Introduction

Cyclic Sedimentation of Appalachian Devonian and Midcontinent Pennsylvanian Black Shales: Analysis of Ancient Marine Anoxic Systems

Ancient organic-rich mudstones (black shales) are the most important type of source rock for oil and gas. Black shales are, however, highly variable in their lithologic and geochemical character and in the environmental controls responsible for their formation. Although water-column stratification and bottomwater oxygen depletion are features common to most environments favoring accumulation of organic sediments, other parameters that are more poorly constrained and intrinsically variable, e.g., primary productivity rates, watermass circulation patterns, and terrigenous clastic and organic matter fluxes, also significantly influence the potential economic value of an organic-rich deposit. Determination of the roles of these factors in the formation of a given black shale requires detailed stratigraphic, petrographic, and geochemical analysis.

A fundamental problem in the analysis of black shales is that compositional variation exists at stratigraphic length scales ranging from mm-thick laminae to the thickness of the entire formation. Because geochemical analysis of fine-scale variation over long stratigraphic intervals is prohibitively costly, a sampling strategy must be designed that yields the maximum information for a given level of analytical effort. Our research program on black shales has utilized an innovative approach based on whole-core X-radiography combined with hierachical sampling of short core intervals for detailed petrographic and geochemical analysis (Fig. 1). Major advantages of an Xradiography-based approach are (1) patterns of compositional variation can be "previewed" prior to sampling, permitting sample collection to be targeted at representative stratigraphic intervals, (2) environmental controls are more likely to be successfully isolated when compositional analysis is undertaken on closely-spaced samples than on widely-spaced ones, which are more likely to have recorded changes in multiple environmental parameters, and (3) X-radiograph gray-scale densities (GSD) provide high-resolution data series for time series analysis, facilitating analysis of cyclicity in black shales at both fine (mm) and coarse (m) length scales (Fig. 2). These methodological advances have, in turn, permitted an improved understanding of the depositional conditions under which black shales form.

In this combined field and core workshop, we will examine patterns of compositional variation in Paleozoic black shales. On the fieldtrip, we will visit exposures of the Upper Devonian Ohio Shale and the Lower Mississippian Sunbury Shale. Patterns of compositional variation in these black shales will be compared with those in gray shales and siltstones of the Mississippian Borden Formation and the Lower Pennsylvanian Breathitt Formation. In the core workshop, we will focus on compositional cyclicity in black shales of the Cleveland Member of the Ohio Shale from Kentucky and Ohio and of Upper Pennsylvanian core shales (Hushpuckney, Stark, and Muncie Creek) of Midcontinent cyclothems from Kansas. Although both sets of shales exhibit dm-scale cyclicity, these Devonian and Pennsylvanian units differ in other significant respects, e.g., formation thickness (5-30 m vs. <1 m), organic matter types (marine- vs. terrestrial-dominated), and authigenic component abundances (e.g., low vs. high phosphate), and these dissimilarities in character imply

differences in depositional mechanisms (rapid vs. slow sedimentation; clastic vs. organic dilution processes).

The characteristics of these shales are described in four papers. The two contributions by Jaminski et al. reconstruct environmental conditions within the Upper Devonian Cleveland Member of the Ohio Shale. The first paper considers patterns of dm-scale compositional cyclicity, and the second paper examines broad regional and stratigraphic trends in shale geochemistry. The two contributions by Algeo et al. reconstruct environmental conditions within Upper Pennsylvanian core black shales of Midcontinent cyclothems. The first paper provides a complete description of the X-radiography-based methodology of compositional analysis that forms the basis of our research program on ancient marine anoxic systems, and the second paper analyzes environmental controls on organic matter accumulation and authigenic phosphate precipitation in the study units.

Our research program on ancient anoxic marine systems would not have been possible without contributions from many individuals, whom we would like to acknowledge herein. In particular, we would like to thank James Hower of the Center for Applied Energy Research for assistance with organic petrography, Lisa Pratt of Indiana University for access to LECO and mass spectrometer facilities, Darrell Taulbee, Mark Thompson, Julie Primack, and Volker Brüchert for analytical assistance, and Lisa Trump for drafting. We also would like to thank Tom Robl and the Center for Applied Energy Research for loan of the KEP-2 and KEP-3 cores, Scott Brockman and the Ohio Geological Survey for loan of the OHRS-5 and OHDW-1 cores, and Lynn Watney and the Kansas Geological Survey for loan of a set of nine cores containing Pennsylvanian core black shales. A number of colleagues have provided helpful discussions of work in progress, including Thomas Anderson, Philip Heckel, Timothy Lyons, James Ogg, Lisa Pratt, Brad Sageman, and Arndt Schimmelmann. Additional insights on marine anoxic systems have been gained through related research projects by graduate students at the University of Cincinnati, including Adam Woods, Steven Lev, Patrick Mickler, Michael Cherny, William Hartwell, Thomas Kuhn, Erika Elswick, Rick Schultz, and Mike Lewan.

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FIGURE CAPTIONS

- FIG. 1. Hierarchical sampling strategy for the Upper Devonian Cleveland Member of the Ohio Shale. (A) Lateral variation in shale composition was investigated through analysis of four cores along a ca. 210-km-long transect from northern Kentucky to central Ohio. (B) Stratigraphic variation at the scale of the entire 15-20-m-thick formation was examined via whole-core X-radiography. (C) Fine-scale stratigraphic variation was studied in detail for several short (15-20-cm-thick) intervals using multiple analytical techniques (Fig. 2).
- FIG. 2. Methodological flowchart for analysis of compositional characteristics of study units. Step 1: patterns of compositional variation (e.g., dm-scale cycles) were identified using wholecore X-radiography; image analysis allowed conversion of X-radiograph images to digital data series for subsequent time series analysis. Step 2: in each study core, several representative short (15-20-cm-thick) stratigraphic intervals were chosen for detailed geochemical and petrographic analysis, including C and S elemental concentrations (Leco), major- and trace-element concentrations (XRF), DOP (chromium reduction), clay mineralogy (XRD), organic petrography, and S isotopes. Step 3: identification of depositional processes and cycle forcing mechanisms was carried out through stastical analysis of geochemical and petrographic data and time series analysis of X-radiograph grayscale records.



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