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Project Title: A Chemostratigraphic Study of Regional and Global Controls on Deposition and Preservation of Late Cambrian Shales of the Conasauga Formation

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Black shales in the geologic record are significant sinks of organic carbon, and the source rocks for most oil and gas resources. Because preservation of organic carbon requires low-oxygen conditions at the time of deposition, the occurrence of widespread deposition of black shale facies in the geologic past has been linked to global marine anoxia events [1]. One possible such event is the Upper Cambrian Steptoean Positive Carbon Isotope Excursion, or SPICE [2]. The SPICE event initiated rapidly and persisted for about 4 Myr. It is associated with a large (4-6‰) increase in $\delta^{13}\text{C}_{\text{carb}}$, as well as positive $\delta^{34}\text{S}$ and negative $\delta^{238}\text{U}$ excursions, and is bookended by episodes of biological turnover [2-4]. The event may have contributed to dramatic increases in atmospheric pO_2 [5], and concomitant changes in ocean chemistry that have been recorded in upper Cambrian platform carbonates in other parts of the world [4]. With the support of ACS-PRF, we carried out an investigation of the Late Cambrian Conasauga group of the Central Appalachian Basin, portions of which have been recent targets of hydrocarbon exploration, and which previous work has shown was deposited during the SPICE event [6]. We investigated core material of shale and adjacent carbonates deposited on the Laurentian continental shelf to establish a baseline chemostratigraphy of the Upper Cambrian Conasauga Group in southeastern Ohio. At the time of deposition, this location was on the continental shelf inboard of a major structural feature consisting of a series of steep normal faults forming an extensive basin known as the Rome Trough. This study integrated stratigraphy, $\delta^{13}\text{C}_{\text{carb}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ with trace element data to establish a chemostratigraphy of the Upper Cambrian Conasauga Group, in the Central Appalachian region prior to and during SPICE.

The Ohio Geological Survey provided core material from an exploratory well (API# 3414560141) in Scioto County, Ohio (38.59, -82.82). The cored interval provides a continuous section that contains the Upper Cambrian SPICE based on its correlation with other coeval rock units deposited on the Laurentia passive margin (Fig. 1) [6-8]. A selective leaching method was used to obtain the carbonate-hosted trace element concentrations [9]. This method extracts both biogenic and cement carbonate, but minimizes the contribution from silicate components of the sample. Whole rock and leachate samples were analyzed by Activation Laboratories Ltd. Powdered samples were digested using sodium peroxide fusions (precluding Na_2O and LOI analysis) and analyzed by ICP-MS. To determine mineralogy, powdered samples were homogenized with ~10% by weight ZnO standard, back-loaded into a powder mount, and analyzed on a PANalytical X'Pert Pro diffractometer using Cu $K\alpha$ radiation. Total clay content was inferred qualitatively by comparing thin sections, hand specimens and diffraction patterns of powdered samples.

Aliquots of powdered, bulk carbonate samples were analyzed at the University of California, Davis, Stable Isotope Laboratory for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopic composition. All strontium preparation was performed in a clean lab under a HEPA filtered hood, following the procedure of Wall et al. [10]. Samples were analyzed on Thermo Scientific Neptune Plus® double-focusing MC-ICP-MS at the University of Pittsburgh. NIST SRM 987 was measured repeatedly throughout the sample analyses, and all $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are normalized to a SRM 987 value of 0.710240, and corrected for ^{87}Rb decay to 497 Ma based on the measured Rb/Sr.

The sample interval shows a $\delta^{13}\text{C}_{\text{carb}}$ excursion (Fig. 2) comparable in magnitude to those in other Cambrian age correlative sections around the globe [e.g., 2, 3]. The $\delta^{13}\text{C}_{\text{carb}}$ excursion measured in this study seems to be relatively unaffected by diagenetic alteration, having a continuous positive progression in both biogenic carbonate and matrix cement components. Despite individual sample scatter, the positive $\delta^{13}\text{C}_{\text{carb}}$ values persist through siliciclastic-dominant subtidal, peritidal and finally supratidal facies. In addition, the values measured in the study section conform well to

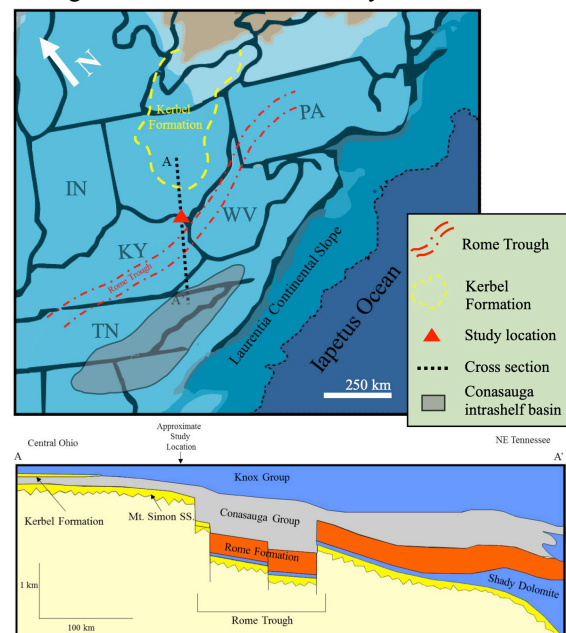


Figure 1. Top: Reconstructed Late Cambrian carbonate platform of Eastern Laurentia, modified from [7]. Bottom: Cross section of across A-A', modified from [8].

$\delta^{13}\text{C}_{\text{carb}}$ values measured in the Conasauga Group ~200 miles south, on the other side of the Rome Trough [6]. We interpret the positive $\delta^{13}\text{C}_{\text{carb}}$ trend in our data set as the result of a global trend of increased organic carbon burial and preservation. In the carbonate facies, the $^{87}\text{Sr}/^{86}\text{Sr}$ of acetic acid-leachable minerals (*i.e.*, calcite, dolomite) tracks reasonably well with expected Cambrian seawater values [11] (Fig. 2). However, the ratios diverge significantly within the clastic material of the Nolichucky Formation, which likely reflects diagenetic leaching of Sr from the clastic portion and subsequent incorporation in carbonate cement. This is consistent with the rare earth element (REE) data, which show that carbonate cement extracted from the Nolichucky Formation has significantly different REE patterns than carbonate from limestone.

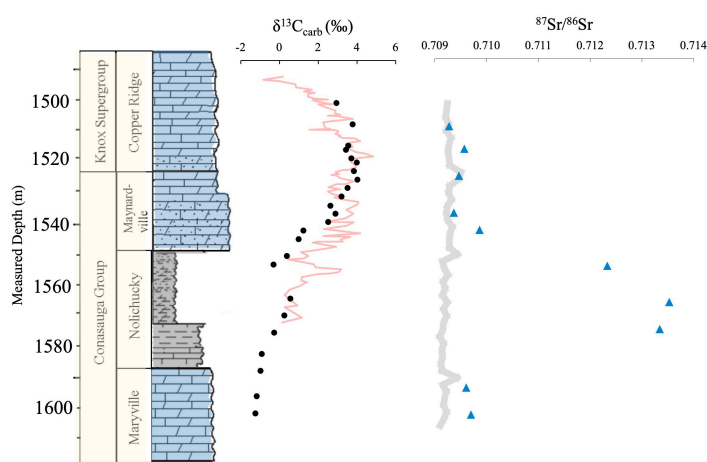


Figure 2. $\delta^{13}\text{C}$ values of the study samples (black circles) plotted with depth-adjusted values of [6] in red. Blue triangles are age corrected $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios measured in leached carbonate of our sample set. Gray line is depth-adjusted Late Cambrian seawater [11].

The correlation of dual authigenic enrichments of U and Fe within shales of the Nolichucky Formation strongly suggests the presence of an anoxic water column prior to the onset of the SPICE at the study site. This was followed by a relative sea level fall and a shift to a more oxic depositional environment. A decrease in carbonate-hosted U concentrations starting in the Nolichucky Formation and up through the overlying Maynardville and Copper Ridge Formations contemporaneous with the SPICE could indicate a drawdown in soluble trace metals in response to extensive black shale deposition. While the Nolichucky Shale in this section has low TOC content (<0.5%) and Mo (<3 ppm), decreasing trace element concentrations (Ni and V) in the leached carbonate portion could point to a regional drawdown of trace nutrients resulting from euxinic conditions conducive to black shale deposition deeper in the Rome Trough and the adjacent Conasauga intrashelf basin.

The work reported here constituted the bulk of the Masters thesis for Mr. Justin Mackey [12], who is currently a Research Fellow at the DOE National Energy Technology Laboratory. The funding for this project also partially supported three other graduate students who contributed to this project: one received a Masters degree [13] and currently works at Vanderbilt University; another received a Masters degree [14] and currently works for the U.S. Army Corps of Engineers; and a third is completing his Ph.D. at the University of Pittsburgh. A manuscript based on Mr. Mackey's work on this project has gone through review and is currently awaiting a final decision [15]. Funding from PRF also helped support eight undergraduate research assistants (six of whom have graduated with a B.S. degree in Geology) who assisted with the lab work on this project.

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