



HAL
open science

CO₂ and temperature decoupling at the million-year scale during the Cretaceous Greenhouse

Abel Barral, Bernard Gomez, François Fourel, Véronique Daviero-Gomez, Christophe Lecuyer

► **To cite this version:**

Abel Barral, Bernard Gomez, François Fourel, Véronique Daviero-Gomez, Christophe Lecuyer. CO₂ and temperature decoupling at the million-year scale during the Cretaceous Greenhouse. Scientific Reports, 2017, 7, 10.1038/s41598-017-08234-0 . hal-02329276

HAL Id: hal-02329276

<https://univ-lyon1.hal.science/hal-02329276v1>

Submitted on 30 Dec 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NoDerivatives 4.0 International License

SCIENTIFIC REPORTS



OPEN

CO₂ and temperature decoupling at the million-year scale during the Cretaceous Greenhouse

Abel Barral¹ , Bernard Gomez¹, François Fourel¹, Véronique Daviero-Gomez¹ & Christophe Lécuyer^{1,2}

CO₂ is considered the main greenhouse gas involved in the current global warming and the primary driver of temperature throughout Earth's history. However, the soundness of this relationship across time scales and during different climate states of the Earth remains uncertain. Here we explore how CO₂ and temperature are related in the framework of a Greenhouse climate state of the Earth. We reconstruct the long-term evolution of atmospheric CO₂ concentration (*p*CO₂) throughout the Cretaceous from the carbon isotope compositions of the fossil conifer *Frenelopsis*. We show that *p*CO₂ was in the range of ca. 150–650 ppm during the Barremian–Santonian interval, far less than what is usually considered for the mid Cretaceous. Comparison with available temperature records suggest that although CO₂ may have been a main driver of temperature and primary production at kyr or smaller scales, it was a long-term consequence of the climate-biological system, being decoupled or even showing inverse trends with temperature, at Myr scales. Our analysis indicates that the relationship between CO₂ and temperature is time scale-dependent at least during Greenhouse climate states of the Earth and that primary productivity is a key factor to consider in both past and future analyses of the climate system.

Greenhouse gas emissions resulting from human activity are considered to be an important driver of the current global warming. Accurate understanding of this cause-effect relationship is essential to propose realistic scenarios of the future evolution of Earth's climate, but the human monitoring history of these variables may be very tenuous to properly take into account the relative importance of their large time-scale dynamics into the climate system. Geological records offer an opportunity to address this time-scale issue as they provide track of the long-term dynamics of atmospheric greenhouse gas contents and surface temperature throughout Earth's history. An analysis of this relationship throughout the whole Phanerozoic pointed out atmospheric *p*CO₂ as the main multi-scale driver of global warming¹. However, recent improvement and refining of methods to reconstruct *p*CO₂ evidence that this conclusion was based on outdated imprecise estimates^{2,3}. Additionally, some factors involved in long-term climate dynamics such as O₂ have been put forward to challenge this paradigm⁴. This raises questions about the extent to which we are correctly interpreting the relative influence of atmospheric *p*CO₂ forcing on climate⁵.

The analysis of the relationship between *p*CO₂ and temperature for the Phanerozoic as a whole may not be pertinent because it comprised shifts between drastically different climate states of the Earth in which the relative impact and the dynamics of atmospheric CO₂ may have strongly differed. Of these, Greenhouse is considered to be the default planetary climate state of the Earth, prevailing in more than 70% of the Phanerozoic⁶. The Cretaceous is one of the longest and most studied Greenhouse periods of Earth's history, with an extensive background of *p*CO₂^{7–10} and temperature^{11–13} reconstructions. This makes the Cretaceous an exceptional 'laboratory' of the past to explore the relationship between the two factors. Nevertheless, *p*CO₂ reconstructions made so far for the Cretaceous defined temporal trends that are not consistent with those described for temperature^{11–13} or the carbon cycle dynamics evidenced by carbon isotopes^{14–16}. This raises questions about how accurate are *p*CO₂ reconstructions made so far and how significant was the relative contribution of *p*CO₂ to temperature evolution during the Cretaceous.

¹Laboratoire de Géologie de Lyon, CNRS UMR 5276, Université Lyon 1, Villeurbanne, 69622, France. ²Institut Universitaire de France, Paris, France. Correspondence and requests for materials should be addressed to A.B. (email: abel.barral.cuesta@gmail.com)

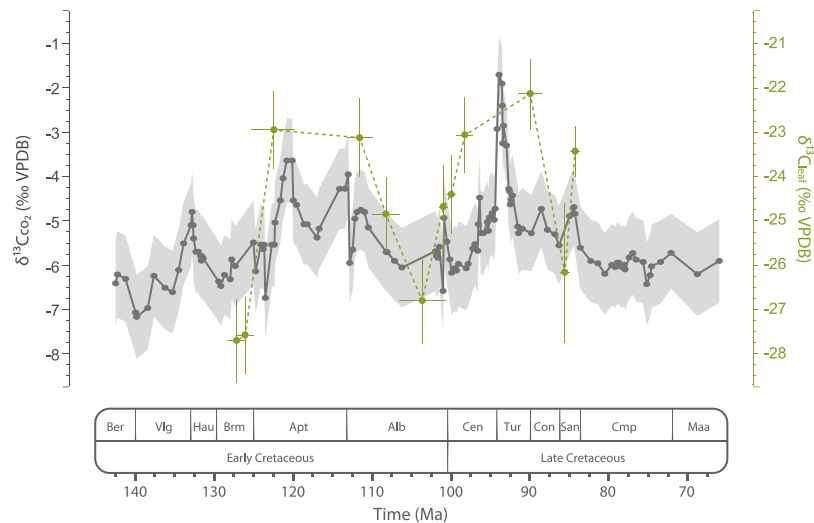


Figure 1. Comparison of the carbon isotope compositions of leaves of the fossil conifer *Frenelopsis* ($\delta^{13}\text{C}_{\text{leaf}}$) obtained for each studied episode with the evolution of the carbon isotope composition of atmospheric CO_2 ($\delta^{13}\text{C}_{\text{CO}_2}$) throughout the Cretaceous estimated by Barral *et al.*¹⁶. Envelopes and bar errors correspond to $\pm 1\sigma$.

Carbon isotopes are relevant tools for describing past carbon cycle and CO_2 dynamics^{14–20}. Carbon isotope compositions of terrestrial plants are particularly interesting as they are strongly linked to atmospheric CO_2 , which is the main source of carbon assimilated by plants via photosynthesis. The recent construction of models relating carbon isotope fractionation by plants and $p\text{CO}_2$ ^{19–21} coupled with the good preservation of the pristine carbon isotope signal within plant fossil materials^{22–25}, make carbon isotope compositions of plant fossils valuable proxies to analyze the evolution of atmospheric $p\text{CO}_2$ during past periods.

Herein the long-term evolution of atmospheric $p\text{CO}_2$ during the Cretaceous is reconstructed based on the carbon isotope compositions of leaves of the fossil conifer *Frenelopsis* ($\delta^{13}\text{C}_{\text{leaf}}$). $p\text{CO}_2$ is estimated from twelve stages spanning the Barremian–Santonian interval (129.4–83.6 Ma) during which major disturbance events of the carbon cycle related to CO_2 release to the atmosphere^{14, 15, 18} and major variations in temperature^{11–13} described for the Cretaceous took place. We explore the correspondence between estimated $p\text{CO}_2$ trends and those previously published for temperature to analyze the relative influence of $p\text{CO}_2$ forcing on climate during the Cretaceous.

Results and Discussion

Carbon isotope compositions of the fossil conifer *Frenelopsis*. $\delta^{13}\text{C}_{\text{leaf}}$ values from the twelve studied stages range from -27.7 to -22.1 ‰ in average (Fig. 1; Table 1). In most of these stages, $\delta^{13}\text{C}_{\text{leaf}}$ values show similar standard deviations (ca. 0.9‰), thus reflecting a similar range of local environmental variability. Santonian stages are the only exceptions, which may reflect higher climatic instability related to the development of Oceanic Anoxic Event (OAE) 3. Carbon isotope compositions of *Frenelopsis* in the Barremian, upper Albian and lower Santonian stages are notably ^{13}C -depleted compared to others, even though it is not significant in the latter case (Fig. 1). These lower $\delta^{13}\text{C}_{\text{leaf}}$ values are consistent with decreases in the carbon isotope composition of atmospheric CO_2 ($\delta^{13}\text{C}_{\text{CO}_2}$) recently described by Barral *et al.*¹⁶ (Fig. 1). Overall, there is a good agreement between $\delta^{13}\text{C}_{\text{leaf}}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ curves, though trends in the former are generally magnified. This magnification is more pronounced during the Cenomanian–Turonian interval, coinciding with a critical increase in global temperatures¹¹, which may have slightly reduced carbon isotope fractionation by plants ($\Delta^{13}\text{C}_{\text{leaf}}$) by reducing the discrimination effect of RuBisCO against ^{13}C ^{26, 27}.

Atmospheric CO_2 concentration during the Cretaceous. $\Delta^{13}\text{C}_{\text{leaf}}$ values inferred from $\delta^{13}\text{C}_{\text{leaf}}$ and concomitant $\delta^{13}\text{C}_{\text{CO}_2}$ values (Table 1) were used to estimate $p\text{CO}_2$ values. $p\text{CO}_2$ estimates are in the range of ca. 150–650 ppm for the Barremian–Santonian interval, and the resolution is better than 55 ppm (i.e. 1σ , standard deviation) for most of the stages (Fig. 2; Table 1). This range of values is consistent with the conclusions by Franks *et al.*²⁰ from a method based on universal equations of leaf gas exchange using stomatal anatomy and carbon isotope ratios of fossil leaves suggesting $p\text{CO}_2$ values below 1000 ppm during most of the Phanerozoic, although their conclusions remain controversial^{28–30}. Our $p\text{CO}_2$ estimates average ca. 300 ppm for the studied interval, which is in accordance with the most recent revision of GEOCARBSULF model³ and the range of values obtained in most recent works dealing with proxy-based reconstructions^{7–10} (Fig. 2). All these reconstructions suggest that atmospheric CO_2 concentrations were comparable to those of present-day atmosphere, which is a conclusion in deep contrast with the classical view that the Cretaceous period was characterized by atmospheric CO_2 concentrations considerably higher than today³¹. This is also consistent with several other approaches. Boron isotope compositions ($\delta^{11}\text{B}$) of marine biogenic carbonates are closely related to $p\text{CO}_2$ and pH^{32–34}. Higher atmospheric concentrations would imply more CO_2 dissolution into the ocean, causing a lowering of seawater pH and $\delta^{11}\text{B}$ of marine biogenic carbonates^{33, 34}. However, $\delta^{11}\text{B}$ of Cretaceous and present-day brachiopods as well as ophiolitic serpentinites are close to each other³⁵, thus suggesting that seawater pH and atmospheric $p\text{CO}_2$ were of similar

| Locality | Age | $\delta^{13}\text{C}_{\text{leaf}}$ (‰) | | | $\delta^{13}\text{C}_{\text{CO}_2}$ (‰) | | $\Delta^{13}\text{C}_{\text{leaf}}$ (‰) | | $p\text{CO}_2$ (ppm) | |
|----------------------|--|---|----------|----|---|----------|---|----------|----------------------|----------|
| | | μ | σ | n | μ | σ | μ | σ | μ | σ |
| Hautrage | upper lower Barremian– lower upper Barremian | −27.7 | 0.9 | 30 | −6.1 | 0.5 | 22.3 | 1.1 | 476.5 | 135.2 |
| Uña | upper Barremian | −27.6 | 0.9 | 30 | −5.7 | 0.7 | 22.5 | 1.1 | 502.2 | 155.1 |
| Mas de la Parreta | uppermost Barremian– lower Aptian | −23.0 | 0.9 | 30 | −5.8 | 0.7 | 17.6 | 1.1 | 191.6 | 37.6 |
| El Soplao | lower Albian | −23.1 | 0.9 | 30 | −5.0 | 0.3 | 18.6 | 1.0 | 225.6 | 39.4 |
| San Just | lower–middle Albian | −24.9 | 0.8 | 30 | −5.8 | 0.5 | 19.6 | 1.0 | 272.3 | 53.8 |
| Reillo | upper Albian | −26.8 | 1.0 | 30 | −5.8 | 0.3 | 21.6 | 1.1 | 408.9 | 99.0 |
| Archingeay (A1sl–A) | uppermost Albian | −24.7 | 1.0 | 26 | −5.7 | 0.4 | 19.5 | 1.1 | 265.8 | 53.3 |
| Archingeay (A2sm1–2) | lowermost Cenomanian | −24.4 | 0.9 | 30 | −5.9 | 0.4 | 18.9 | 1.0 | 240.9 | 43.9 |
| La Buzinie | uppermost lower– lowermost middle Cenomanian | −23.1 | 0.9 | 30 | −5.9 | 0.5 | 17.6 | 1.0 | 190.5 | 34.5 |
| Infiesto | upper Turonian– Coniacian | −22.1 | 0.8 | 30 | −5.1 | 0.4 | 17.4 | 0.9 | 185.0 | 30.1 |
| Piolenc | lower Santonian | −26.2 | 1.6 | 17 | −5.2 | 0.6 | 21.5 | 1.7 | 432.5 | 220.3 |
| Belcodème | upper Santonian | −23.4 | 0.6 | 30 | −4.8 | 0.5 | 19.1 | 0.8 | 246.0 | 34.5 |

Table 1. $\delta^{13}\text{C}_{\text{leaf}}$, $\delta^{13}\text{C}_{\text{CO}_2}$, $\Delta^{13}\text{C}_{\text{leaf}}$ and $p\text{CO}_2$ values for the twelve studied Cretaceous stages. μ and σ correspond to mean and standard deviation, respectively.

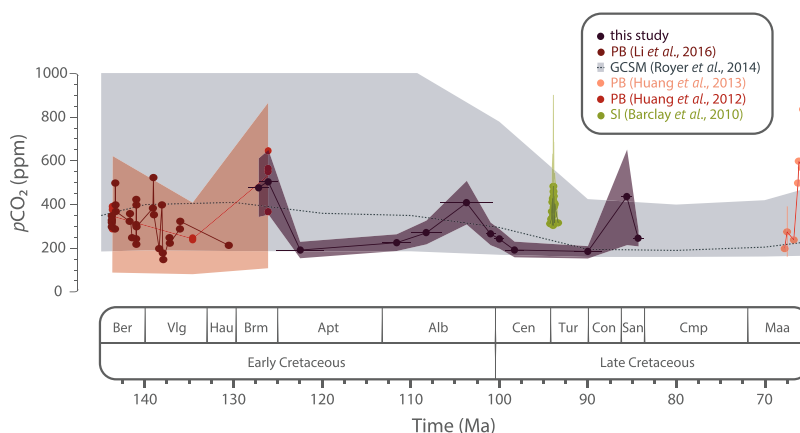


Figure 2. Comparison of the $\delta^{13}\text{C}_{\text{leaf}}$ -based $p\text{CO}_2$ estimates with most recent proxy-based and model-based $p\text{CO}_2$ reconstructions for the Cretaceous^{3,7–10}. Envelopes and bar errors represent $\pm 1\sigma$. GCSM: GEOCARBSULF Model reconstructions; PB: Paleosol Barometer reconstructions; SI: Stomatal Index reconstructions.

magnitude. Analysis of reef abundance and diversity throughout the Phanerozoic also agrees with our results, indicating that during the Cretaceous no significant long-term rise in ocean acidification, reflecting a long-term rise in $p\text{CO}_2$, took place³⁶. Only discrete short-term events of ocean acidification have been described during the Cretaceous based on marine calcifiers, associated with major Cretaceous OAEs and Hothouse episodes^{37,38}.

Was $p\text{CO}_2$ a long-term driver of temperature during the Cretaceous? Several events of volcanic CO_2 release into the atmosphere linked to the emplacement of large igneous provinces have been inferred from pronounced negative shifts of both carbon and strontium isotope compositions of marine carbonates^{14,38} associated with the main Cretaceous OAEs^{14,18,37}. These CO_2 release events are also evident regarding the evolution of $\delta^{13}\text{C}_{\text{CO}_2}$ throughout the Cretaceous¹⁶ (Fig. 1) and are most likely responsible for temperature increases at the kyr scale^{12,13}. The biggest of these CO_2 release events in terms of the magnitude of carbon isotope excursions was related to OAE1b and lasted ca. 25 kyr^{14,39}. This event was responsible for a fast warming of the atmosphere of ca. 0.3 °C and followed by cooler climatic conditions during a period of ca. 45 kyr³⁹. Greater kyr-scale increases in temperature of ca. 6–7 °C have been described associated with the CO_2 release events related to OAE1a^{12,13} and OAE2¹¹ (Fig. 3). However, our results indicate that drastic Myr-scale $p\text{CO}_2$ drawdowns took place during the warmest time intervals described for the Cretaceous^{11–13}: a drawdown of ca. 310 ppm (from ca. 500 to ca. 190 ppm) during the upper Barremian–lower Aptian interval (ca. 7.5 Myr), and ca. 225 ppm (from ca. 410 ppm to ca. 190 ppm) during the upper Albian–lower Cenomanian interval (ca. 5 Myr) (Fig. 3). In fact, at the Myr-scale,

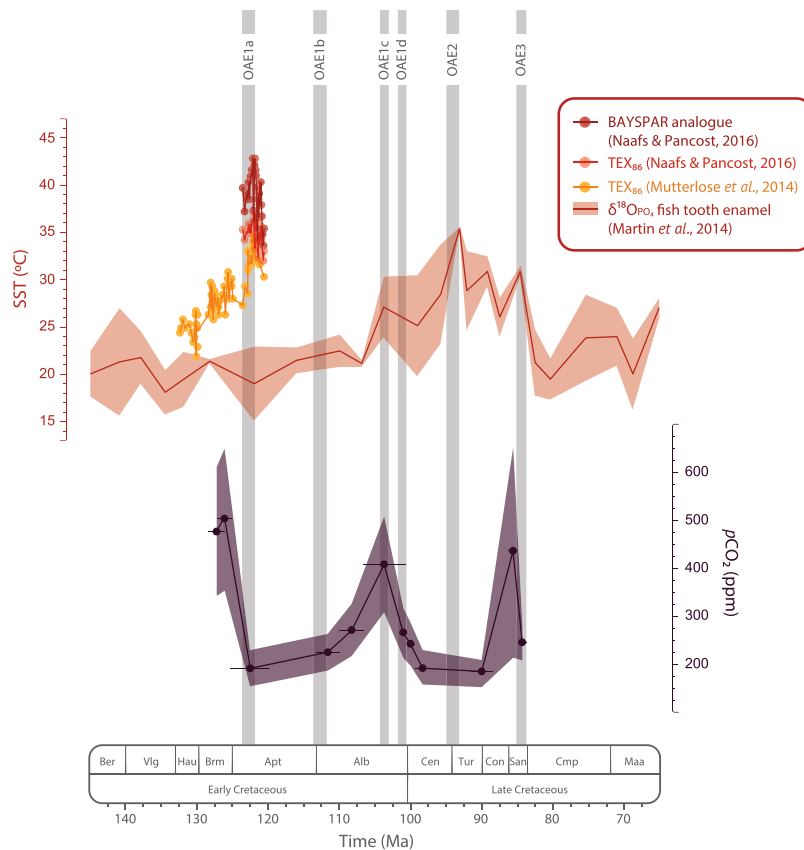


Figure 3. Reconstructed $p\text{CO}_2$ compared with available sea surface temperature (SST) records^{11–13} for the Cretaceous. Vertical grey bars represent major Oceanic Anoxic Events (OAE) occurring during the Cretaceous¹⁸. Envelopes represent $\pm 1\sigma$.

trends in $p\text{CO}_2$ are even inverse compared to temperature during significant time intervals such as the upper Barremian–lower Aptian (considering the higher resolution temperature curves based on TEX_{86} proxy^{12,13}) and the upper Albian–Santonian in which $p\text{CO}_2$ minima are coeval with thermal maxima (Fig. 3). If $p\text{CO}_2$ was rather low and usually decoupled from temperature at the Myr-scale, it may not have been the main long-term driver of global warming during the Cretaceous.

Time scale dependency of the relationship between $p\text{CO}_2$ and temperature. Episodes of enhanced primary production have been associated with the kyr-scale CO_2 release events that took place during major OAEs and the warmest intervals of the Cretaceous^{40–44}. Barclay *et al.*⁷ showed that a 20% increase in $p\text{CO}_2$ during OAE2 triggered extensive primary productivity leading to a global increase in rates of organic carbon burial, which eventually resulted in a $p\text{CO}_2$ decrease down to 26% in ca. 100 kyr. This indicates that, as a consequence of a critical CO_2 release event to the atmosphere, primary productivity can account for $p\text{CO}_2$ drawdowns of at least up to the 10^5 yr scale. The time resolution of our record is not high enough to fully discuss $p\text{CO}_2$ trends on the kyr scale; however, when the time uncertainty of our estimates allows clear perusal, $p\text{CO}_2$ levels are consistently low well after the events of CO_2 release to the atmosphere described in the literature^{18,45} (Fig. 3). This indicates that the aforementioned primary productivity effect may exceed the kyr scales resulting in a negative balance or a low-level stasis of $p\text{CO}_2$ up to the Myr scales. If primary production were responsible for a long-term decrease in atmospheric $p\text{CO}_2$ during the Cretaceous, we should find a co-varying increase in atmospheric $p\text{O}_2$ as a product of long-term enhanced photosynthesis. This is in accordance with the long-term trends obtained by the recent revision of the GEOCARBSULF model, which describes both a drawdown of $p\text{CO}_2$ and an increase in $p\text{O}_2$ levels from the earliest stages of the Cretaceous up to the mid Cretaceous³. Poulsen *et al.*⁴ emphasized the importance of O_2 in long-term climate dynamics as under low $p\text{O}_2$ conditions shortwave scattering by clouds and air molecules is reduced; this implies a significant increase in surface shortwave forcing, leading to increase of atmospheric water vapour and consequent enhanced greenhouse forcing which increases global surface temperatures. Thus, their simulations predict that temperature increases under low $p\text{O}_2$ and high $p\text{CO}_2$ conditions. However, during the Cretaceous temperature was maintained high during the late Albian–Santonian interval coinciding with relatively high $p\text{O}_2$ ³ and low $p\text{CO}_2$ conditions^{3,7} (Fig. 3). This observation reflects that both $p\text{O}_2$ and $p\text{CO}_2$ parameters may not be enough to explain long-term evolution of temperature.

In addition to the conclusions of previous work on atmospheric CO_2 dynamics at kyr time scales⁷ our results indicate that the relationship between CO_2 and temperature was probably scale-dependent during the Cretaceous. In the framework of a Greenhouse climate state functioning, CO_2 appears to have been a main driver of global

warming and primary production at timescales up to the kyr⁷. However, our results indicate that it was decoupled from temperature and most likely a long-term consequence of the climate-biological system at Myr scales. Direct extrapolation of these conclusions to time intervals corresponding to different climate states of the Earth is not pertinent because C cycle dynamics, and thus the evolution of $p\text{CO}_2$, might be strongly modulated by different global scale functioning of climate factors. For instance, temperature strongly affects carbon sequestration by living organisms^{26,27}, and global oceanic and atmospheric circulation patterns are involved in heat transport⁴⁶ and distribution of climate zones⁴⁷ that strongly influence primary productivity. Different dynamics and relative effects of those factors within different climate states of the Earth⁶ may result in different functioning of atmospheric CO_2 dynamics. However, nowadays anthropogenic CO_2 release into the atmosphere also constitutes a main driver of climate change at a human time scale. At larger scales, primary productivity appears to have been an important driver of atmospheric CO_2 concentration during both interglacial⁴⁸ and glacial intervals⁴⁹. Further work on the Myr-scale interrelationships between primary productivity, CO_2 and temperature within these different climate state intervals of the Earth is needed to explore how universal are the conclusions obtained herein. Primary production constitutes a major factor involved in climate dynamics and that regulates the balance between $p\text{O}_2$ and $p\text{CO}_2$. Thus, productivity must be taken into consideration in the evaluation of the relative effect of O_2 and CO_2 on climate dynamics. Present-days anthropogenic CO_2 release event can be compared in magnitude with those of the Cretaceous, reflected in a ca. -1.8‰ shift in $\delta^{13}\text{C}_{\text{CO}_2}$ since the industrial revolution⁵⁰ against the ca. -2‰ shift associated with OAE1b¹⁶ (Fig. 1). However, its critically shorter time of development makes it a more intense disturbance event, and so its forthcoming consequences are difficult to predict. Evaluating the response time of primary production to cushion CO_2 forcing will be critical to allow the prediction of climate evolution and its impact in the near future of life on Earth.

Methods

Twelve stages corresponding to eleven sites from the Cretaceous of western Europe were used for $p\text{CO}_2$ reconstruction (see Supplementary Fig. S1). The sites represent similar terrestrial environments in which the fossil conifer genus *Frenelopsis* was present, and they are distributed over a narrow palaeolatitude band ($30\text{--}40^\circ\text{N}$) of the same climate zone throughout the time range analyzed⁵¹ (see Supplementary Table S1). These stages and sites were selected to reduce as much as possible environmental biases on $\delta^{13}\text{C}_{\text{leaf}}$.

Frenelopsis was chosen as a $p\text{CO}_2$ proxy because it was frequent and abundant in Cretaceous ecosystems^{52–55}. *Frenelopsis* is a valuable material for performing stable carbon isotope analysis due to its resistance to decay and diagenesis. It provides accurate $\delta^{13}\text{C}_{\text{leaf}}$ values, which are comparable to those of living plant leaves^{25,56,57}.

Frenelopsis leaves were treated with HCl 32% following the protocol recommended by Barral *et al.*²⁵. Thirty *Frenelopsis* leaves per locality were separately reduced to powder using an agate mortar. Three replicates of ca. $100\ \mu\text{g}$ per leaf were randomly selected and weighted using a precision balance Sartorius ME36S and loaded into tin capsules. Carbon isotope analyses were performed using a continuous flow IRMS configuration, being He the carrier gas, using a EuroEA3028TM-HT elemental analyzer working in combustion mode and interfaced with an IP60 isotope ratio mass spectrometer. Carbon isotope ratios were calibrated against the international standard IAEA-C4 ($\delta^{13}\text{C} = -23.96\text{‰}$) and casein ($\delta^{13}\text{C} = -22.67\text{‰}$) as an internal reference. Based on repeated analysis of standards, analytical reproducibility was better than $\pm 0.2\text{‰}$.

$p\text{CO}_2$ values were estimated for each stage using the equation relating $p\text{CO}_2$ to $\delta^{13}\text{C}_{\text{leaf}}$ described by Schubert and Jahren^{19,21} ($r = 0.94$):

$$\Delta^{13}\text{C}_{\text{leaf}} = [(28.26)(0.22)(p\text{CO}_2 + 23.9)]/[28.26 + (0.22)(p\text{CO}_2 + 23.9)]$$

$\Delta^{13}\text{C}_{\text{leaf}}$ values were estimated from $\delta^{13}\text{C}_{\text{leaf}}$ and concomitant $\delta^{13}\text{C}_{\text{CO}_2}$ values by using the equation proposed by Farquhar *et al.*⁵⁸:

$$\Delta^{13}\text{C}_{\text{leaf}} = \delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{leaf}}/1 + (\delta^{13}\text{C}_{\text{CO}_2}/1000)$$

$\delta^{13}\text{C}_{\text{CO}_2}$ values were taken from the $\delta^{13}\text{C}_{\text{carb}}$ -based $\delta^{13}\text{C}_{\text{CO}_2}$ estimates provided by Barral *et al.*¹⁶. We avoid discrimination bias due to different physiological functioning related to taxonomic specificity by using always the same taxon, and thus $\delta^{13}\text{C}_{\text{leaf}}$ faithfully represents environmental variability. In order to avoid misrepresented $p\text{CO}_2$ estimates due to subtle uncorrelations between the beds from which $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{13}\text{C}_{\text{leaf}}$ were obtained, we accounted for $\delta^{13}\text{C}_{\text{CO}_2}$ variability in the uncertainty timespan of the *Frenelopsis* localities by averaging and estimating cumulated error for each stage. This was made by randomly drawing 10,000-repetition Gaussian distributions for each single case within the interval of uncertainty of a given stage, defined by the pre-determined means and standard deviations of each case, and calculating the mean and the standard deviations of the 10,000 randomly generated sets. This procedure was also implemented to include the associated errors to each $\delta^{13}\text{C}_{\text{leaf}}$, $\delta^{13}\text{C}_{\text{CO}_2}$ and $\Delta^{13}\text{C}_{\text{leaf}}$ values into the aforementioned equations to account for all sources of error in the resolution of $p\text{CO}_2$ estimates.

References

- Royer, D. L., Berner, R. A., Montañez, I. P., Tabor, N. J. & Beerling, D. J. CO_2 as a primary driver of phanerozoic climate. *GSA Today* **14**, 4–10 (2004).
- Breecker, D. O., Sharp, Z. D. & McFadden, L. D. Atmospheric CO_2 concentrations during ancient greenhouse climates were similar to those predicted for AD 2100. *Proc. Natl. Acad. Sci.* **107**, 576–580 (2010).
- Royer, D. L., Donnadiu, Y., Park, J., Kowalczyk, J. & Godd eris, Y. Error analysis of CO_2 and O_2 estimates from the long-term geochemical model GEOCARBSULF. *Am. J. Sci.* **314**, 1259–1283 (2014).
- Poulsen, C. J., Tabor, C. & White, J. D. Long-term climate forcing by atmospheric oxygen concentrations. *Science* **348**, 1238–1241 (2015).
- Pepp e, D. J. & Royer, D. L. Can climate feel the pressure? *Science* **348**, 1210–1211 (2015).

6. Kidder, D. L. & Worsley, T. R. Phanerozoic large igneous provinces (LIPs), HEATT (haline euxinic acidic thermal transgression) episodes, and mass extinctions. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **295**, 162–191 (2010).
7. Barclay, R. S., McElwain, J. C. & Sageman, B. B. Carbon sequestration activated by a volcanic CO₂ pulse during Ocean Anoxic Event 2. *Nat. Geosci.* **3**, 205–208 (2010).
8. Huang, C. M., Retallack, G. J. & Wang, C. S. Early Cretaceous atmospheric pCO₂ levels recorded from pedogenic carbonates in China. *Cretac. Res.* **33**, 42–49 (2012).
9. Huang, C., Retallack, G. J., Wang, C. & Huang, Q. Paleatmospheric pCO₂ fluctuations across the Cretaceous–Tertiary boundary recorded from paleosol carbonates in NE China. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **385**, 95–105 (2013).
10. Li, J., Wen, X. Y. & Huang, C. M. Lower Cretaceous paleosols and paleoclimate in Sichuan Basin, China. *Cretac. Res.* **62**, 154–171 (2016).
11. Martin, J. E., Amiot, R., Lécuyer, C. & Benton, M. J. Sea surface temperature contributes to marine crocodylomorph evolution. *Nat. Commun.* **5** (2014).
12. Mutterlose, J., Bottini, C., Schouten, S. & Damsté, J. S. S. High sea-surface temperatures during the early Aptian Oceanic Anoxic Event 1a in the Boreal Realm. *Geology* **42**, 439–442 (2014).
13. Naafs, B. D. A. & Pancost, R. D. Sea-surface temperature evolution across Aptian Oceanic Anoxic Event 1a. *Geology* **44**, 959–962 (2016).
14. Erba, E. Calcareous nannofossils and Mesozoic oceanic anoxic events. *Mar. Micropaleontol.* **52**, 85–106 (2004).
15. Jarvis, I. A. N., Gale, A. S., Jenkyns, H. C. & Pearce, M. A. Secular variation in Late Cretaceous carbon isotopes: a new δ¹³C carbonate reference curve for the Cenomanian–Campanian (99.6–70.6 Ma). *Geol. Mag.* **143**, 561–608 (2006).
16. Barral, A., Gomez, B., Legendre, S. & Lécuyer, C. Evolution of the carbon isotope composition of atmospheric CO₂ throughout the Cretaceous. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **471**, 40–47 (2017).
17. Cerling, T. E. In *Palaeoweathering, palaeosurfaces and related continental deposits* (eds. Thiry, M. & Simon-Coinçon, R.) International Association of Sedimentologists Special Publication **27**, 43–60 (1999).
18. Jenkyns, H. C. Geochemistry of oceanic anoxic events. *Geochem. Geophys. Geosystems* **11** (2010).
19. Schubert, B. A. & Jahren, A. H. The effect of atmospheric CO₂ concentration on carbon isotope fractionation in C₃ land plants. *Geochim. Cosmochim. Acta* **96**, 29–43 (2012).
20. Franks, P. J. *et al.* New constraints on atmospheric CO₂ concentration for the Phanerozoic. *Geophys. Res. Lett.* **41**, 4685–4694 (2014).
21. Schubert, B. A. & Jahren, A. H. Global increase in plant carbon isotope fractionation following the Last Glacial Maximum caused by increase in atmospheric pCO₂. *Geology* **43**, 435–438 (2015).
22. Bocherens, H., Friis, E., Mariotti, A. & Pedersen, K. R. Carbon isotopic abundances in Mesozoic and Cenozoic fossil plants: Palaeoecological implications. *Lethaia* **26**, 347–358 (1993).
23. De Leeuw, J. W., Frewin, N. L., Van Bergen, P. F., Damsté, J. S. & Collinson, M. E. In *Marine palaeoenvironmental analysis from fossils* (eds. Bosence, D. W. J. & Allison, P. A.) **83**, 43–71 (Geological Society Special Publications, 1995).
24. Arens, N. C., Jahren, A. H. & Amundson, R. Can C₃ plants faithfully record the carbon isotopic composition of atmospheric carbon dioxide? *Paleobiology* **26**, 137–164 (2000).
25. Barral, A., Lécuyer, C., Gomez, B., Fourel, F. & Daviero-Gomez, V. Effects of chemical preparation protocols on δ¹³C values of plant fossil samples. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **438**, 267–276 (2015).
26. Crafts-Brandner, S. J. & Salvucci, M. E. Rubisco activase constrains the photosynthetic potential of leaves at high temperature and CO₂. *Proc. Natl. Acad. Sci.* **97**, 13430–13435 (2000).
27. Falkowski, P. *et al.* The global carbon cycle: a test of our knowledge of Earth as a system. *Science* **290**, 291–296 (2000).
28. McElwain, J. C., Montañez, I., White, J. D., Wilson, J. P. & Yiotis, C. Was atmospheric CO₂ capped at 1000ppm over the past 300 million years? *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **441**, 653–658 (2016).
29. Franks, P. J. & Royer, D. L. Comment on ‘Was atmospheric CO₂ capped at 1000ppm over the past 300 million years?’ by McElwain J. C. *et al.* [Palaeogeography, Palaeoclimatology, Palaeoecology **441** (2016) 653–658]. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* (2017).
30. McElwain, J. C., Montañez, I. P., White, J. D., Wilson, J. P. & Yiotis, C. Reply to Comment on ‘Was atmospheric CO₂ capped at 1000ppm over the past 300 million years?’ [Palaeogeography, Palaeoclimatology, Palaeoecology **441** (2016) 653–658]. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* (2017).
31. Wang *et al.* Paleo-CO₂ variation trends and the Cretaceous greenhouse climate. *Earth-Sci. Rev.* **129**, 136–147 (2014).
32. Pearson, P. N. & Palmer, M. R. Middle Eocene seawater pH and atmospheric carbon dioxide concentrations. *Science* **284**, 1824–1826 (1999).
33. Pearson, P. N. & Palmer, M. R. Atmospheric carbon dioxide concentrations over the past 60 million years. *Nature* **406**, 695–699 (2000).
34. Lécuyer, C., Grandjean, P., Reynard, B., Albarède, F. & Telouk, P. ¹¹B/¹⁰B analysis of geological materials by ICP–MS Plasma 54: Application to the boron fractionation between brachiopod calcite and seawater. *Chem. Geol.* **186**, 45–55 (2002).
35. Simon, L., Lécuyer, C., Maréchal, C. & Coltice, N. Modelling the geochemical cycle of boron: implications for the long-term δ¹¹B evolution of seawater and oceanic crust. *Chem. Geol.* **225**, 61–76 (2006).
36. Kiessling, W. & Simpson, C. On the potential for ocean acidification to be a general cause of ancient reef crises. *Glob. Change Biol.* **17**, 56–67 (2011).
37. Erba, E., Bottini, C., Weissert, H. J. & Keller, C. E. Calcareous nannoplankton response to surface-water acidification around Oceanic Anoxic Event 1a. *Science* **329**, 428–432 (2010).
38. Arkhipkin, A. I. & Laptikhovskiy, V. V. Impact of ocean acidification on plankton larvae as a cause of mass extinctions in ammonites and belemnites. *Neues Jahrb. Geol. Paläontol.-Abh.* **266**, 39–50 (2012).
39. Wagner, T., Wallmann, K., Herrle, J. O., Hofmann, P. & Stuesser, I. Consequences of moderate 25,000 yr lasting emission of light CO₂ into the mid-Cretaceous ocean. *Earth Planet. Sci. Lett.* **259**, 200–211 (2007).
40. Schlanger, S. O. & Jenkyns, H. C. Cretaceous oceanic anoxic events: causes and consequences. *Neth. J. Geosci. En Mijnb.* **55**, 179–184 (1976).
41. Kuypers, M. M., Pancost, R. D., Nijenhuis, I. A. & Sinningh-Damsté, J. S. Enhanced productivity led to increased organic carbon burial in the euxinic North Atlantic basin during the late Cenomanian oceanic anoxic event. *Paleoceanography* **17**, 1051 (2002).
42. Adams, D. D., Hurtgen, M. T. & Sageman, B. B. Volcanic triggering of a biogeochemical cascade during Oceanic Anoxic Event 2. *Nat. Geosci.* **3**, 201–204 (2010).
43. Gomes, M. L., Hurtgen, M. T. & Sageman, B. B. Biogeochemical sulfur cycling during Cretaceous oceanic anoxic events: a comparison of OAE1a and OAE2. *Paleoceanography* (2016).
44. Tessin, A., Sheldon, N. D., Hendy, I. & Chappaz, A. Iron limitation in the Western Interior Seaway during the Late Cretaceous OAE 3 and its role in phosphorus recycling and enhanced organic matter preservation. *Earth Planet. Sci. Lett.* **449**, 135–144 (2016).
45. Leckie, R. M., Bralower, T. J. & Cashman, R. Oceanic anoxic events and plankton evolution: Biotic response to tectonic forcing during the mid-Cretaceous. *Paleoceanography* **17**, 13–1 (2002).
46. Hay, W. W. Evolving ideas about the Cretaceous climate and ocean circulation. *Cretac. Res.* **29**, 725–753 (2008).
47. Hasegawa *et al.* Drastic shrinking of the Hadley circulation during the mid-Cretaceous Supergreenhouse. *Clim. Past* **8**, 1323–1337 (2012).
48. Adams, J. M., Faure, H., Faure-Denard, L., McGlade, J. M. & Woodward, F. I. Increases in terrestrial carbon storage from the Last Glacial Maximum to the present. *Nature* **348**, 711714 (1990).

49. Montañez *et al.* Climate, $p\text{CO}_2$ and terrestrial carbon cycle linkages during late Palaeozoic glacial–interglacial cycles. *Nat. Geosci.* **9**, 824–828 (2016).
50. National Oceanic and Atmospheric Administration, Earth System Research Laboratory, Global Monitoring Division. U.S. Department of Commerce. <http://www.esrl.noaa.gov/>.
51. Chaboureau, A.-C., Sepulchre, P., Donnadieu, Y. & Franc, A. Tectonic-driven climate change and the diversification of angiosperms. *Proc. Natl. Acad. Sci.* **111**, 14066–14070 (2014).
52. Gomez, B., Martín-Closas, C., Barale, G., Thévenard, F. & Guignard, G. *Frenelopsis* (Coniferales: Cheirolepidiaceae) and related male organ genera from the Lower Cretaceous of Spain. *Palaeontology* **45**, 997–1036 (2002).
53. Gomez, B. *et al.* Floristic assemblage from the Albian–Cenomanian of Charente–Maritime (SW France). *Ann. Paléontol.* **90**, 147–159 (2004).
54. Mendes, M. M., Dinis, J. L., Gomez, B. & Pais, J. Reassessment of the cheirolepidiaceae conifer *Frenelopsis teixeirae* Alvin et Pais from the Early Cretaceous (Hauterivian) of Portugal and palaeoenvironmental considerations. *Rev. Palaeobot. Palynol.* **161**, 30–42 (2010).
55. Barral, A. *et al.* Local-scale analysis of plant community from the Early Cretaceous riparian ecosystem of Hautrage, Belgium. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **443**, 107–122 (2016).
56. Nguyen, T. T. T. *et al.* Ecological distribution of Cenomanian terrestrial plants based on $^{13}\text{C}/^{12}\text{C}$ ratios. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **145**, 79–93 (1999).
57. Nguyen, T. T. T. *et al.* Isotope reconstruction of plant palaeoecology. Case study of Cenomanian floras from Bohemia. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **183**, 43–70 (2002).
58. Farquhar, G. D., Ehleringer, J. R. & Hubick, K. T. Carbon isotope discrimination and photosynthesis. *Annu. Rev. Plant Biol.* **40**, 503–537 (1989).

Acknowledgements

This work was financially supported by the CNRS-UMR 5276 and the projects CGL2013-42643-P, CGL2014-52163-C2, CGL2015-68363-P and CGL2015-60805-P funded by the Ministerio de Economía y Competitividad of the Spanish government and 2014SGR-251 funded by the AGAUR, Catalan Research Authority.

Author Contributions

A.B. conceived the original idea for this study and led the writing of the manuscript under the advising of B.G. and C.L. Plant fossil materials were provided by B.G. and V.D.-G. $\delta^{13}\text{C}_{\text{leaf}}$ measurements were made by A.B., F.F. and C.L. All the authors contributed to data interpretation and manuscript editing.

Additional Information

Supplementary information accompanies this paper at doi:[10.1038/s41598-017-08234-0](https://doi.org/10.1038/s41598-017-08234-0)

Competing Interests: The authors declare that they have no competing interests.

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2017