.52	0.269	-8.67	-7.84	22.6 (2.3)	-6.0 (0.46)	1187 (220)
65.69	0.287	-8.69	-7.93	23.6 (3.2)	-5.9 (0.66)	1048 (302)
65.78	0.297	-9.07	-9.15	25.1 (2.3)	-6.8 (0.47)	1180 (217)
65.79	0.298	-8.57	-9.54	30.6 (3.5)	-6.1 (0.67)	1075 (374)
65.81	0.300	-7.99	-8.87	24.6 (2.4)	-6.5 (0.49)	938 (250)
65.82	0.301	-7.07	-8.81	27.2 (3.3)	-6.0 (0.67)	1238 (488)
65.88	0.307	-8.82	-7.28	24.9 (3.3)	-5.0 (0.66)	800 (283)
65.92	0.311	-8.17	-8.39	24.2 (3.2)	-6.2 (0.66)	1251 (352)
65.98	0.316	-7.16	-7.97	21.0 (3.1)	-6.5 (0.65)	806 (381)
66.11	0.327	-6.60	-7.17	15.2 (2.5)	-6.9 (0.53)	701 (329)
66.22	0.336	-8.83	-9.48	27.7 (3.4)	-6.6 (0.67)	1059 (307)
66.26	0.339	-8.25	-8.97	28.5 (3.4)	-5.9 (0.67)	1468 (382)
66.31	0.343	-7.36	-11.68	26.6 (4.2)	-9.0 (0.83)	863 (414)
66.39	0.349	-6.75	-9.08	22.6 (2.0)	-7.1 (0.41)	1285 (308)
66.60	0.366	-6.37	-10.97	20.9 (1.5)	-9.5 (0.32)	870 (237)
66.78	0.380	-8.38	-10.85	17.9 (3.1)	-10.0 (0.65)	348 (189)
66.92	0.387	-7.15	-11.19	19.9 (3.4)	-9.9 (0.72)	665 (317)
67.24	0.403	-7.37	-9.58	16.7 (3.0)	-9.0 (0.64)	806 (281)
67.39	0.411	-6.78	-11.72	30.1 (3.4)	-8.4 (0.67)	587 (476)
68.00	0.445	-6.64	-9.50	30.3 (3.5)	-6.1 (0.67)	1228 (523)
68.12	0.451	-6.53	-8.48	19.0 (3.1)	-7.4 (0.65)	987 (387)
68.45	0.466	-6.62	-8.64	24.9 (3.3)	-6.3 (0.66)	1333 (451)
68.50	0.471	-6.66	-8.53	20.9 (3.1)	-7.1 (0.65)	1686 (422)
68.61	0.478	-7.56	-9.29	25.4 (3.2)	-6.9 (0.63)	1132 (286)
68.62	0.479	-6.80	-9.26	23.4 (3.2)	-7.3 (0.66)	1212 (411)
68.87	0.498	-6.39	-8.02	24.2 (4.9)	-5.9 (1.00)	1609 (516)
68.93	0.503	-6.43	-8.26	25.2 (3.3)	-5.9 (0.66)	1850 (499)
69.18	0.523	-7.12	-10.71	16.8 (4.6)	-10.1 (0.97)	813 (316)
69.39	0.539	-7.79	-11.71	23.4 (3.2)	-9.7 (0.66)	894 (309)
69.64	0.558	-6.37	-10.80	24.8 (3.3)	-8.5 (0.66)	2175 (534)
69.88	0.577	-5.83	-13.11	27.1 (4.8)	-10.4 (0.96)	1856 (647)
70.08	0.594	-6.59	-13.83	28.6 (3.4)	-10.8 (0.67)	1264 (532)
70.36	0.627	-7.05	-12.94	29.0 (4.1)	-9.8 (0.80)	1248 (492)
71.05	0.668	-5.06	-11.95	22.3 (3.2)	-10.2 (0.65)	3460 (719)
71.43	0.699	-7.87	-11.65	34.0 (3.0)	-7.6 (0.56)	1553 (454)
72.10	0.753	-8.13	-11.35	16.0 (3.0)	-10.9 (0.64)	680 (237)
72.28	0.765	-8.06	-9.93	20.5 (3.1)	-8.5 (0.65)	992 (291)
72.55	0.784	-6.66	-14.00	42.1 (6.1)	-8.4 (1.10)	2454 (885)
72.98	0.814	-6.27	-11.43	26.5 (3.3)	-8.8 (0.66)	1473 (521)
73.83	0.861	-6.84	-9.88	30.2 (7.1)	-6.5 (1.39)	1660 (609)
74.23	0.887	-6.84	-11.81	26.7 (6.9)	-9.2 (1.36)	1396 (533)

Table DR5 A summary of climatic parameters.

75.36	0.968	-6.20	-10.25	38.2 (3.7)	-5.4 (0.69)	2203 (775)
75.77	1.001	-6.66	-10.90	32.9 (5.6)	-7.0 (1.08)	1738 (616)

* Age model see Supplementary text.

[†] VPDB = Vienna Pee Dee Belemnite. Uncertainties on δ^{13} C and δ^{18} O are < 0.07‰ and 0.06‰ respectively.

[‡] Calculated using the Equation (5) in Passey and Henkes (2012). Uncertainty is reported in parentheses.

[§] VSMOW = Vienna Standard Mean Ocean Water. Calculated using the equation reported in Kim and O'Neil (1997). Uncertainty is reported in parentheses.

[¶]Calculated using the equations of Breecker and Retallack (2014). Uncertainty is reported in parentheses.