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Stable isotopes, trace elements, and tiny fossils: A Multi-Proxy deep dive into the Late Devonian Lower Kellwasser Event in the Appalachian Basin

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The Late Devonian biotic crisis (LDBC) occurred from the Frasnian-Fammenian boundary to the Devonian-Carboniferous boundary and led to sharp reductions in diversity, with up to 35% of benthic marine invertebrate genera going extinct including in the Appalachian Basin (AB) of North America. In the AB, the first pulse of the LDBC is the Lower Kellwasser Event (LKE), expressed as organic-rich black shales of the Pipe Creek Formation. Here, we combine $\delta^{13}C_{org}$ and $\delta^{15}N_{bulk}$, with single-fossil $\delta^{13}C_{org}$ data, trace metal proxies, and microfossil abundance to reconstruct paleoenvironmental and paleoecological conditions before, during, and after the LKE through the Pipe Creek. We document a dramatic ~5‰ drop in bulk $\delta^{13}C_{org}$ at the onset of the LKW at Pipe Creek which is mirrored in $\delta^{15}N_{bulk}$. This is correlated with elevated TOC, Mo and U concentrations, which together indicate an increase in dysoxic/anoxic conditions.This negative excursion is coeval with a significant increase in the absolute abundance of organic-walled microfossils inferred to be planktonic algae. We hypothesize that these coupled records were driven by episodic overturning of the AB, leading to an increase of nutrients such as sub-chemocline phosphorus and dissolved inorganic nitrogen [1]. These increases in limiting nutrients would then have led to an increase in primary productivity in the surface waters while also leading to a depletion in bulk $\delta^{13}C_{org}$ due to the mixing of CO_2 from organic carbon respired at depth [1]. Single-fossil $\delta^{13}C_{org}$ roughly follow the bulk $\delta^{13}C_{org}$ record, as would be expected for a time-averaged signal of short-lived planktonic organisms. We do not see any signal of the commonly identified LKE positive carbon isotope excursion in either fossil or bulk records.

Our work provides a more nuanced view of the LKE in the AB and shows that this extinction did not negatively impact planktonic communities and was thus spatially and ecologically heterogeneous, consistent with bottom water dysoxia and anoxia as a kill mechanism.

[1]Uveges, Benjamin T., et al. "Biogeochemical controls on black shale deposition during the Frasnian-Famennian biotic crisis in the Illinois and Appalachian Basins, USA, inferred from stable isotopes of nitrogen and carbon." *Palaeogeography, Palaeoclimatology, Palaeoecology* 531 (2019): 108787.