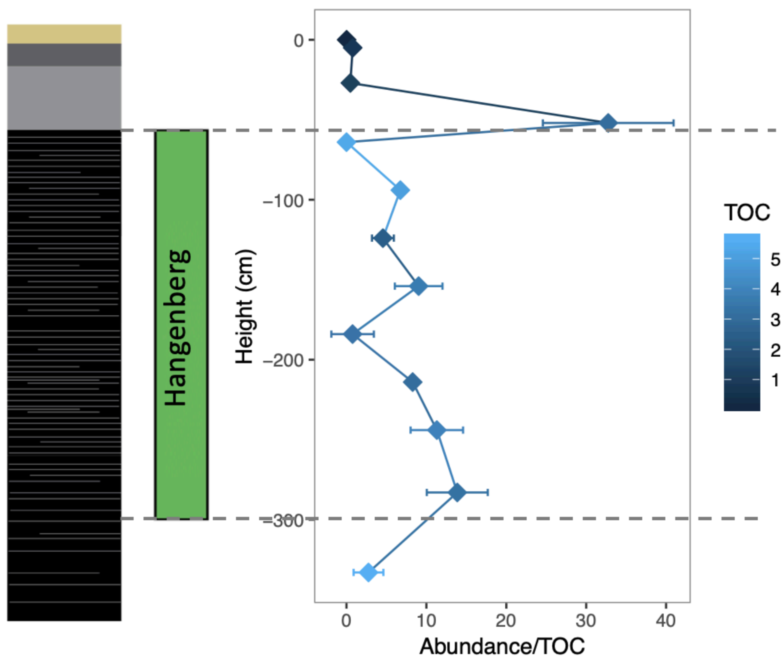
ACS PRF 56967-UR8

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 pulses of Late Devonian extinctions occurs at the Frasnian-Fammenian (F-F) boundary and at an interval known as the Hangenberg event. The causes of both of these extinctions are poorly understood and remain a topic of some controversy, but it is widely believed that low oxygen conditions, possibly driven by volcanism, 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. 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. Our project has sought to answer many of these unknowns by examining the OWM record in detail - including looking at morphology, taxonomy, and geochemistry – through the late Devonian extinctions. This year, our work mainly focused on the latest extinction interval, the Hangenberg event.

The Hangenberg event is one of the major pulses of extinction associated with the late Devonian mass extinction. This global crisis devastated entire ecosystems and represents a major turning point in the evolution of many faunal groups. Multiple triggers of the event have been proposed, among them periodic or sustained anoxic conditions, volcanism leading to ocean acidification and/or hypercapnia, wildfires, perturbations of the carbon cycle, eustatic sea level changes, or some combination of these causes.

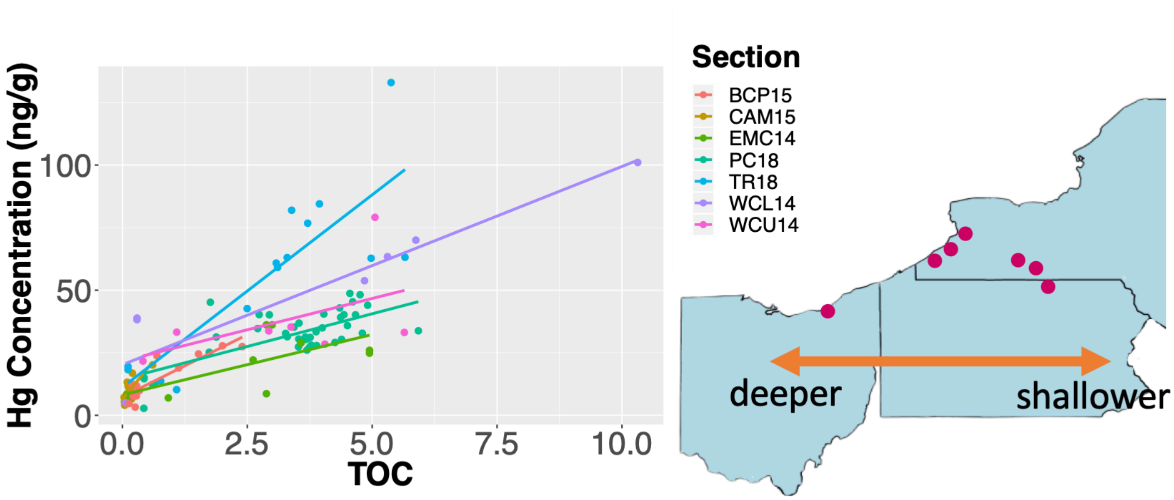


OWM abundance scaled to TOC through the Hangenberg Event in NE OH showing low abundance followed by a peak right after the extinction interval.

The Hangenberg event is primarily associated with the Hangenberg Black Shale in Europe, though correlating black shale horizons have been found globally. The palynological record of the Hangenberg crisis has been used by researchers in Poland's Holy Cross Mountains to decipher local causes of extinction, but little palynological study of the Hangenberg event has been done outside of Europe. We analyzed the microfossil record in a section of the Cleveland Shale in northeastern Ohio that captures the Hangenberg event. We looked at acritarch and miospore abundance and diversity throughout the end of the Hangenberg event, as well as geochemical analysis of mercury (Hg) records in this section, which is used as a potential proxy for volcanic activity. In our work, both Hg and fossil abundance are normalized to total organic carbon (TOC) to account for preservation biases.

The presence of miospore index species *Retispora lepidophyta* and *Verrucosisporites nitidus*, as well as the overall assemblage composition, correlates our section of the Cleveland Shale with the Hangenberg Black Shale and the Western European miospore zone LN. In particular, *R. lepidophyta* is uncommon but present in upper Cleveland shale layers and the Hangenberg Black Shale, but rises to dominance in samples taken from just above the black shale in both Poland and Ohio. This correlation of palynological records in the Cleveland Shale with the Hangenberg Black Shale shows consistency of miospore response to the cause or causes of the Hangenberg event.

Microfossil abundance varies throughout the studied section, culminating in a complete lack of microfossils at the top of the Cleveland Shale. Acritarch and miospore abundances generally parallel one another, though miospores are more abundant than acritarchs in our youngest samples, possibly due to regression and decreased water depth. We see no clear association between Hg and fossil abundance in the Cleveland Shale. Additionally, there are no Hg/TOC spikes that might represent volcanism during the Hangenberg event, a trend that continues at sites in nearby Western New York. We instead suggest that changes in oxygen and redox cycling, or local conditions like water depth and sea level change, are more likely causes of the Hangenberg event.



Hg vs TOC cross plot for 7 stratigraphic sections through the late Devonian across the Appalachian Basin, shown on the map at right. Note the relatively strong linear relationship, which potentially indicates a lack of support for a major volcanic event.

In addition to our work on the Hangenberg, we are continuing to analyze Hg data for all of the late Devonian extinction intervals in order to better determine potential triggers for this mass extinction. To do this, we are analyzing sulfur via our in-house elemental analyzer and sending samples off for trace metal analyses in order to learn more about the Hg system and figure out if the Hg measurements we have made could be entirely driven by redox variability, or could be due at least in part to volcanism.

Finally, we continue to synthesize all of the OWM data we have collected over the last three years – morphology, taxonomy, fossil abundance, fossil carbon isotope values, mercury data, and more – to create a more detailed and comprehensive picture of the paleoecology and paleoenvironmental conditions of the late Devonian extinctions.