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GEOCHEMICAL ANALYSIS OF THE MIDDLE TO UPPER DEVONIAN ANTRIM SHALE, KROCKER 1-17 CORE, MICHIGAN BASIN

MIKAYLA C. GIEHLER, Macalester College Project Advisor: Kelly R. MacGregor

INTRODUCTION

The Middle to Upper Devonian is distinguished by global biotic events attributed to marine anoxia (black shale) and perturbations in the carbon cycle (Becker et al. 2020). While previous studies had documented these events in the North American Appalachian Basin (see House, 2002), less attention has been directed toward discerning analogous global events within the neighboring Michigan Basin. This investigation aims to reconstruct the paleoredox conditions and organic matter production and preservation within the Antrim Shale from the Krocker 1-17 drill core located in the north-central Michigan Basin. Since black shale organic matter is derived from a combination of marine and terrestrial sources, this study utilizes elemental proxies for sedimentation and paleoredox to distinguish terrestrial organic matter input to the basin from primary marine organic matter accumulation.

METHODS

This study focuses on the Krocker 1-17 core (core location and detailed geologic setting provided in Zambito and Voice, this volume). Core measurements and detailed lithological observations were made at the Michigan Geological Repository for Research and Education (MGRRE). A Dremel equipped with a diamond-tipped drill bit (model 7123) was used to cleanse the exterior of the core (to mitigate potential contamination introduced during the coring process). A total of 96 powdered samples from the Krocker 1-17 core were collected (~3 to 4 ft. apart) using a Dremel tool with a tungsten carbide drill bit (model 9906).

Portable x-ray fluorescence (pXRF) analysis was

conducted at the Beloit College Department of Geology to discern the elemental composition of the samples obtained from both cores utilizing the Thermo Fisher Scientific Niton XL3t GOLDD+ Handheld XRF Analyzer (see methods in Zambito et al. 2016). Uranium (U), molybdenum (Mo), silicon (Si), and aluminum (Al) were collected by pXRF analysis. Borehole log data including total gamma, potassium (K) and thorium (Th) spectral gamma, as well as Total Organic Carbon (TOC) were provided by MGRRE. U and Mo are used as paleoredox proxies given their tendency to attach to organic matter, which is preserved under low oxygen conditions (Tribovillard et al. 2006). The Si/Al ratio is used as a proxy for detrital sediment input to the study area, with higher values indicating increased quartz influx (Sageman et al. 2003).

RESULTS AND DISCUSSION

As shown in Figure 1, total gamma, U, TOC, and Mo show consistent patterns through the Antrim Shale. For all of these profiles, higher values are observed in the Norwood and Lachine members of the Antrim Shale, while lower values occur in the Paxton Member. In contrast, both K and Th are relatively consistent through the Antrim Shale. The profile of Si/ Al shows elevated values in the Norwood Member and consistently low values in the Paxton, similar to the gamma log and concentrations of U, TOC, and Mo; however, whereas the gamma log and concentrations of U, TOC, and Mo all show decreasing trends through the Lachine Member, the Si/Al trend shows an increase. The values of Mo observed, which range well above 200 ppm in the Norwood Member, suggest anoxic conditions on the seafloor (Tribovillard et al.



Figure 1. Well logs and geochemical results from the Krocker 1-17 core.

2006).

The similarity of the gamma log and concentrations of U, TOC, and Mo indicate that the gamma log pattern is related to the natural radioactivity of U, and not K and Th in this succession. Correspondence of the concentrations of U, TOC, and Mo is interpreted to suggest that the U and Mo are preserved attached to organic matter (see Tribovillard et al. 2006). The elevated value of Si/Al in the Norwood, which corresponds to elevated TOC values, and slight decrease in values of K when Si/Al is highest is interpreted to represent an interval of high productivity and silica accumulation via the skeletons of radiolarians rather than sediment influx to the basin; indeed, radiolarians are known from this stratigraphic interval (Gutschick and Sandberg, 1991). The increasing trend observed in Si/Al through the Lachine Member coincident with decreasing TOC values may indicate that marine organic matter accumulation is being diluted through this part of the succession due to increased detrital sediment input, though it is unclear if terrestrial organic matter is fluxing to the basin with the detrital sediment. Future analysis of this core will

include organic carbon isotopic analysis to analyze sources of organic matter within the basin.

CONCLUSIONS

This study demonstrated that in the Michigan Basin, organic matter preservation is closely associated with anoxic sea floor conditions and because of seafloor geochemical conditions, U and Mo patterns are closely associated with that of TOC. The data set presented herein suggests that most organic matter in the Antrim Shale was likely derived from marine sources, but further isotopic work is necessary to confirm this.

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REFERENCES

Becker, R. T., Marshall, J. E. A., Da Silva, A.-C.,
Agterberg, F. P., Gradstein, F. M., and Ogg, J.
G., (2020) The Devonian Period. In Gradstein,
F. M., Ogg, J. G., Schmitz, M. D., and Ogg, G.
M. (Eds.) Geologic Time Scale 2020. Elsevier, p. 733-810

Gutschick, R. C., & Sandberg, C. A. (1991). Upper Devonian biostratigraphy of Michigan Basin. In Catacosinos, P. A. and Daniels, P. A., Jr. (Eds.), Early Sedimentary Evolution of the Michigan Basin, Geological Society of America Special Paper, 256:155–180. https://doi.org/10.1130/ spe256-p155

House, M.R. (2002) Strength, timing, setting and cause of mid-Paleozoic extinctions. Palaeogeography, Palaeoclimatology, Palaeoecology, 181(1-3):5-25 https://doi. org/10.1016/S0031-0182(01)00471-0

Sageman, B. B., Murphy, A. E., Werne, J. P., Ver Straeten, C. A., Hollander, D. J., & Lyons, T. W. (2003). A tale of shales: The relative roles of production, decomposition, and dilution in the accumulation of organic-rich strata, Middle-Upper Devonian, Appalachian Basin. Chemical Geology, 195(1–4), 229–273. https://doi. org/10.1016/s0009-2541(02)00397-2

Tribovillard, N., Algeo, T.J., Lyons, T., and Riboulleau, A. (2006) Trace metals as paleoredox and paleoproductivity proxies: An update. Chemical Geology, 232(1–2), 12-32 https://doi. org/10.1016/j.chemgeo.2006.02.012

Zambito IV, J.J., and Voice, P.J., this volume, Integrated stratigraphic and paleoenvironmental study of the Middle-Late Devonian carbonate to black shale transition in the Michigan Basin.

Zambito, J.J., McLaughlin, P.I., Haas, L.D., Stewart, E.K., Hurth, M.J., and Bremmer, S.E., 2016b, Sampling Methodologies and Data Analysis Techniques for Geologic Materials Using Portable X-Ray Fluorescence (pXRF) Elemental Analysis: Wisconsin Geological and Natural History Survey, Open-File Report WOFR2016-02, 5 appendices, 12 p.