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Building a High Resolution Record of Organic-walled Microfossils in Upper Devonian Shales: Paleoenvironmental and Ecological Implications

Phoebe A. Cohen, Williams College

The Late Devonian was a time of highly elevated biodiversity loss, turnover, and ecological restructuring. The largest pulse of Late Devonian extinctions occurs at the Frasnian-Fammenian (F-F) boundary. The causes of the F-F extinctions are poorly understood and remain a topic of some controversy, but it is widely believed that low oxygen conditions played a role. Although an extinction in the marine invertebrate fossil record is well documented, less research has been done to understand the record of organic-walled microfossils (OWMs) both in terms of their diversity and their paleoenvironmental significance in light of data suggesting lowered oxygen levels during these intervals. Organic-walled microfossils (OWMs) are microscopic, close-walled fossils made of recalcitrant organic material (Figs 1). They likely represent structures made by a variety of eukaryotic organisms including algae and animals. Many OWM forms are poorly understood. We often do not know what kinds of organisms made these structures, why they form them, or how preservational processes affects their diversity and abundance in the fossil record. Despite these issues, OWMs are often used to interpret patterns in deep time such as overall biological diversity and marine primary productivity.

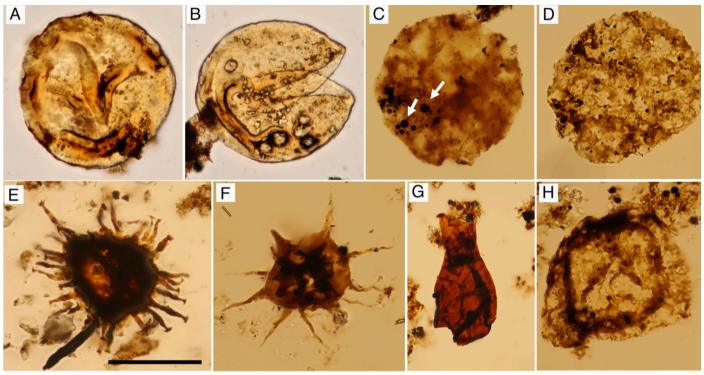


Figure 1. Microphotographs of representative OWM fossils. A) Large smooth leiosphere from WCU-32. B) Large smooth leiosphere with possible excyst- ment structure from WCU-32. C) Rough acritarch from WCL-58 with pyrite framboids (marked by white arrows). D) Rough acritarch from WCU- 87. E) Large acanthomorphic acritarch from BC-5.8. F) Small acanthomorphic acritarch from BC-2.3. G) Chitinozoan from BC-2.3. H) Ptero- morph-type acritarch from BC-2.3. Scale bar in E is A) 70 microns; B) 70 microns; C) 70 microns; D) 100 microns; E) 90 microns; F) 50 microns; G) 180 microns; H) 70 microns. From Kelly et al. in review

We have discovered that organic-walled microfossils are abundant before, during, and after the F-F extinction event in strata exposed in Western New York (Fig 2). These events are captured in organic-rich black shale horizons known as the Kellwasser Events. We have measured the absolute abundance of OWMs in beds below, during, and after the Kellwasser extinction events in five measured stratigraphic sections across Upstate New York (two are shown in Fig. 2). In all localities, the peak in fossil abundance is within the Kellwasser beds, even when accounting for differences in total organic carbon. This suggests that the fossil taxa are responding in some way to the trigger of the mass extinction, potentially low oxygen. The abundance and morphology of OWMs changes on a stratigraphic scale small enough to capture a meaningful signal across the Kellwasser events. In addition, morphological variation is present throughout the events and between sections as well, most notably variation between deeper and shallower water localities in an east-west transect across the state. This work was the senior thesis project of Abby Kelly, who is now a second year graduate student at the University of Cincinnati. Abby has been leading our publication of this work.

This summer we also measured the amount of mercury in all of the samples we have collected across update New York. Mercury (Hg) is emitted by volcanoes during eruptions, and is used as a proxy for volcanism, one of the proposed triggers of the late Devonian extinctions. However, our research shows that Hg enrichments are not significant during the Kellwasser events when scaled to TOC (Fig. 2) indicating that there is another trigger for this extinction interval. This work was led by two undergraduate students at Williams, who participated in the field work, prepped the samples for analysis, and analyzed the results.

The biggest discovery we have made this year has been the ability to measure the carbon isotopic composition of individual OWMs from our sections with collaborator Chris Junium at Syracuse University. In these samples, which span the major extinction events, we have found a consistent offset between the $\delta^{13}C_{org}$ of OWMs and associated bulk organic matter, where the OWMs are $^{13}C$-enriched by an average of 2–6‰ (Fig 3). This is not a taxonomic

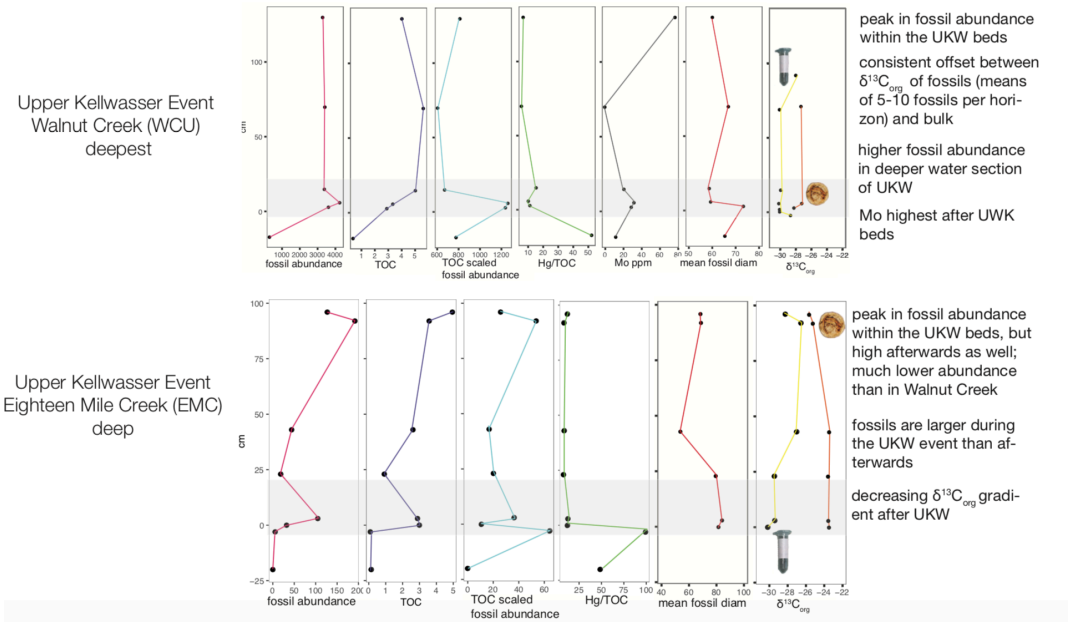


Figure 2. Abundance, TOC, Hg, fossil diameter data, and isotopic data from two stratigraphic sections in Upstate New York

signal because, in this case, all acritarchs are $^{13}$C-enriched regardless of their morphology (Fig 3). Instead, it suggests that all OWMs are sampling a pool of dissolved inorganic carbon with a distinct isotopic signal and are ecologically and metabolically distinct from the organisms that supplied most of the bulk organic matter. While the signal within OWMs is consistent, preliminary data indicate that chitinozoans (thought to be metazoan egg cases) plot in between the bulk and OWMs signal (Fig 3). In addition, within the black shales of the Kellwasser horizons the isotopic difference between microfossils and the bulk organic matter is greater than in the surrounding gray shales. We hypothesize that these differences could be the results of a strong biological pump leading to a large $\delta^{13}C_{org}$ gradient with shallow $^{13}$C-enrichment and $^{13}$C-depetion at depth. If OWMs were assimilating carbon in the surface ocean, they will have an enriched $\delta^{13}C_{org}$ value, whereas chinitozoans, presumably living in deeper waters, would $^{13}$C-depleted. The bulk $\delta^{13}C_{org}$ value would be lighter still because it represents the averaging of the carbon fixed in the entire water column, including lighter carbon from deeper in the water column and biomass produced by processes such as methanotrophy. We hypothesize that this evidence for a strong biological pump could be partially responsible for the frequent episodes of anoxia and dysoxia associated with the end-Devonian extinction. This work was led by senior thesis student Ezekiel King Phillips '18, who is preparing to apply to graduate schools for the fall of 2019 and is working on writing up our results. In addition, I submitted a NSF proposal this fall to continue this work on other time periods. Thus, the ACS PRF grant has enabled me to expand my research and move in new directions.

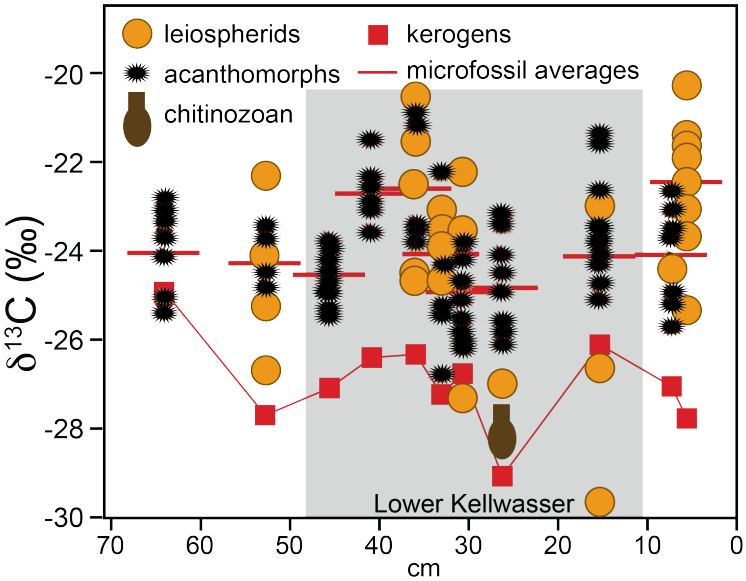


Figure 3. Multi-taxa microfossil and kerogen $\delta^{13}$C data from the Late Devonian, Lower Kellwasser (Pipe Creek Shale) from Cameron, New York. The gray band demarcates the black shale associated with the Lower Kellwasser horizon.