Carbon isotopic evidence for rapid methane clathrate release recorded in coals at the terminus of the Late Palaeozoic Ice Age

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The end of the Late Palaeozoic Ice Age (LPIA) ushered in a period of significant change in Earth’s carbon cycle, demonstrated by the widespread occurrence of coals worldwide. In this study, we present stratigraphically constrained organic stable carbon isotope (δ13Corg) data for Early Permian coals (312 vitrain samples) from the Moatize Basin, Mozambique, which record the transition from global icehouse to greenhouse conditions. These coals exhibit a three-stage evolution in atmospheric δ13C from the Artinskian to the Kungurian. Early Kungurian coals effectively record the presence of the short-lived Kungurian Carbon Isotopic Excursion (KCIE), associated with the proposed rapid release of methane clathrates during deglaciation at the terminus of the Late Palaeozoic Ice Age (LPIA), with no observed disruption to peat-forming and terrestrial plant communities.

δ13Corg variations in coals from the Moatize Basin are cyclic in nature on the order of 103–105 years and reflect changes in δ13Corg of ~±1‰ during periods of stable peat accumulation, supporting observations from Palaeozoic coals elsewhere. These cyclic variations express palaeoenvironmental factors constraining peat growth and deposition, associated with changes in base level. This study also demonstrates the effectiveness of vitrain in coal as a geochemical tool for recording global atmospheric change during the Late Palaeozoic.

The end of the Late Palaeozoic Ice Age (LPIA) represents one of the most extreme climate transformations in geological history, transitioning from icehouse to greenhouse conditions 1–3. This global event is critical to understanding changes in the carbon cycle associated with the highest rates of global organic carbon burial (up to 6.5 × 1018 mol/Myr) in the past half billion years 4, and coal formation across the terrestrial lithosphere.

The terminal deglaciation of the LPIA was an irregularly distributed, asynchronous event occurring from the Late Palaeozoic, where polar ice melted due to continental scale warming at high-latitudes over Gondwana 1,5,6. The multiple ice centres of the LPIA across Gondwana are evidenced by widespread glacial deposits in Palaeozoic-aged basins of Australia, Antarctica, South America, Arabia, India and Africa 1,2,7. Recently, growing evidence suggests that the LPIA may have been triggered, and subsequently terminated, by uplift and erosion of the Hercynian Mountains 8.

δ13C data has been increasingly utilised to understand both palaeoclimatic and palaeoenvironmental changes associated with the LPIA 5,6,9–11. Recently, a negative isotopic shift in δ13C was observed in both inorganic and organic carbon sources, in sediments from high and low latitude Palaeozoic basins 11. This δ13C excursion has been proposed as the Kungurian Carbon Isotopic Excursion (KCIE), and hypothesised to record the release of extremely depleted (ca. −35‰) methane clathrates during glacial melting 11.

Despite coal occurrence recording the high rates of carbon burial during this period, high-resolution δ13Corg records of coals deposited during the LPIA have not yet been used to demonstrate changes in the global carbon cycle. The slow accumulation of peat, ~0.9 mm/yr in modern high-latitude settings 12, allows subsequently formed coals to continuously record palaeoclimate and palaeoenvironmental change at high-temporal resolutions.

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This study investigates if the proposed KCIE is evidenced in δ¹³C_{org} of Early Permian coals of the Moatize Basin, Mozambique. These coals were selected for this investigation as they are associated with the final occurrence of widespread glacial deposits, and interbedded with deglacial lacustrine sediments, noted throughout other stratigraphically equivalent basins in Southern Africa.

Samples from core recovered by Vale Moçambique were utilised from available core across eight (8) locations in the Moatize Basin, Tete Province, central Mozambique (Fig. 1A). These cores intersect target stratigraphy for the Vale Moçambique mine, that include thick (>10 m) coal accumulations. Coals occur within both the Permian Matinde and Moatize formations (Fig. 1B), although the thickest accumulation of coals is within the lower Moatize Formation (net coal ~52.9 m). Coals were sampled from the lower Moatize Formation that conformably overlies the glacial sediments of the Vúzi Formation marking local glacial to deglacial transition. The glacial sediments and the lacustrine sediments above the first correlatable coal seam, Sousa Pinto seam, to the base of the Chipanga seam, aided in the correlations between drill cores across the basin, in the absence of better chronostratigraphic markers (e.g., volcanic ash).

Results

The range of δ¹³C_{org} for the coals of the Moatize Formation falls within the typical range of C3 plant organic matter, ranging from an absolute maximum of −20.0‰, to an absolute minimum of −26.9‰. The data were collected across all locations domained by each respective ply within the Bananeiras, Chipanga, and Sousa Pinto seams (Fig. 2A). From observing the range of data within these domains, three distinctive ply-dominated stages are interpreted.

Stage 1 – Initiation of peat accumulation. Stage 1 coals, encapsulate the Sousa Pinto seam (plys SPB, SPM, SPU). The average δ¹³C_{org} value for this stage is −23.5‰ (σ = 0.8‰, n = 75), exhibiting a shift to more positive δ¹³C_{org} with time.

Stage 1, Artinskian coals of the Sousa Pinto seam exhibit variable ranges of δ¹³C_{org}, suggesting some variation in palaeoenvironmental factors controlling low-magnitude (~±1‰) δ¹³C cycling. A weak (~1.5‰) positive shift in δ¹³C_{org} of Stage 1 coals suggests a more long-lived change in atmospheric CO₂ concentrations and δ¹³C. These changes are concurrent with the development of widespread peat deposits, resulting in increased rates of carbon burial coincident with the Artinskian.

Stage 2 – Terminal deglaciation. Stage 2 coals, encapsulate the basal Chipanga seam ply only (BCB). The mean δ¹³C_{org} value for this stage is −24.7‰, with a high standard deviation (σ = 1.5‰, n = 15). Stage 2 coals have the most negative δ¹³C_{org} of all the data domains. A striking, high-magnitude (~3.5‰) negative excursion is observed δ¹³C_{org} in Stage 2, coincident with the base of the Chipanga seam in the early Kungurian. This negative excursion is relatively short-lived compared to smaller-scale δ¹³C_{org} cycles (~±1‰) in Stage 1 coals of the Artinskian, and Stage 3 coals of the Kungurian. The compiled δ¹³C_{org} record from the Moatize Formation coals is time equivalent to other, continuous δ¹³C_{org} records from sediments in both low and high-latitude sediments (Fig. 3), suggesting the observed negative carbon shift may be the globally recorded KCIE.
Figure 2. (A) Compiled data of Moatize Formation coals by ply domain (SPB - Sousa Pinto base, SPM - Sousa Pinto middle, SPU - Sousa Pinto upper, BCB - basal Chipanga, LUCB - lower Chipanga base, LUCT - lower Chipanga top, MCM - middle Chipanga, UCB - Upper Chipanga base, UCT - Upper Chipanga top, BNL - Bananeiras lower, BNU - Bananeiras upper). (B) compiled data of Moatize Formation coals normalised by sample distribution within each ply domain, grey shading highlighting Stage 1/3 $\delta^{13}$C cycling and Stage 2 negative $\delta^{13}$C excursion.

Figure 3. Comparison of geochemical data from other studies$^{5,11,37}$, with this study; grey shading highlighting the proposed Kungurian Carbon Isotopic Excursion (KCIE) interval.
Stage 3 – Cyclic pluvials. Stage 3 coals, encapsulate the lower Chipanga seam, through to the upper Bananeira seams (plys LUCB, LUCT, MCM, UCB, UCT, BNL and BNU). The average $\delta^{13}C$ value for this stage is $-22.6\%$ ($n = 0.6\%$, $n = 222$), and remains stable throughout each ply domain, regardless of seam and age distribution. When the total sample set (excluding statistical outliers, $n = 305$) is normalised for each ply domain, the cyclic variation of $\delta^{13}C_{org}$ within these coals can be observed (Fig. 2B). Mechanisms for these $\delta^{13}C_{org}$ cycles are further discussed below.

Discussion
The Early Permian coals of the Moatize Formation exhibit a three-stage evolution in atmospheric $\delta^{13}C$ from the Artinskian to the Kungurian. In this study, $\delta^{13}C_{org}$ cycles (particularly striking in Stage 3, see Fig. 2B), indicate a $\pm 1\%$ shift in $\delta^{13}C_{org}$ over discrete, regular spacing at normalised depths, from which time intervals may be estimated.

Cyclic variation of $\delta^{13}C_{org}$ in coal at similar scales has been previously observed in high-resolution isotopic studies from Eastern Australia18–20. In these works, the primary control on the distribution of $\delta^{13}C$ cycles within coal is attributed to palaeoenvironmental factors controlling peat accumulation, including water availability, salinity, pH and atmospheric temperature21. However, the timescales over which these cycles occur have not yet been addressed.

The accumulation rates of peat are dependent on both depositional environment, and biological productivity, often genetically linked with peat-forming plant communities22. In the Moatize Formation coals of Stage 3, it is demonstrated that both the plant community, and depositional environment controlling peat accumulation and burial linked with uplift and subsequent erosion of the Hercynian range demonstrate what maybe a more profound and long-lived impact on global climate34. Additionally, the lack of observable effects on land plant communities despite significant carbon cycle perturbation during the KCIE event further supports the resilience of terrestrial flora to the effects of global scale atmospheric perturbation34.

The observed KCIE is equivalent to the duration of a $10^3$–$10^5$ year cycle. The short-lived nature of this isotopic excursion suggests the rapid injection of $^{13}C$-depleted carbon into the atmosphere, rather than any relatively long-lived changes in CO$_2$ concentration. It is possible that this negative carbon isotopic shift is due to the release of methane clathrates (CH$_4$) into the atmosphere during terminal deglaciation. Furthermore, the contribution of deep soil organic carbon (SOC) loss and CH$_4$ from terrestrial permafrost may also have contributed to widespread $\delta^{13}C$ perturbation31.

The timing of this rapid CH$_4$ release is equivalent to the development of euxinic lake deposits across Southern Africa as a result of deglaciation marking the end of the LPIA13–15. The stratigraphic equivalent of these euxinic lacustrine deposits is represented by organic rich black shale separating the Sousa Pinto and Chipanga seams, at variable thickness at each sample location (Fig. 1B).

The accumulation of peat, evidenced by the occurrence of the Sousa Pinto seam during Stage 1, implies that more gradual global scale warming and glacial retreat resulting in base-level rise had initiated in the Artinskian, prior to evidence of any catastrophic CH$_4$ release. Furthermore, atmospheric CH$_4$ injection indicated by the KCIE seems to have little to no observable effect on peat accumulation subsequent to the ultimate terminus of the LPIA, suggesting peat-forming terrestrial ecosystems remained relatively stable during this period.

This estimated time-frame of carbon cycle perturbation during the KCIE is relatively short lived, corresponding to the short residence time of CH$_4$ in the atmosphere30. This brief time-period of potential methane clathrate release, and subsequently rapid oxidation to CO$_2$, is not accompanied by any known mass extinctions, or terrestrial ecosystem catastrophe during the Early Permian33.

These observations suggest that whilst CH$_4$ release may have contributed to enhanced global warming during the terminus of the Late Palaeozoic Ice Age, the proposed effects of continental weathering and organic carbon burial linked with uplift and subsequent erosion of the Hercynian range demonstrate what maybe a more profound, and long-lived impact on global climate6. Additionally, the lack of observable effects on land plant communities despite significant carbon cycle perturbation during the KCIE event further supports the resilience of terrestrial flora to the effects of global scale atmospheric perturbation34.

The authors suggest an understanding of the global carbon cycle across geological time may greatly benefit from further research into $\delta^{13}C_{org}$ from coals.

| Peat Accumulation Rate (mm/yr) | Coal:Peat Compaction Ratio |
|--------------------------------|----------------------------|
|                               | 1:1.2$^{23}$               |
| 0.9$^{23}$                    | 13333                      |
| 1.3$^{24}$                    | 9231                       |
|                               | 1:5.7$^{25}$               |
|                               | 65333                      |
|                               | 43846                      |
|                               | 1:7$^{26}$                 |
|                               | 77777                      |
|                               | 53846                      |
|                               | 1:10$^{27}$                |
|                               | 111111                     |
|                               | 76923                      |

Table 1. Approximation of the duration (yrs) of a single $\delta^{13}C$ cycle observed over ~10 m of coal in Stage 3.
Methods

Samples were taken from plies of the Bananerias (n = 62, average seam thickness = 8.5 m), Chipanga (n = 175, average seam thickness = 31.3 m) and Sousa Pinto (n = 75, average seam thickness = 13.1 m) coal seams (δ13Corg = 312‰). Great care was taken to only sample bright (vitrain) bands from coals, as to minimise δ13Corg variation with coal lithotype or biochemical composition. Vitrains were hand-picked at a millimetre scale to avoid any potential carbonate contamination from mineralised cleats. The typical low taphonomic diversity of peat-forming ecosystems, minimises the likelihood of δ13Corg variation dependent on taxa.

The δ13Corg values were determined in the Stable Isotope Geochemistry Laboratory (SIGL) at the University of Queensland using a stable isotope ratio mass spectrometer (Isoprime), coupled in continuous flow mode with an elemental analyser (Elementar Cube) (EA-CF-IRMS). Calibration was performed by use of two standards, USGS244 (−16.1‰ δ13CPDB) and NAT76H1 (−29.26‰ δ13CPDB), interspersed throughout analytical runs. Each sample was analysed in duplicate, using 50–200 μg of concentrate combusted at 1020 °C in 3.5 mm × 5 mm tin capsules. Any sample with a beam size outside the working range of 1 × 10−9 to 9 × 10−9 Å, or with a δ13Corg result variation between duplicates of >0.4‰, was re-analysed, in accordance with laboratory quality control practices. Final data values were normalised and are reported in ‰ VPDB.

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Nikola Van de Wetering (Vale-UQ Coal Geosciences Program, School of Earth and Environmental Sciences, University of Queensland): substantial contributions to the conception and design of the work, acquisition, analysis, interpretation of data, writing, drafting and revision. Joan S. Esterle (Vale-UQ Coal Geosciences Program, School of Earth and Environmental Sciences, University of Queensland): substantial contributions to the conception and design of the work, interpretation of data, drafting and revision of work. Suzanne D. Golding (School of Earth and Environmental Sciences, University of Queensland): interpretation of data, drafting and revision of work. Sandra Rodrigues (Vale-UQ Coal Geosciences Program, School of Earth and Environmental Sciences, University of Queensland): the acquisition, analysis, interpretation of data, drafting and revision of work. Annette E. Götz (Technische Universität Ilmenau): interpretation of data, drafting and revision of work. The above authors have communicated and agreed on the approval of the submitted manuscript and associated material, and agreed to be personally accountable for the author's own contributions and to ensure that questions related to the accuracy or integrity of any part of the work.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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