δ^{13}C of terrestrial vegetation records Toarcian CO₂ and climate gradients

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Throughout Earth’s history, variations in atmospheric CO₂ concentration modulated climate. Understanding changes in atmospheric carbon cycle is therefore pivotal in predicting consequences of recent global warming. Here, we report stable carbon isotopes (δ^{13}C) of molecular land plant fossils complemented by bulk organic and inorganic carbon fractions for early Toarcian (Early Jurassic) sediments that coincided with global warming and a carbon cycle perturbation. The carbon cycle perturbation is expressed by a negative excursion in the δ^{13}C records established for the different substrates. Based on differences in the magnitude of the carbon isotope excursion recorded in land plants and marine substrates we infer that the early Toarcian warming was paralleled by an increase in atmospheric CO₂ levels from ~500 ppmv to ~1000 ppmv. Our data suggest that rising atmospheric CO₂ levels resulted from the injection of 12C-enriched methane and its subsequent oxidation to CO₂. Based on the cyclic nature of the CIE we concluded that methane was released from climate sensitive reservoirs, in particular permafrost areas. Moderate volcanic CO₂ emissions led to a destabilization of the labile permafrost carbon pool triggering the onset of Toarcian climate change only. The main carbon cycle perturbation then subsequently was driven by a self-sustained demise of a carbon-rich cryosphere progressing from mid to high latitudes as reflected by latitudinal climate gradients recorded in land plant carbon isotopes.

Anthropogenic fossil carbon emissions steadily increase atmospheric CO₂ levels and thereby impact on Earth’s climate and carbon cycle¹. As a consequence rising global temperatures can lead to a reactivation of carbon stored in permafrost regions that upon its release to the atmosphere will further accelerate global warming². Melting polar ice caps and sea level rise, climate extremes and enhanced stress for marine and continental ecosystems have been proven to be direct consequences of global warming³–⁵. Predictions on the evolution of Earth’s climate system, the carbon cycle and the response of ecosystems are, however, problematic. Thus, investigation of sediment archives that record ancient climate perturbation can serve as analogues for recent climate change and can thereby guide in predicting consequences of global warming and its cascade of consequences.

Here, we address changes in Earth’s climate and carbon cycle that occurred in conjunction with the early Toarcian Oceanic Anoxic Event (Early Jurassic; ~183 Ma). This study utilizes stable carbon isotopes recorded in different substrates, facilitating the reconstruction of changes in the global carbon cycle, atmospheric CO₂ levels and latitudinal climate gradients during the early Toarcian global warming.

Background

Around the globe, sediment archives that span the early Toarcian record profound environmental changes. A rapid high-amplitude sea level rise paralleled by a decline in oxygen isotope values of macrofossil calcite, has been interpreted to reflect a rise in sea water temperatures that was potentially accompanied by a reduction in the volume of land-based ice caps⁶–⁹. Rising global temperatures evolved parallel to an increase in atmospheric CO₂ level inferred from stomata data¹⁰. In the marine realm global warming led to expansion of marine death zones and triggered the genesis of the Toarcian Oceanic Anoxic Event (T-OAE)¹¹, whereas on land it caused substantial shifts in floral assemblages¹²–¹³. A hallmark of the early Toarcian is a negative carbon isotope excursion (CIE) that is interpreted to reflect a global carbon cycle perturbation, caused by injections of 12C-enriched carbon into Earth’s hydro-atmosphere.

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system\textsuperscript{9,14–18}. Carbon sources are debated controversially and comprise a volcanic CO\textsubscript{2} and/or thermogenic CH\textsubscript{4} associated with the emplacement of the Karoo-Ferrar Large Igneous Province of southern Gondwana\textsuperscript{10,19}, destabilization of methane hydrates\textsuperscript{14,16}, increased rates of wetland methanogenesis\textsuperscript{17}, or permafrost decay and thermokarst blowout events during global warming\textsuperscript{9}. The CIE has been reported in marine and terrestrial organic matter as well as in marine carbonates\textsuperscript{10,12,14,15}, suggesting that the carbon cycle perturbation affected the entire exchangeable carbon reservoir. A decline in $\delta^{13}$C documented in land plant-derived lipids indicates atmospheric $^{13}$C depletion and substantiates a perturbation of the atmospheric carbon cycle\textsuperscript{18,20,21}. However, current $\delta^{13}$C records of land plant-derived lipids cover only a brief stratigraphic interval and provide no information on the recovery phase of the CIE and on the long-term evolution of the atmospheric carbon reservoir. Moreover, information on atmospheric CO\textsubscript{2} concentration and its absolute change during the early Toarcian warming event are based on stomata data from a single section only and span the onset of the CIE\textsuperscript{10}. Reconstruction of atmospheric CO\textsubscript{2} concentration may further be complicated by stratigraphic gaps and methodological limitation\textsuperscript{10,22}.

Here we utilize compound-specific carbon isotope data of land plant wax lipids to reconstruct changes in the atmospheric carbon reservoir across the early Toarcian carbon cycle perturbation and the associated climate event. The $\delta^{13}$C analysis of land plant-derived wax lipids, compounds not affected by the differential preservation of fossilized wood fragments\textsuperscript{15}, provide a robust method for reconstructing changes in the isotopic composition of the atmospheric carbon reservoir. The compound-specific $\delta^{13}$C record is complemented by $\delta^{13}$C data from marine calcite that reflect changes in the oceanic carbon reservoir. The reconciliation of $\delta^{13}$C excursions in land plant and marine substrates allows reconstruction of changes in the entire exchangeable carbon reservoir. Moreover, parallel evaluation of marine and terrestrial carbon isotope excursions provide information not only on changes in atmospheric CO\textsubscript{2} concentration but also on absolute atmospheric CO\textsubscript{2} levels prior to and during the early Toarcian carbon cycle perturbation\textsuperscript{23,24}.

**Study site.** In this study we investigated upper Pliensbachian to lower Toarcian sediments, represented by the *Emaciatum* to *Serpentinum* ammonite zones and the NJT5b to NJT6 nanofossil zones, cropping out at La Cerradura (Subbetic, southern Spain)\textsuperscript{25}. Ammonite assemblages in combination with coccolithophore-based biostratigraphic data indicate that the sediments can be correlated with the T-OAE\textsuperscript{26}, which is further supported by paleontological and geochemical data\textsuperscript{25}. Sediments, mainly marlstone-limestone alternation, were deposited in a fragmented marine platform with hemipelagic sedimentation at a paleolatitude of about 26°N at the southern Iberian paleomargin. Floral assemblages suggest that during the Early Jurassic (183 Ma) the study site was located in the semi-arid climate belt\textsuperscript{27} (Fig. 1).

**Results and Discussion**

**An atmospheric record of the toarcian carbon cycle perturbation.** The early Toarcian carbon cycle perturbation is expressed in $\delta^{13}$C\textsubscript{org} and $\delta^{13}$C\textsubscript{carb} data by negative excursions of $\sim$3.4‰ and $\sim$1.2‰, respectively (Table 1 in the SI). A shift towards lower $\delta^{13}$C values occurred in a stepwise manner at
the Polymorphum-Serpentinum zonal transition (Fig. 2). Stratigraphic position as well as pattern and pacing of the CIE at La Cerradura match trends from other locations documenting a multiphasic carbon cycle perturbation9,15,16. The δ13C signatures of terrestrial n-alkanes recording a negative CIE with a magnitude of −3.7‰ (−3.1‰ on average) (Fig. 2) parallel the high-resolution δ13C bulk data (Table 2 in the SI). The stepped CIE character is documented in the δ13Cn-alkane record, confirming that the CIE reflects multiple re-occurring carbon injections into the Earth’s ocean-atmosphere system9,16. Moreover our data unequivocally demonstrates that the Toarcian carbon cycle perturbation affected not only the marine but also the atmospheric carbon reservoir, as previously shown by Pienkowski et al. (ref. 12) and Hesselbo et al. (refs. 14,15). The −3.7‰ magnitude of the CIE at La Cerradura is similar to that reported in long chain n-alkanes from the Sichuan Basin (China)18, but is slightly lower than the −5.3‰ CIE (−4.2‰ on average) determined for terrigenic n-alkanes from the Cleveland Basin (UK)20 (Fig. 2). Differences in the magnitude may originate from low stratigraphic coverage of compound-specific δ13C values and/or stratigraphically incompleteness of the sections. Higher and variant magnitudes in the range from −3.5 to −8.0‰ reported in δ13Cwood (Table 3 in the SI)12,14,15,21 can be attributed to differential preservation states (e.g. jet, charcoal), molecular heterogeneity, or taxonomic impact on the isotopic signature of fossil wood15. Moreover, when preserved as jet (degraded wood), microbial reworking and impregnation by marine taxa during exposure to seawater, can alter the initial δ13C signature15.

While δ13Cn-alkane records for different basins show similar trends and magnitudes of the CIE, their absolute δ13C values differ. The δ13Cn-alkane records from the Cleveland and Sichuan basins both show base values more depleted in 13C by about 4 to 5‰ when compared with base values from La Cerradura (Fig. 2). This offset relates to latitudinal climate gradients associated with different floral assemblages and precipitation rates impacting on δ13C of land plants23,26–30 (Fig. S4 in the SI). During the Early Jurassic the Cleveland and Sichuan basins were located in a winter-wet temperate climate belt, while southern Iberia was situated in the winter-wet to semi-arid climate belt27 (Fig. 1). Lower precipitation rates in the latter are expressed in a dominance of xerophytic flora31,32 and are evident in clay mineral assemblages33. Accordingly, differences in the δ13Cn-alkane values from the different basins reflect a strong latitudinal climate gradient. A dominance of exceptionally long n-alkanes in samples from La Cerradura (Figs. S1, S2 in the SI) confirms organic matter contributions from xerophytic flora. Therefore, δ13Cn-alkane at La Cerradura records the terrestrial δ13C pool as part of the global carbon cycle.

Quantifying atmospheric CO2 levels across the early Toarcian CIE. The early Toarcian CIE was associated not only with changes in the isotopic composition of the exchangeable C-reservoir, but also with changes in atmospheric pCO2 levels. Based on stomata data McElwain et al. (ref. 12) reported pCO2 values in the range 350 to
An alternative approach for determining ancient pCO₂ levels is based on the observation that the isotopic fractionation of C3 land plants will vary not only with precipitation rates, but also with pCO₂. This CO₂ effect results in a higher isotopic fractionation when pCO₂ levels increase and thereby cause higher CIE magnitudes in terrigenic than in marine substrates. Offsets in CIE magnitude of terrigenic versus marine substrates thus facilitate determination of absolute atmospheric pCO₂ levels (for details we refer to the supplementary information). However, as pointed out by Schubert & Jahren (ref. 25) and Lomax et al. (ref. 30) under enhanced water stress the carbon isotopic signatures of C3 plants vary as a function of precipitation rates and then do not unambiguously reflect past atmospheric CO₂ concentration. According to recent observations, a strong impact of precipitation rates on δ¹³C of land plant biomass has been documented for vegetation in areas with mean annual precipitation rates < 2200 mm/year. On the contrary, precipitation seems to have no significant impact on the land plant δ¹³C in areas with high mean annual precipitation rates (ref. 24). The dominance of xerophytic flora in the southern Iberian paleomargin, which here is represented by the La Cerradura section, suggests low paleo-precipitation rates and eventually enhanced paleo-water stress (ref. 42). When compared to localities at higher latitudes, lower paleo-precipitation rates also manifested themselves in the δ¹³C-enrichment of the land plant biomass. We can, however, speculate only about absolute paleo-precipitation rates at the southern Iberian paleomargin, which complicate evaluating the impact of water stress on the δ¹³C land plant biomass.

In order to calculate pCO₂ levels and to minimize the effect of different paleo-precipitation rates, we compared data from the La Cerradura section, located in a semi-arid climate (Table S1 in the SI), from Yorkshire (UK) (ref. 25) and from China (ref. 18) that were both situated in a humid climate belt (Fig. 1). In particular the δ¹³C data of the La Cerradura section, and δ¹³C data from sites situated in a humid climate are supposed to vary in dependency of changing atmospheric CO₂ levels (ref. 33). Moreover, a CO₂ dependence of the land plant δ¹³C has also been documented for vegetation growing under low water treatment (ref. 29). It is therefore reasonable to assume that changes in δ¹³C, at all sites will also vary as a function of changes in the atmospheric CO₂ concentration. This assumption is underpinned by the consistent evolution and similar magnitudes of the CIE seen in the δ¹³C at all sites investigated (Fig. 2).

Based on δ¹³C data from La Cerradura (this study), Yorkshire (ref. 25) and China (ref. 18) we calculated a maximal magnitude in the CIE of -4.2‰ (−3.1% on average). A higher CIE, of −5.4‰ is achieved when including δ¹³C data of fossil wood and phytoclasts (Table 3 in the SI). Following the approach of Schubert & Jahren (ref. 25), we determined the magnitude of the CIE in marine substrates (CIEmarine) by using δ¹³C data from oxygenated marine basins only. This includes data from organic matter-lean sediments deposited at the southern part of the West Tethys Shelf. At these areas the seafloor preferentially remained oxygenated throughout the early Toarcian (ref. 34). For such settings organic matter-induced carbonate diagenesis and/or CO₂ recycling in stratified water bodies that may alter the δ¹³C signature can assumed to be minimal or can even be excluded (ref. 30,33). Carbon isotope data from marine organic matter is not included in our calculation, as δ¹³C values can be affected by mixing of organic matter of marine phototrophic and non-phototrophic organisms or land plants (ref. 26). We calculated an average CIEmarine of −2‰ (Table 3 in the SI), which is similar to the −2 to −3‰ estimate by Suan et al. (ref. 40). Using the δ¹³Cmarine based CIEterragenesis and the CIEmarine we calculated a ΔCIE (ΔCIE = CIEterragenesis - CIEmarine) of −1.5 and −2.2‰, for average and maximal values of the CIEterragenesis, respectively. Including δ¹³C data from fossil wood yields a ΔCIE of about −3.4‰.

Calculation of pCO₂ levels prior to the CIE (pCO₂init) and during the climax of the CIE (pCO₂CIE) further requires an estimation for the pre-CIE pCO₂ that here is derived from mass balance calculations in dependency of the CIEmarine and the isotopic signature of the respective carbon source. We calculated ΔpCO₂ values for carbon sources with isotopic signatures characteristic for: i) biogenic methane emissions (δ¹³C: −70‰ (ref. 41)), ii) gas hydrates (δ¹³C: −60‰ (ref. 45)), iii) thermogenic methane (δ¹³C: −35‰ (ref. 45)) and iv) a source dominated by volcanogenic CO₂ (δ¹³C: −10‰ (ref. 42)) (for details see supplementary information).

For an isotopically-light carbon source (−70 to −50‰) and a ΔCIE of −2.2‰ and −3.4‰, we calculated values for pCO₂init ~600 ppmv and of ~400 ppmv, respectively, whereas for pCO₂CIE we obtained 1200 and 850 ppmv, respectively (Fig. 3). Initially low pre-CIE CO₂ estimates will be affected by a maximum uncertainty of about ±350/−100 ppmv, while a high maximum uncertainty of about ±1000/−400 ppmv must be assumed for CO₂ estimates during the CIE (ref. 44). Errors result from uncertainties in the model-curve fit of the experimental data (ref. 36) and from uncertainties in the input parameters used to calculate pCO₂ (Fig. 3). The error range also includes uncertainties arising from unknown paleoenvironmental conditions under which fossil plants grew (ref. 46).

The uncertainty can be assumed to be comparable to those associated with other methods for past pCO₂ reconstruction (ref. 24,25). Isotope-based estimates are close to the stomata-based pCO₂ assessment (ref. 10). However, in contrast to McElwain et al. (ref. 30), our data attest to a doubling in pCO₂ instead of a threefold increase (Fig. 3). Our results strongly suggest that an early Toarcian carbon cycle perturbation was caused by carbon release in form of δ¹³C-enriched methane from a cryosphere collapse or, alternatively, from marine gas hydrates (ref. 17) or wetlands (ref. 17).

With respect to uncertainties in the ΔCIE value and in the δ¹³C-based CO₂ reconstruction, the thermogenic methane release from thermal alteration of organic matter-rich sediments during the Karoo-Ferrar emplacement (ref. 10) would be plausible as well. Such a scenario is, however, not supported by geochemical data (ref. 46). and is further difficult to reconcile with the orbitally-forced cyclic pattern of the CIE that is only explained by carbon release from climate-sensitive reservoirs responding to changes in Earth’s solar orbit (ref. 16). On the contrary, the release of biogenic and thermogenic methane from glacier- and permafrost-capped reservoirs would be a plausible scenario that is supported by recent observations (ref. 41).

Assuming volcanic CO₂ emission as being the major driver of the early Toarcian climate change would require the release of enormous amounts of CO₂ that would have shifted pCO₂ levels from about 1000 ppmv during...
pre-event times to more than 4000 ppmv during the CIE (Fig. 3). Thus, direct volcanic CO₂ emissions fail in explaining both, the magnitude of the CIE and of climate change (Fig. 3). A plausible scenario would be that the emplacement of the Karoo-Ferrar Large Igneous province released small quantities of volcanic CO₂ and eventually some thermogenic methane from Gondwana coals. Both initiated a moderate rise in global temperatures, triggering the release of 12C-enriched carbon from mid-latitudinal climate-sensitive reservoirs. In combination with changes in Earth’s solar orbit this atmospheric carbon increase stimulated a self-sustaining cryosphere demise prograding to higher latitudes and thereby releasing even more cryosphere-stored carbon, a process assumed to be the major driver of the early Toarcian climate and environmental change9. Our results allow us to postulate that the early Toarcian carbon cycle perturbation and associated climate changes were driven primarily by the release of huge quantities of 12C-enriched methane from climate sensitive cryosphere reservoirs.

**Conclusions**

The compound-specific carbon isotope record for land plant-derived long-chain n-alkanes from Iberia provides a robust long-term record of changes in the atmospheric carbon reservoir that occurred in concert with the early Toarcian global warming. The presence of a negative CIE in long-chain n-alkanes that parallels bulk organic and inorganic 13C trends confirms 13C-depletion of the entire exchangeable carbon reservoir, in particular atmospheric 13C-depletion. Based on offsets in the magnitude of the CIE reported in terrigenic and marine substrates, we calculated a doubling in atmospheric CO₂ levels paralleled the carbon cycle perturbation and global warming. Carbon added to the ocean-atmosphere system was strongly enriched in 12C derived from climate-sensitive cryosphere reservoirs. Karoo-Ferrar volcanism may have triggered global warming but volcanic CO₂ emissions fail to explain the magnitude of the carbon cycle perturbation. Accordingly, volcanic CO₂ was only a trigger but not the driver of the early Toarcian climate change, which was caused by successive and self-attenuating cryosphere collapse. Our data suggest that environmental changes that occurred concomitant to the T-CIE were linked to the release of huge amount of cryosphere methane to the Earth’s ocean-atmosphere system.

**Material and Methods**

**Sampling.** Geochemical analysis have been performed at sample material that has been taken at the La Cerradura section after removal of surface rocks that potentially experience alteration due to weathering. All samples have been taken at least 30 cm below surface. Rock samples were crushed and powdered in order to obtain a homogenous and representative sample. Prior to geochemical analysis the powdered sample material was dried in an oven at 40 °C for 48 h.

**Stable carbon isotope analysis of the bulk organic matter and carbonate.** Stable carbon isotope analysis for bulk organic carbon (δ13Corg) were performed on decalcified sample material. Decalcification was achieved by treating the sample material with hydrochloric acid (HCl, 10% and 25%) to remove carbonate-bound and if present dolomite-bound carbon. Afterwards, samples were washed, neutralized with deionized water and dried in an oven at 40 °C for 48 h. Stable carbon isotope analysis was performed using a Thermo Finnigan Delta V isotope ratio mass spectrometer coupled to a Flash EA via a Conflow III interface.

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**Figure 3.** (A) Reconstruction of atmospheric pCO₂ prior to and during the early Toarcian CIE. In dependency of the carbon source and its isotopic signature different and partly contrasting CO₂ scenarios can be proposed. The best fit scenario is achieved for carbon sources enriched in 12C, suggesting that CIE and climate change were driven by carbon injections from cryosphere collapse, or gas hydrates and wetlands17 (low pCO₂ scenario, blue asterisks). Such a scenario agrees with stomata-based pCO₂ estimates10. Contribution from thermogenic methane released from fossil hydrocarbon sources would be plausible as well (moderate pCO₂ scenario, green and red asterisks). On the contrary, scenarios invoking volcanic CO₂ emissions as primary driver of the early Toarcian carbon cycle perturbation are not supported by our data (high pCO₂ scenario, orange and red asterisks). Vertical grey bars indicate uncertainties of pCO₂ determinations. (B) Impact of pCO₂ levels and precipitation rates on the δ13C of land plant biomass (T-J: Triassic-Jurassic boundary; see supplementary information for additional information and references). Latitudinal climate and vegetation gradients cause offsets in δ13C absolute values.
The carbonate fraction was measured for its carbon isotopes using a Kiel III carbonate preparation line connected to a Thermo Fisher 252 mass spectrometer. Powered and homogenized samples were treated with 103% phosphoric acid at 70 °C\(^\circ\). Carbon isotope ratios of the organic matter and the carbonate are expressed in conventional delta notation: \(\delta^{13}C_{\text{sample}}(\%) = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] \times 1000\), where R is the ratio of \(^{13}\text{C} / ^{12}\text{C}\) of the sample and the V-PDB standard for carbon. Reproducibility and accuracy were monitored by replicate standard and sample analysis and are better than 0.1‰.

**Stable carbon isotope analysis of land plant n-alkanes.** Total lipid extracts for selected samples were obtained from solvent extraction using a Soxhlet apparatus. As extraction solvent we used a mixture of dichloromethane (DCM) and methanol (MeOH) (9:1, v/v). Similar to the method applied by Ruesbsam et al. (ref. 48) total bitumen extracts were separated into aliphatic, aromatic and polar hydrocarbon fractions by silica gel-column chromatography (8 ml SPE column, 2.8 g Silica 60 mesh, 25–40 μm) using solvents with increasing polarity in an LCTECH automated SPE system. The aliphatic hydrocarbon fractions were treated with activated copper turnings in order to remove elemental sulfur. GC–MS measurements of the aliphatic hydrocarbon fractions were performed on an Agilent 5975B MSD interfaced to an Agilent 7890 A GC equipped with a quartz capillary (Agilent DB1-HT; 60 m length, 0.25 mm inner diameter, 0.25 μm film thickness). The temperature program of the GC oven used was: 70 °C (5 min isothermal) to 140 °C at 10 °C/min, then to 325 °C at 3 °C/min (held for 7 min). The quadrupole MS was operating in scan mode in the m/z 50 to 750 range. Compounds of interest were identified via characteristic mass spectra and were integrated manually using the GC/MS Masshunter Software (Agilent Technologies)\(^\text{48}\).

Aliphatic hydrocarbon fractions of all samples analyzed are clearly dominated by odd-numbered long-chain n-alkanes (Fig. S1 in the SI), originated in land plants\(^\text{49}\). Cyclic aliphatic hydrocarbons (steroids, hopanoids) are present as well, but occur at very low abundances (acyclic/cyclic > 10; Figs. S1 and S2 in the SI). Moreover, the temperature program of the GC oven was modified to minimize co-elution of the odd-numbered n-alkanes with cyclic aliphatic hydrocarbons (Fig. S2 in the SI). Due to the clear dominance of long-chain n-alkanes and the absence of co-elution with cyclic aliphatic hydrocarbons compound-specific \(^{13}\text{C}\) analysis for the long-chain n-alkanes was performed on untreated aliphatic hydrocarbon fractions, without previous m/e-sieving as commonly applied\(^\text{49}\).

Gas chromatography–isotope ratio mass spectrometry (GC–irMS) was performed following the methodology described in Plet et al. (ref. 48) using a Thermo Scientific Trace GC Ultra interfaced to a Thermo Scientific Delta V Advantage mass spectrometer via a GC isolink and a Conflow IV. The \(^{13}\text{C}\) values of the compounds were determined by integrating the ion currents of masses 44, 45 and 46, and are reported in permil (‰) relative to the VPDB standard. Reported values are the average of at least two analyses with standard deviation of <0.5‰.

**Calculation of pCO\(_2\) levels.** Calculation of pCO\(_2\) levels follows the approach by Schubert & Jahren (ref. 24) and is based on the differences in the magnitude of a CIE reported in land plant organic matter and marine substrates. Assessment of methodical uncertainties is based on the work by Cui and Schubert (ref. 49) and varies as a function of absolute pCO\(_2\) concentration. Details on the calculations are provided in the supplementary information.

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Author contributions

W.R. and L.S. designed the research, carried out the laboratory work, performed analyzes. W.R. and M.R. carried out the field work. M.R. provided biostratigraphic data. All authors contributed to the interpretation of the results, the discussion and manuscript writing.

Competing interests

The authors declare no competing interests.

Additional information

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