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Assessing the Role of Nitrogen Cycling on Black Shale Formation
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Summary: This study aims to constrain the role of nitrogen cycling and post-depositional alteration on organic carbon preservation and burial in two contrasting settings, marginal vs. distal of the Western Interior Seaway with differing thermal histories, by studying the stable carbon and nitrogen isotope composition of porphyrins (the degradation products of algal pigments). While the processes leading to black shale formation have been studied for decades, the role of oxygen-depletion and marine productivity on organic carbon accumulation and preservation remain highly debated. This is largely due to the fact that our understanding of how nutrient cycling controls these two processes is rather poor because of the scarcity of geochemical tools that can trace changes in nitrogen cycling at a fine scale. Results from this project will allow us to reconcile current discrepancies regarding the processes controlling black shale formation and the long-term cycling of carbon and nitrogen in sedimentary systems.

Progress of the research: A total of 87 samples from the SH-1 core, collected in 2014 near Grand Staircase – Escalante National Monument, and covering the Cenomanian-Turonian boundary (~94 Ma; OAE2), were prepared for elemental (calcium carbonate, total organic carbon, total nitrogen) and stable isotope ($\delta^{13}N$ and $\delta^{15}N$) analysis (Fig. 1). Samples were decalcified using 10% HCl, then rinsed and neutralized with deionized water, and later dried at 50°C for 4 days. Calcium carbonate was calculated by weight difference before and after decalcification. Samples were analyzed via a Thermo Elemental Analyzer - Isotope Ratio Mass Spectrometer (EA-IRMS) in the CU Boulder Earth Systems Stable Isotope Lab. Before analysis, our team tested the EA-IRMS response to varying sample sizes and C/N ratios. Additionally, we have also analyzed 90 samples from the GC-3 core (Texas) for carbon isotope analysis of bulk carbonate. About half of the GC-3 core samples will also be prepared and analyzed for $\delta^{15}N$.
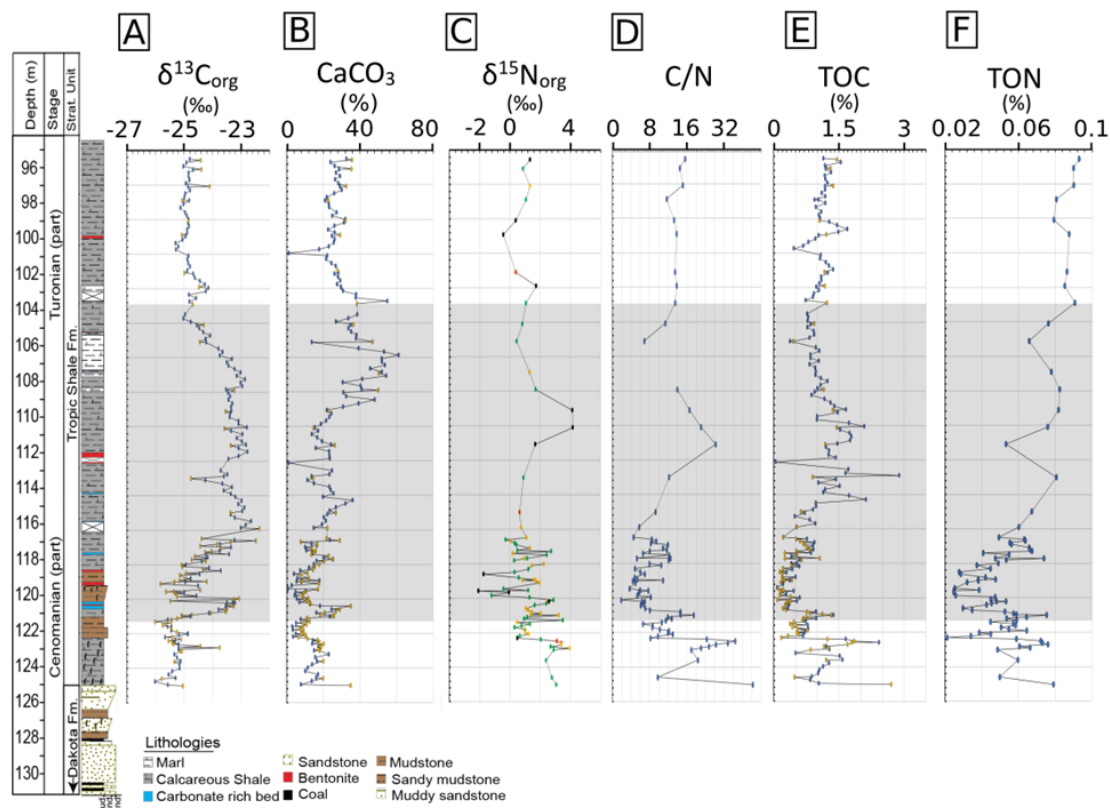

Figure 1: Elemental and stable isotope data from the SH1 core. The stratigraphic column is adapted from Jones et al. (2019). (A) $\delta^{13}Corg$; (B) CaCO3%; (C) $\delta^{15}Norg$; (D) C/N ratio; (E) TOC%; (F) TON%. OAE2 interval is indicated by the gray shaded region. Records include data from Jones et al. (2019; blue symbols) and this study (orange symbols).

Furthermore, our team established the analytical method for the analysis of porphyrins by high performance liquid chromatography – mass spectrometry (HPLC-MS) (Fig. 2). So far, we have been confirmed the present and quantified the abundance of porphyrins in 35 samples from core SH1. Additionally, we plan to analyze porphyrins in 13 samples from the GC-3 core.
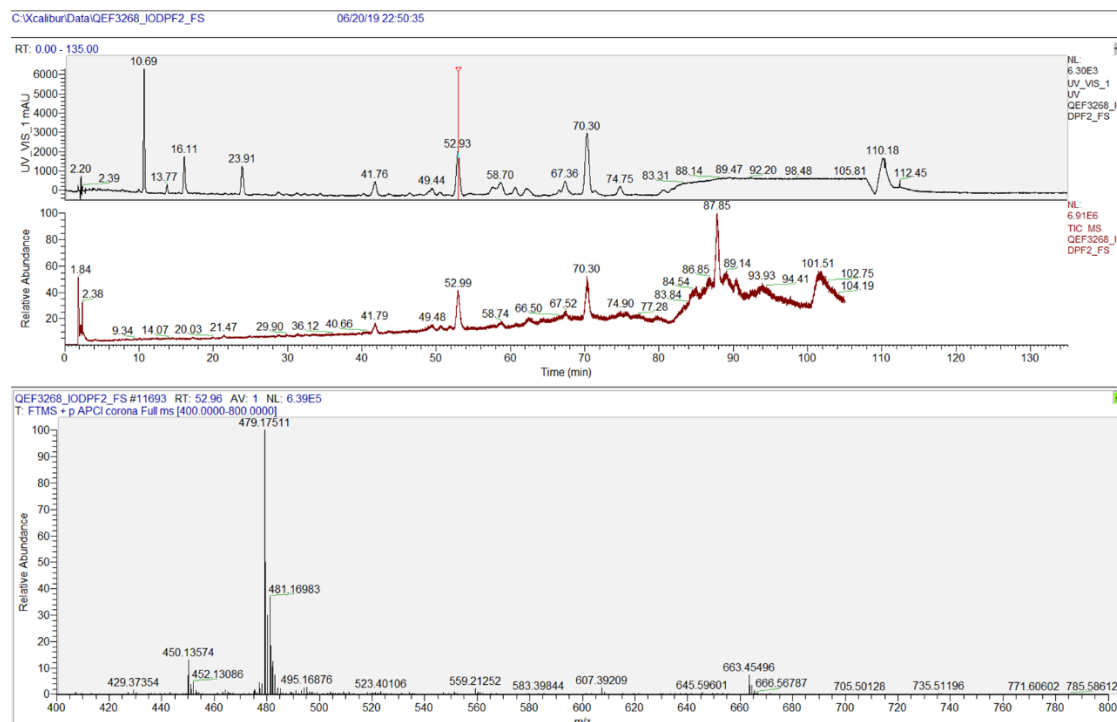

Figure 2: UV chromatogram of an SH1 sample (top), Mass Spectra of peak at 52.93 minutes showing spectra for nickel ETIO porphyrin (bottom).

Impact of the research on the PI's career and that of students: This grant has funded the PhD work of a graduate student who is currently on track to complete his dissertation in summer 2020. Additionally, this grant also supported the honors thesis of a GEOL major at CU Boulder who graduated in Spring 2019, and who presented results of his research in a poster at the American Geophysical Union Fall Meeting in December 2018. The PI has benefited from the establishment of the analytical method for porphyrin analysis in his own laboratory. Our team has made significant progress towards the isolation of porphyrins using preparatory HPLC for subsequent compound-specific stable isotope analysis. This work will be performed at Penn State University in collaboration with Prof. Kate Freeman, which is allowing the PI and his group to expand their analytical expertise and their network of collaborators. Finally, the PI and his group have strengthened their collaboration with Prof. Katie Snell and the CU Boulder Earth Systems Stable Isotope Lab at CU Boulder that she directs.