



# Isotopic evidence for long term warmth in the Mesozoic

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Atmospheric CO<sub>2</sub> concentrations appear to have been considerably higher than modern levels during much of the Phanerozoic and it has hence been proposed that surface temperatures were also higher. Some studies have, however, suggested that Earth's temperature (estimated from the isotopic composition of fossil shells) may have been independent of variations in atmospheric CO<sub>2</sub> (e.g. in the Jurassic and Cretaceous). If large changes in atmospheric CO<sub>2</sub> did not produce the expected climate responses in the past, predictions of future climate and the case for reducing current fossil-fuel emissions are potentially undermined. Here we evaluate the dataset upon which the Jurassic and Cretaceous assertions are based and present new temperature data, derived from the isotopic composition of fossil brachiopods. Our results are consistent with a warm climate mode for the Jurassic and Cretaceous and hence support the view that changes in atmospheric CO<sub>2</sub> concentrations are linked with changes in global temperatures.

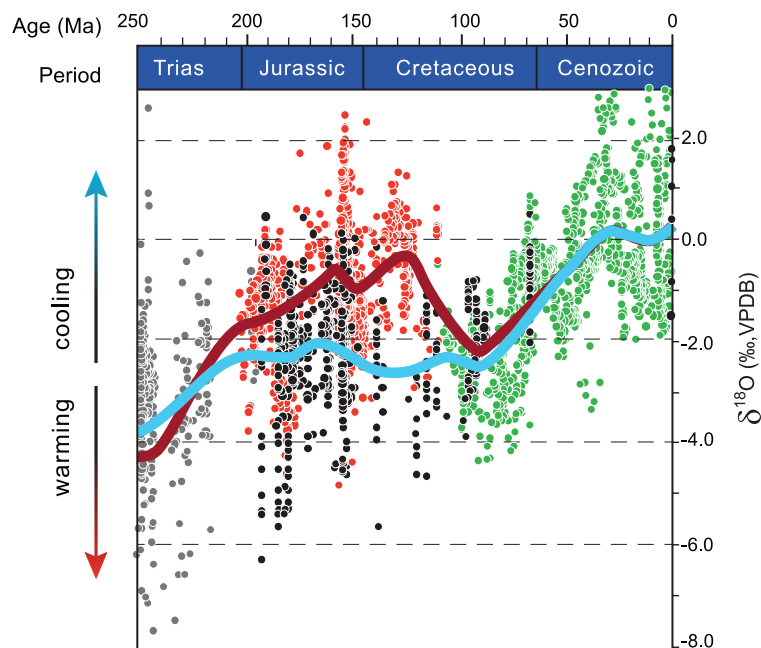
During the Phanerozoic, climate has alternated between states characterised by widespread glaciation (ice-houses) and largely ice-free hothouse (or warmhouse) conditions<sup>1–6</sup>. Quasi-periodic icehouse-hothouse cycles of varying length have been proposed<sup>7–9</sup> and many<sup>2,8,10</sup> have suggested that these major changes in Phanerozoic climate are linked to variations in atmospheric CO<sub>2</sub>. A number of studies have, however, cast doubt on the CO<sub>2</sub>-climate link<sup>4</sup> and suggest instead that the galactic cosmic ray flux is the main driver of Phanerozoic climate change<sup>5,11</sup>. Although not fully accepted by many<sup>3,12,13</sup>, if correct, then this view has significant implications for our predictions of future climate change and the case for reducing anthropogenic carbon emissions<sup>6</sup>.

The basis for this assertion is a putative temperature record<sup>5,14,15</sup> based upon the oxygen isotopic composition of well-preserved marine fossils (principally brachiopods, belemnites and planktonic foraminifera). This temperature record<sup>5</sup> shows two mismatches between temperature and atmospheric CO<sub>2</sub>: during the Late Ordovician glaciation (~445 million years ago) and the Early Jurassic to Early Cretaceous interval (~180–100 million years ago), both of which coincided with model<sup>2,16</sup> and proxy indications<sup>10,18</sup> of high levels of atmospheric CO<sub>2</sub>. The Late Ordovician paradox has been particularly well studied<sup>17–20</sup>. A lower solar luminosity at this time suggests that the CO<sub>2</sub> threshold for initiating a glaciation may have been higher<sup>18</sup>. Moreover, if the cooling pulse that led to ice volumes to expand to a similar size as those of the Pleistocene was relatively short-lived<sup>19</sup>, atmospheric CO<sub>2</sub> proxies may not have recorded this brief reduction in CO<sub>2</sub> levels. Furthermore, it has also been suggested that tropical ocean temperatures in excess of 30°C during the Late Ordovician coexisted with substantial south polar ice sheets<sup>19</sup>. Significant differences in the geosphere, e.g. the distribution of the continents, and biosphere, e.g. the absence of significant terrestrial vegetation and calcareous plankton, during the Late Ordovician suggest that the links between CO<sub>2</sub> and climate may well have operated differently to more recent times.

The Early Jurassic to Early Cretaceous anomaly presents a more critical test of the relationship between CO<sub>2</sub> and temperature change, given that Earth's palaeogeography and biota were more similar to those of the present-day. Although the Mesozoic is not a direct analogue for future greenhouse warming, such warm intervals in Earth history provide important insights into processes operating in the climate system<sup>21</sup>. Isotope derived temperature curves for this interval<sup>4</sup> suggest significant cooling at this time, whereas CO<sub>2</sub> proxy and model data typically indicate that atmospheric CO<sub>2</sub> reached peaks not recorded since the Devonian<sup>2</sup>. Here we present extensive temperature data, derived from the isotopic composition of fossil brachiopods in order to evaluate the hypothesized Jurassic-Cretaceous cooling trends and re-assess Phanerozoic trends.

## Results

Over 170 new oxygen isotope measurements from Mesozoic calcitic brachiopods are presented, combined with a further 300 brachiopod-derived measurements from published data<sup>22–25</sup> (Figs. 1, 2) in order to test the robustness



**Figure 1 | Evolution of Mesozoic-Cenozoic  $\delta^{18}\text{O}$  values.** Smoothed curves (red curve<sup>12,13</sup> and brachiopod-foraminifera only isotope data, blue curve) are generated using Kernel regressions with a bandwidth (h) of 10 Myr. Abbreviation: Trias = Triassic. Grey dots = brachiopod data, red circles = belemnite data and green circles = planktonic foraminifera<sup>12,13</sup> and black circles = brachiopod data compiled in this study.

of cooling events suggested in previous studies<sup>4,5</sup>, and test whether galactic cosmic ray flux is potentially a driver of Phanerozoic climate change. The new dataset (see SI) covers the Jurassic to Cretaceous time interval. Almost all shells are derived from shallow epicontinental seas of the European region representing the tropical to subtropical Tethys. The data are constrained by ammonite biozone resolution (~0.4 to 1 Myr on average) allowing the generation of a reliable temporal series calibrated to numerical ages<sup>26</sup>. Our cathodoluminescence (CL) and petrographic analyses (SI) of the calcitic shells demonstrate excellent ultrastructure preservation of the analysed material. The trace element concentrations of each of the brachiopod shells corresponds to the results of the petrographic and CL analyses, whereby relatively low concentrations of Mn and Fe also argues for well-preserved fossils<sup>3,14,15</sup>.

## Discussion

Our new brachiopod-derived  $\delta^{18}\text{O}$  isotope data from the Jurassic and Early Cretaceous are consistently more negative than coeval published data<sup>14,15</sup> (Fig. 1). The most likely explanation is that the published data derive from different fossil taxa; the Jurassic and Early Cretaceous portion of the published database is dominated by data derived from belemnites (Cephalopoda, Coleoidea). Studies<sup>24,25,27</sup> have also shown that belemnites typically display relatively more positive  $\delta^{18}\text{O}$  values than brachiopods; a difference possibly related to a combination of factors. Firstly, belemnites are interpreted as migratory nektonic organisms that were hence able to tolerate deeper and cooler waters, just as extant coleoids do<sup>28</sup>. Secondly, they may not have precipitated their calcite in isotopic equilibrium with seawater<sup>25</sup>. Furthermore, belemnites within the database are derived from a range of low, mid and high palaeolatitudes<sup>15</sup> whereas the brachiopod data are derived predominantly from low (tropical and subtropical) palaeolatitudes<sup>14,15</sup>.

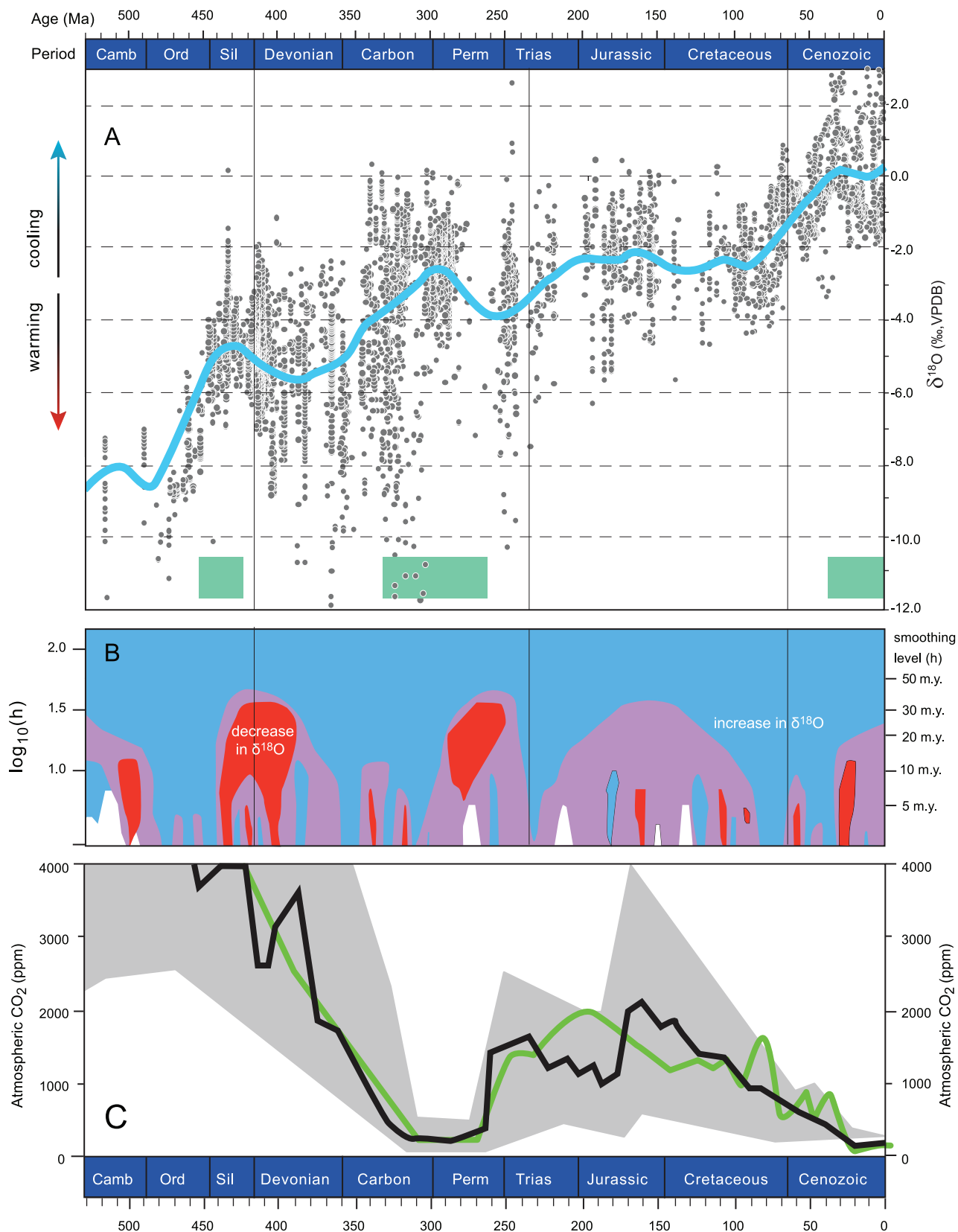
In contrast, the Late Cretaceous-Cenozoic proportion of the published database<sup>14,15</sup> consists of isotope measurements derived largely from planktonic foraminifera. Where our new data and published brachiopod data<sup>24</sup> are coeval with these planktonic data they show a good correspondence. The shells of planktonic foraminifera and brachiopods of similar age record comparable  $\delta^{18}\text{O}$  signatures,

whereas coeval belemnites do not. Has, therefore, the inclusion of belemnite data in previous datasets<sup>14</sup> resulted in erroneous temperature estimates for the Early Jurassic-Early Cretaceous interval?

As we have excluded a diagenetic influence (and assuming shell calcite is precipitated in isotopic equilibrium with seawater<sup>22-25</sup>), the  $\delta^{18}\text{O}$  composition of the brachiopods and planktonic foraminifera must reflect both the isotopic composition of the seawater in which the organisms lived and the water temperature at the time of shell growth. The isotopic composition of the seawater reflects changes in the size of ice-sheets, (ice-sheet growth preferentially removes <sup>16</sup>O from seawater), the pH of seawater and possibly a long term change in seawater caused by tectonic processes<sup>29</sup>. Recent research using the ‘carbonate clumped isotope’ method<sup>3,19</sup> is, however, inconsistent with such a secular variation in the  $\delta^{18}\text{O}$  of sea water. For this reason we have not adjusted the isotope data to accommodate for this (Figs. 1, 2), and the curve is interpreted in terms of temperature change. Given the potential problems with including belemnite data, we have combined our new data with the brachiopod- and foraminifera-derived data<sup>14,15</sup> only, without including any belemnite data, to produce a novel, high resolution Mesozoic temperature curve.

When the critical Early Jurassic to Early Cretaceous interval is examined, it is clear that the new curve of mean temperature diverges significantly from the previous one (Fig. 1). The maximum difference in  $\delta^{18}\text{O}$  is 2.5 ‰, equivalent to ca. 8 °C mean temperature change. We suggest the inclusion of belemnite data<sup>4</sup> skews interpretations by creating the impression that temperatures were some 8 °C cooler than the new data suggest.

The excellent agreement between our new Mesozoic brachiopod data and the published data derived from coeval planktonic foraminifera enables us to confidently link the published Palaeozoic dataset<sup>4</sup> (derived almost entirely from brachiopods) with Cenozoic data (derived almost entirely from planktonic foraminifera), providing a new Phanerozoic  $\delta^{18}\text{O}$  (temperature) curve that is free of biases related to the use of belemnite data in the Mesozoic. To test the relationship between temperature and  $\text{CO}_2$  at various temporal scales through the Phanerozoic, we use the ‘SiZer’ statistical approach (Significance of Zero Crossings of the Derivative<sup>30</sup>). This method is based on the construction of curves fitting time series



**Figure 2 | Evolution of Phanerozoic  $\delta^{18}\text{O}$  values.** (A): Smoothed brachiopod-foraminifera only curve generated using Kernel regressions with a bandwidth (h) of 10 Myr. Abbreviations: Camb = Cambrian; Ord = Ordovician; Sil = Silurian; Carbon = Carboniferous; Perm = Permian; Trias = Triassic. Green shaded boxes represent glaciations and icehouses<sup>12</sup>. (B): SiZer map of the isotope data derived from brachiopods and foraminifera only. Blue shading indicates a statistically significant increase in isotopic values (i.e. cooling), and the confidence interval is completely above a slope of 0. Red shading indicates that the confidence interval is completely below a slope of 0, and there is a significant decrease (i.e. warming). Purple shading indicates where the confidence interval for the derivative contains 0. White fill indicates where the data are too sparse. The lower panel C shows the atmospheric  $\text{CO}_2$  concentration record as determined from multiple proxy reconstructions<sup>16</sup> (green curve), and  $\text{CO}_2$  estimates (yellow curve) from GEOCARB III<sup>2</sup>.



using different levels of temporal smoothing (h). The first derivatives of each curve (i.e., the slopes) are computed with their 95% confidence intervals, allowing the signs of derivative estimates to be statistically tested. The results of these multiple tests reported in the form of SiZer maps (Fig. 1) enable significant features to be identified at different time scales. SiZer has been successfully applied to studies of the Quaternary<sup>31</sup> and of the Jurassic<sup>27</sup>, but this is the first Phanerozoic-scale analysis.

The long-term, first-order Phanerozoic trend is one of overall cooling (i.e. increase in  $\delta^{18}\text{O}$ ) from the Cambrian/Ordovician boundary to the present day, which matches the first-order decline in  $\text{CO}_2$  over the same interval (Fig. 2). Our SiZer analysis of the Palaeozoic record indicates two major cooling episodes (through the Ordovician and from the mid-Devonian to end-Carboniferous), both of which culminate with well-known glacial maxima<sup>9</sup>. Significant repeated shorter-term trends are apparent within the Ordovician and Silurian, a time characterised by warming and cooling/glacial and interglacial cycles<sup>19,20</sup>. We are therefore confident that our approach will provide a robust means to evaluate Mesozoic–Cenozoic trends.

Our SiZer analysis reveals warming during the Permian corresponding closely to rising  $\text{CO}_2$  levels, reaching a peak around the Permian/Triassic boundary<sup>32</sup>. Following the Permian/Triassic temperature maximum, our new Mesozoic brachiopod  $\delta^{18}\text{O}$  record suggests an overall cooling trend through most of the Triassic, mirroring the  $\text{CO}_2$  estimates from the GEOCARB III model<sup>2</sup> and the GEOCLIM<sup>32</sup> and COPSE models<sup>33</sup>. There is less agreement between our data and other proxy  $\text{CO}_2$  estimates<sup>18</sup> in particular those derived from paleosol carbonates<sup>10</sup>. Through the Jurassic, the long term temperature trend is one of relative stasis. Evidence for long lived and extensive ice sheets during this time is lacking, although short transient events may characterise this time<sup>8,34</sup>. The SiZer analysis only records one cooling episode in the Jurassic. Indeed, for this interval a wealth of data is available suggesting that high latitude warmth is the norm<sup>1,8,18</sup>. The apparent long term climatic stasis continues through to the Late Cretaceous (ca. 95 Ma), when a return to increasing  $\delta^{18}\text{O}$  values indicate the onset of another cooling trend, consistent with temperature predictions from the COPSE model<sup>33</sup>. The transition from equable temperatures to long-term cooling is observed as  $\text{CO}_2$  levels fell below 1000 ppm. The long-term trend of climatic stability for at least 100 million years (largely encompassing the Jurassic and Early Cretaceous) recorded in our brachiopod  $\delta^{18}\text{O}$  data is also reconcilable with the  $\text{CO}_2$  predictions for this interval, although there is some disagreement between model and proxy estimates of atmospheric  $\text{CO}_2$  levels<sup>10,16,18</sup> (Fig. 2C).

Our new brachiopod-derived  $\delta^{18}\text{O}$  isotope curve overturns the earlier and contentious suggestions that during the Early Jurassic to Early Cretaceous Earth experienced a cool climate mode. Inclusion of belemnite  $\delta^{18}\text{O}$  data is shown to bias the temperature interpretation towards cooler estimates. Whilst the data are consistent with two icehouse-hothouse intervals lasting tens of millions of years within the Palaeozoic, the Mesozoic–Cenozoic shows a different pattern. The lack of a prolonged cooling episode leading to glacial conditions may be a consequence of elevated atmospheric  $\text{CO}_2$  coupled with changing continental positions and higher solar luminosity. The Permo–Triassic hence appears as a major turning point in the climatic, as well as biotic<sup>35</sup>, history of the Earth. Carbon cycle modelling estimates of  $\text{CO}_2$  changes over the Mesozoic, in particular, correlate well with these changes in temperature. Together our observations support the assertion that atmospheric  $\text{CO}_2$  is consistent with patterns of past global climate change on a Phanerozoic time scale, and serves to invalidate claims against a long-term  $\text{CO}_2$ –climate link.

## Methods

For stable isotope ratios we use the conventional terminology and  $\delta$ -notation:  $\delta^{18}\text{O} = (\text{R}_{\text{sample}}/\text{R}_{\text{standard}} - 1) * 1000$ .  $\text{R}_{\text{sample}}$  and  $\text{R}_{\text{standard}}$  are the  $^{18}\text{O}/^{16}\text{O}$  ratio in the sample and standard, respectively. Positive or negative  $\delta^{18}\text{O}$  values mean that the sample has more or less  $^{18}\text{O}$  in the standard in parts per thousand (permil, ‰). The

PDB standard, is a Cretaceous marine fossil (*Belemnitella americana*), and has now been exhausted and replaced by the V-PDB standard. Stable isotopes were determined on a VG Instruments Optima Isotope Ratio Mass Spectrometer (at the University of Plymouth) using 200–300  $\mu\text{g}$  carbonate. Isotopic results were calibrated against NBS-19. Reproducibility for both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  was better than 0.1‰, based upon multiple sample analysis. Trace element geochemistry in conjunction with optical petrography and cathodoluminescence (CL) was used to determine the state of preservation of each of the brachiopods analysed. Cold cathode CL analysis was undertaken using a CITL CL MK 3A, mounted on a Nikon petrological microscope. Sub-samples for chemical analysis weighing 1–2 mg were dissolved in nitric acid and analysed using a Varian 725-ES ICP-AES. Based upon analysis of duplicate samples, reproducibility was better than  $\pm 3\%$  of the measured concentration of each element.

- Huber, B. T. Tropical Paradise at the Cretaceous Poles? *Science* **282**, 2199–2200 (1998).
- Berner, R. A. & Kothavala, Z. GEOCARB III: A revised model of atmospheric  $\text{CO}_2$  over Phanerozoic time. *American Journal of Science* **301**, 182–204 (2001).
- Came, R. E. *et al.* Coupling of surface temperatures and atmospheric  $\text{CO}_2$  concentrations during the Palaeozoic era. *Nature* **449**, 198–201 (2007).
- Veizer, J., Godderis, Y. & François, L. M. Evidence for decoupling of atmospheric  $\text{CO}_2$  and global climate during the Phanerozoic eon. *Nature* **408**, 698–701 (2000).
- Shaviv, N. J. & Veizer, J. Celestial driver of Phanerozoic climate? *GSA Today* **13**, 4–10 (2003).
- Kump, L. R. What Drives Climate? *Nature* **408**, 651–652 (2000).
- Fischer, A. G. Climatic oscillations in the biosphere, in *Biotic Crises in Ecological and Evolutionary Time*. Nitecki, M. ed., Academic, New York, pp. 103–131 (1981).
- Frakes, L. A. *Climates throughout geologic time*. Elsevier, 310 p. (1979).
- Crowell, J. C. Pre-Mesozoic ice ages; their bearing on understanding the climate system. *Geol. Soc. Am. Mem.* **192**, 106 p. (1999).
- Breecker, D. O., Sharp, Z. D. & McFadden, L. D. Atmospheric  $\text{CO}_2$  concentrations during ancient greenhouse climates were similar to those predicted for A. D. 2100. *PNAS* **107**, (2010).
- Gies, D. R. & Helsel, J. W. Ice age epochs and the sun's path through the Galaxy. *Astrophysical Journal* **626**, 844–848 (2005).
- Royer, D. L., Berner, R. A., Montañez, I. P., Tabor, N. J. & Beerling, D. J.  $\text{CO}_2$  as a primary driver of Phanerozoic climate. *GSA Today* **14**, 4–10 (2004).
- Fletcher, B. J., Brentnall, S. J., Anderson, C. W., Berner, R. A. & Beerling, D. J. Atmospheric carbon dioxide linked with Mesozoic and early Cenozoic climate change. *Nature Geoscience* **1**, 43–48 (2008).
- Veizer, J. *et al.*  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  evolution of Phanerozoic seawater. *Chemical Geology* **161**, 59–88 (1999).
- Prokoph, A., Shields, G. A. & Veizer, J. Compilation and time-series analysis of a marine carbonate  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{34}\text{S}$  database through Earth history. *Earth-Science Reviews* **87**, 113–133 (2008).
- Berner, R. A. Addendum to “Inclusion of the weathering of volcanic rocks in the GEOCARBSULF model”. *American Journal of Science* **308**, 100–103 (2008).
- Poussart, P. F., Weaver, A. J. & Barnes, C. R. Late Ordovician glaciation under high atmospheric  $\text{CO}_2$ : a coupled model analysis. *Paleoceanography* **14**, 542–558 (1999).
- Royer, D. L.  $\text{CO}_2$ -forced climate thresholds during the Phanerozoic. *Geochimica et Cosmochimica Acta* **70**, 5665–5675 (2006).
- Finnegan, S. *et al.* The magnitude and duration of Late Ordovician–Early Silurian Glaciation. *Science* **331**, 903–906 (2011).
- Turner, B. R., Armstrong, H. A. & Holt, P. Visions of ice sheets in the early Ordovician greenhouse world: Evidence from the Peninsula Formation, Cape Peninsula, South Africa. *Sedimentary Geology* **236**, 226–238 (2011).
- Crowley, T. J. Are there any satisfactory geologic analogs for a future greenhouse warming? *Journal of Climate* **3**, 1282–1292 (1990).
- Carpentier, C., Martin-Garin, B., Lathuilière, B. & Ferry, S. Correlation of reefal Oxfordian episodes and climatic implications in the eastern Paris Basin (France). *Terra Nova* **18**, 191–20 (2006).
- Martin-Garin, B., Lathuilière, E. B., Geister, J. & Ramseyer, K. Oxygen isotopes and climatic control of Oxfordian coral reefs (Jurassic, Tethys). *Palaios* **25**, 721–729 (2010).
- Suan, G. *et al.* Secular environmental precursors to Early Toarcian (Jurassic) extreme climate changes. *Earth Planet. Sci. Lett.* **290**, 448–458 (2010).
- Voigt, S., Wilmens, M., Mortimore, R. N. & Voigt, T. Cenomanian palaeotemperatures derived from the oxygen isotopic composition of brachiopods and belemnites: evaluation of Cretaceous palaeotemperature proxies. *Int. Jour. Earth Sciences* **92**, 285–299 (2003).
- Gradstein, F. M., Ogg, J. G. & Smith, A. G. (Eds.), *A Geologic Time Scale 2004*. Cambridge University Press, Cambridge, 589 p. (2004).
- Dera, G. *et al.* Climatic ups and downs in a disturbed Jurassic world. *Geology* **39**, 215–218 (2011).
- Price, G. D., Twitchett, R. J., Smale, C. & Marks, V. Isotopic analysis of the life history of the enigmatic squid *Spirula spirula*, with implications for studies of fossil cephalopods. *Palaios* **24**, 273–279 (2009).





29. Jaffrés, J., Shields, G. A. & Wallmann, K. The oxygen isotope evolution of seawater: a critical review of a long-standing controversy and an improved geological water cycle model for the past 3.4 billion years. *Earth-Science Reviews* **83**, 83–122 (2007).
30. Marron, J. S. & Chaudhuri, P. When is a feature really there? The SiZer approach in Firooz, A., ed., *Automatic target recognition VII: Photo optic and Industrial Engineering Proceedings* **3371**, 306–312 (1998).
31. Erästö, P. & Holmström, L. Selection of prior distributions and multiscale analysis in Bayesian temperature reconstructions based on fossil assemblages. *Journal of Paleolimnology* **36**, 69–80 (2006).
32. Donnadieu, Y. *et al.* GEOCLIM simulation of climatic and biogeochemical consequences of Pangea breakup. *Geochem. Geophys. Geosyst.* **7**, Q11019, doi:10.1029 (2006).
33. Bergman, N. M., Lenton, T. M. & Watson, A. J. COPSE: A new model of biogeochemical cycling over Phanerozoic time. *American Journal of Science*, **304**, 397–437.
34. Price, G. D. The evidence and implications of polar ice during the Mesozoic. *Earth-Science Reviews* **48**, 183–210 (1999).
35. Erwin, D. H. *The Great Paleozoic Crisis: Life and Death in the Permian*. Columbia University Press, 327 p. (1993).

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## Author contributions

G.D.P. and R.J.T. designed the study. J.R.W. and G.B. performed isotope and geochemical analyses. G.D.P. and R.J.T. analysed and interpreted the data. The manuscript incorporates comments on content and structure from all authors.

## Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

**Competing financial interests:** The authors declare no competing financial interests.

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