

Using the carbon isotopic composition of general phytoplankton biomarkers to understand the role of carbon dioxide in the Late Devonian mass extinction

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The Late Devonian mass extinction, particularly the Frasnian-Famennian (F-F) transition ~372 million years ago, witnessed a major marine ecological crisis that resulted in the loss of 50% of marine genera. This mass extinction coincided with volcanism, extreme temperature change, and loss of oxygen in the oceans, but the initial trigger for this environmental and biological cascade remains debated. The carbon cycle may hold the key to the timing of events and thus help determine the initial trigger, but there is currently a lack of continuous and high-resolution $p\text{CO}_2$ records to constrain the carbon cycle at this time.

Here, we reconstruct high-resolution and continuous $p\text{CO}_2$ levels across the F-F transition by analysing a well-constrained astronomically-tuned section from the Holy Cross Mountains, Poland. Previous studies examining the carbon isotopic composition ($\delta^{13}\text{C}$) of both inorganic and total organic carbon (TOC), as well as individual organic biomarkers, have reported positive carbon isotope excursions during the F-F extinction, suggesting a possible relationship with $p\text{CO}_2$ fluctuations. However, the presence of unresolved complex mixtures (UCMs) in these samples has previously impeded precise $\delta^{13}\text{C}$ measurements of compound-specific biomarker analyses, thereby limiting the accuracy of $p\text{CO}_2$ estimations.

To address this issue, we developed a preparative liquid chromatography (prep-LC) method and molecular sieve to remove UCMs. Using these preparatory steps, we were able to recover clean fractions for $\delta^{13}\text{C}$ analyses of phytane and pristane, degradation products of the omnipresent photoautotroph pigment chlorophyll-a, to reconstruct high-resolution and continuous $p\text{CO}_2$ values. Our findings reveal the relationship between $p\text{CO}_2$ with the broader climate, environmental, and ecological dynamics that shaped the Late Devonian crisis.