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BLACK SHALE STUDIES IN KENTUCKY

Quarterly Report

September 1978

Work Performed Under Contract No. EY-76-C-05-5202

✓ University of Kentucky
Research Group

355 4000

✓ Lexington, Kentucky

and

Kentucky Geological Survey
Lexington, Kentucky

950 1453

MASTER

U. S. DEPARTMENT OF ENERGY

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BLACK SHALE STUDIES
IN KENTUCKY

QUARTERLY REPORT

SEPTEMBER, 1978

EY-76-C-05-5202

UNIVERSITY OF KENTUCKY
RESEARCH GROUP

DEPARTMENT OF GEOLOGY
KENTUCKY GEOLOGICAL SURVEY

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1.0 Work Package 2300 - Geochemical Characterization

1.1 2300-1 Mineralogic Analyses

- 1.1.2 Bulk mineralogic analyses and data reductions have been completed for the Cincinnati Arch outcrop belt in Kentucky. This data is included in this report (Table 2) and has been encoded and submitted to the EGSP data bank.

Mineralogic analyses have been completed for the Pine Mountain Core described by Michael Miller of the Stratigraphic group. The results of this study are being drafted at this time and will be included in the 1978 Annual Report.

During this quarter, detailed clay mineral studies on the set of outcrop sections measured in detail by the stratigraphic group. This work should be completed by the end of January, 1979 and will be the last unit of data necessary for development of a depositional model for the Devonian black shale in the Appalachian basin.

1.2 2300-2 Elemental Analyses

- 1.2.2 Emission Spectrographic and x-ray fluorescent spectrometric measurements have been completed for all the measured sections in the Appalachian basin in Kentucky. This data is now being drafted for inclusion in the Annual Report for 1978. The data will be presented as geochemical logs and submitted as a milestone deliverable. Data will also be submitted to the EGSP data bank.

We have accumulated a large amount of spectrochemical data, particularly for outcrop sections. The analytic precision has so far been assumed to be the same as for the spectrochemical measurement of other materials, however, this assumption should be tested. Eight replicates of the same black shale sample have been run an introduction to a study of analytic and geologic variance. The elements and their coefficients of variation (C) in this initial work are.

<u>Element</u>	<u>C</u>
B	9.9%
P	11.5
Cu	12.9
Pb	7.0
Cr	13.8
Ga	11.7
Mo	14.4
V	14.6
Co	19.3
Ni	12.8
Zr	15.4

More replicate determinations are planned to provide information on analytic variance for the methods and operators.

Close-spaced samples (10 cm spacing) have been collected from two localities and prepared for analysis. The coefficient of variation for these suites will give the total expectable variance at a sampling site, and this value less that for replicate analysis of a single sample will be the local geochemical variance.

Work on the geochemical and stratigraphic aspects of black shale in eastern Kentucky has progressed to the point that a reorientation of the kerogen discrimination portion of the project can and should be done. Work on kerogen to date has concentrated on the chemical aspects of a limited number of available samples without the benefit of a good geochemical, stratigraphic and paleoenvironmental framework; however, the complementary work of Professors Blackburn and Ettensohn now make it possible to redirect the kerogen program within a firm geological framework.

Studies to date have concentrated on the identification of indicator elements which may be used to distinguish terrestrial from marine-derived kerogen and include comparison of kerogen-kerogen, kerogen-rock, and fossils-rock. Measurement of many elements in whole rock, kerogen, and fossil material have made it clear that, although the provenance of the

kerogenous matter is suggested by the amounts and ratios of certain critical elements, the distinction of plant and animal-derived kerogen cannot be made in a clear cut way at this time. The studies do, however, suggest a continuing change of concentration, ratio, or partition of certain elements as a function of sample position within the basin, i.e. chemical variation is seen as a function of distance from shore, distance from a source of detrital material, depth of water, nature of marine conditions, etc.

Since direct measurements to distinguish terrestrial from marine-derived kerogen have not provided data satisfactory to the investigator, a re-orientation of the program is planned in which kerogen separated from black shale samples from various positions in the basin will be examined and correlated with paleoenvironmental indicators.

Field and laboratory studies by Professor Ettenshon and his students are developing a paleoenvironmental description of black shale sedimentation which will allow a meaningful selection of samples for study while the chemical work of Professor Blackburn and his group has, in general, defined the regional chemical trends. Work in the past month on samples from two sections, Le-1 from Leslie Co. in northern Kentucky and Cu-1 from Cumberland Co. in southern Kentucky, show chemical contrasts in the kerogen which may be useful in the recognition of terrestrial and marine types. The data, Table 1, indicate an (expectable) enrichment of Al, Ti, and Cr shoreward where terrestrially-derived kerogen is presumably more abundant, no partition of Pb and Cu between less and more open marine conditions, and significant enrichment of Ni and Sr in kerogen presumably dominated by material of a marine source.

It is planned to concentrate future work on kerogen separated from black shale samples taken from sites defined by the stratigraphy group and to measure those elements indicated by an asterisk in Table 1.

The shift in emphasis in kerogen discrimination studies from whole rock and fossil fragment sample materials to separated kerogen has been necessitated the development of a rapid means for separating kerogen from its silicate matrix. To this end, we have developed the following procedure and are testing it to determine its reproducibility and freedom from contamination.

Acid Mixture: Working under a fume hood, transfer the contents of a 1-pound bottle of HF (48%) to a 1-liter polyethylene bottle. Chill the HF in a bath of cold water for one hour. Keeping the polyethylene bottle in the cold water bath, add 165 ml of concentrated H₂SO₄, mix and allow to cool. Add 40 ml of concentrated HNO₃ and mix.

Procedure:

1. Transfer 1.00 gm of each sample to special Teflon breakers.
2. Under a fume hood, add 30 ml of the Acid Mixture to each Teflon breaker and swirl to wet the sample.
3. Cover the Teflon breakers with Teflon covers and place the breakers on the steam bath so that most of the breaker is suspended in steam and allow to heat for six hours.
4. Remove the Teflon breakers from the steam bath and dilute the contents to approximately 1-liter with demineralized water using a polyethylene container.
5. Separate the solid liquid fractions using vacuum filtration. Wash filtrate with 0.2N HCl and three times with demineralized water.
6. Dry filtrate.

1.3 2300-3. Radio-element determinations

Measurement of U, Th and K by gamma-ray spectrometry has been completed for all samples collected or received from other investigators.

the data has all been reduced and is now being plotted for submission of the geochemical logs as a milestone deliverable.

Much of the data is from the sections measured by the stratigraphic group along the eastern side of the Cincinnati Arch in Kentucky. Complete chemical and mineralogical data is now available for these samples with the exception of C-H-N. These data are now being acquired under the generous auspices of the Institute for Mining and Minerals Research. This data coupled with inorganic data already compiled will afford a better understanding of the nature of the kerogen. During the next quarter emphasis will be placed on the relationships between the radiochemistry of the shale and the type, amount and maturation of the kerogen.

1.4 2300-4 Statistical Evaluation of Geochemical Data

During the next quarter, the statistical evaluation of geochemical data will begin in earnest. All preliminary steps have been taken in meetings with the University of Kentucky Computing Center for the acquisition of disc space and access to the statistical library. Their recommendations include the use of a remote terminal operating as an interactive unit with the UK Conversational Job System as this is the most rapid and convenient access to stored data files.

Data files are now being stored on disc while awaiting the ordering of a terminal as requested in the Fiscal 1978-79 budget.

TABLE 1

Concentration ratios of various elements in
kerogen from Leslie and Cumberland counties.

<u>Element</u>	<u>Leslie</u> <u>Cumberland</u>
Enriched Landward	
Al	2.19*
Mg	2.03
Ti	1.52*
Cr	1.35*
Pb	1.01*
Cu	1.00*
Enriched Seaward	
Fe	.92
P	.84
Ca	.82
Mn	.79
Ni	.78*
Sr	.57*
Na	.50

TABLE 2

Mineralogy of Outcrop Samples around the
Cincinnati Arch in Kentucky

Sample	1-76	2-76	3-76	4-76	5-76	6-76	7-76	8-76	11-76	13-76	14-76	20-76
Chlorite	6.4		4.9	7.4	2.2	3.6	3.8	3.3	2.7	1.8	1.1	0.8
Illite	52.0	35.1	32.7	29.9	28.0	34.9	38.2	31.9	31.3	44.4	29.5	20.9
Kaolinite	14.1	4.9	3.2	11.2	1.4	0.4		2.3			2.8	0.5
Mixed-layer clay		8.5	1.0	3.9	2.6	9.1			3.9	0.7	0.9	
Quartz	9.9	31.5	40.1	22.6	34.8	26.5	31.5	32.8	33.3	30.6	47.7	24.1
Feldspar	0.4	1.8	7.7	2.2	6.8	7.3	7.9	6.6	4.5	3.9	7.6	0.6
Calcite	3.8	3.5	1.2	1.9	4.9	4.9	4.7	5.8	7.9	8.0	1.1	15.9
Dolomite	5.5				4.6	0.8	2.2	3.2	3.7		1.2	
Pyrite		2.2	1.9	0.6		2.8	1.0	0.7				29.8
Organic	8.4	12.1	7.4	20.2	14.6	11.3	10.6	13.3	12.9	10.6	8.0	6.1
Total												

Sample	29-76	47-76	52-76	58-76
Chlorite	4.5	8.3	0.6	2.3
Illite	27.5	23.3	26.3	32.1
Kaolinite	9.5	7.6	4.9	2.5
Mixed-layer clay	0.9			0.5
Quartz	30.1	24.3	39.9	32.5

TABLE 2 - (Continued)

Sample	29-76	47-76	52-76	58-76
Feldspar	6.3	7.1	8.1	6.2
Calcite	1.0	2.3	0.4	5.4
Dolomite		6.7		
Pyrite	0.9	8.9	7.0	8.5
Organic	7.6	11.4	13.1	10.1
Total

Figure 5

Figure 6

COLUMBIA GAS TRANSMISSION
No. 20336
Martin County, KY

Figure 7

NICHOLAS COMBS No. 7239 PERRY CO. KENTUCKY

Figure 8

PINE MOUNTAIN TUNNEL PROJECT
 Core Hole No.5 CoreCall No.C247
 Letcher County,KY
 Figure 9

Figure 10

Black-Shale Stratigraphy Group

1.0 Executive Summary

This quarter has been largely devoted to final interpretation, integration, and compilation of surface stratigraphic and petrologic data into deliverable documents for D.O.E., M.E.R.C. As of September, two such documents have been prepared. A thesis by Dennis Swager on black-shale outcrop stratigraphy from the two eastern Kentucky outcrop belts has been completed and will be included with the annual report. A thesis by Mike Miller on the thin-section petrology of three eastern Kentucky cores has also been completed and will be included with the annual report.

Also during this quarter we have begun the transition to two new parts of the project: map compilation and the paleontological-paleoecological study. Compilation of isopach, lithofacies, and structural contour maps depends largely on completion of the well-log inventory from which all our data is generated. At present, well-log inventories for 37 of the 41 eastern Kentucky counties (90%) have been completed. Work has begun, however, on compiling data from the completed county inventories. As soon as the inventory is completed, hopefully by the end of October, we will begin generating maps in earnest.

Work has also begun on the paleontological-paleoecological portion of the project. A research assistant has been found to complete a thesis study on this part of the project and he is currently engaged in preliminary research.

2.0 Contract Objectives

- 2.1 Completion of outcrop stratigraphy study.
- 2.2 Completion of subsurface petrologic study.
- 2.3 Progress on isopach, structural contour, and lithofacies maps.
- 2.4 Progress on paleontological-paleoecological study.
- 2.5 Progress toward formulation of depositional model.

3.0 Technical Progress

3.1 Outcrop stratigraphy

- 3.1.1 Correlation and interpretation of outcrop stratigraphy along the two black-shale out-

crop belts in eastern Kentucky is now complete. This data is assembled in a thesis by Dennis Swager which will be included with the annual report. Five of Provo's seven radioactive units have been recognized in various of the 12 outcrops sampled along the east-central Kentucky outcrop belt (Fig. 1), and are correlated along the outcrop belt. Correlation from outcrop to outcrop shows that the lower two units pinch out in a southwesterly direction as the black shales lap onto the Cincinnati Arch (Fig. 2). In addition, lithostratigraphic and biostratigraphic units have been recognized in the black shales (Fig. 3), and the lithostratigraphic units have also been correlated along this outcrop belt (Fig. 4). Similar radioactive and lithostratigraphic units have been identified and correlated along the Pine Mt. outcrop belt (Fig. 5).

3.1.2 One additional section will be measured in southern Ohio for comparative purposes; Possible revision of manuscript for D.O.E. publication.

3.1.3 Measure one more section in southern Ohio.

3.2 Subsurface Petrologic Study

3.2.1 Examination and interpretation of thin-section petrology from the three cored wells is not complete. This data is assembled in a thesis by Mike Miller which will be included in the annual report. Three hundred thin-sections, usually made from samples at 2.5-foot intervals along the core, were made and examined from three cores from eastern Kentucky (Fig. 6, Martin County, Johnson County, and Letcher County). Percentages of organic and inorganic constituents were calculated using point-counts and were plotted against core depth and radioactive units (Figs. 7, 8, and 9). Seven stratification types and 5 types of sedimentary structures were also noted in the thin-sections (Fig. 10). In addition, five persistent microfacies were recognized in these shales. These features and others, as well as their stratigraphic and environmental implications are detailed in the thesis by Miller.

3.2.2. Possible revision of thesis manuscript for D.O.E. publication.

3.3 Progress on isopach, structure contour and lithofacies map.

3.3.1 Well-log inventories, our data source, for the following 15 eastern Kentucky counties were completed this quarter: Rockcastle, Pike, Jackson, Harlan, Cumberland, and Leslie Counties. Picks were made concerning the depths, unit thickness, and radioactivity on all the wells (for which logs are present) penetrating the black shale.

Some of this data is now being compiled and preliminary plotting of the data on maps has begun.

3.3.2 None, except for the extreme amount of time involved in searching through all well logs.

3.3.3 We hope to finish the well-log inventory and produce 5 radioactive isopach (lithofacies) maps during the next quarter.

3.4 Paleontological-paleoecological Study

3.4.1 A computer search and library research has generated over 150 articles relating to the paleontology-paleoecology of the black shales. Fauna and floral lists are being compiled and collections are being made.

3.4.2 None

3.4.3 We intend to do more library research and collecting. We plan on visiting many local museums to examine their collections and beginning photography of the specimens which we already have.

3.5 Paleoenvironmental Model

3.5.1 Work on this continues slowly because we need data generated by other projects. We are currently engaged in a thorough library research and plan to continue this.

Figure 1

A_R

A'_R

LE1

* NOTE:

This distance is not to scale. The correct distance between RW1 and BA1 is 9 miles (14.4 kl).

FEET METERS

40 12
20 6
0 40 80 KILOMETERS
25 50 MILES

Covered Interval

Figure 2

Lithostratigraphic Units (This study)	Biostratigraphic Units (This study)	Radioactive Stratigraphic Units (This study)	Ohio Nomenclature Provo (1977)	New Albany Nomenclature Lineback (1969)	Chattanooga Nomenclature Hass (1956)	Chattanooga Nomenclature Walker (1965)
Uppermost Black Shale	<u>Lingula</u> Zone	Unit S	Sunbury Shale	Jacob's Chapel Bed		Big Stone Gap Member
Green Shale & Light Siltstone		Unit B	Bedford-Berea Sequence	Henryville Bed		
Upper Black Shale	<u>Lingula</u> Zone	Unit 1	Cleveland Member	Underwood Bed		
Upper Interbedded Shale		Unit 2	Three Lick Bed (Chagrin Member)	Falling Run Bed		
				Clegg Creek Member	Upper Gassaway Member	
				Camp Run Member	Middle Gassaway Member	
Lower Black Shale		Unit 3	Upper Huron Member	Morgan Trail Member	Lower Gassaway Member	Middle Gray Siltstone Member
		Unit 4	Middle Huron Member		Upper Dowelltown Member	?
Lower Interbedded Shale	<u>Foerstia</u> Zone	Unit 5	Lower Huron Member	Selmier Member	Lower Dowelltown Member	Lower Black Shale Member
				?
Olentangy Shale	Blöcher Member
			Marcellus (?) Shale			

Figure 3

Figure 4

Characterization Studies

1.0 EXECUTIVE SUMMARY

The significant differences between surface and subsurface stratigraphy of the Shale are identified by comparison of surface and subsurface sections. We have identified two interstate problems: (a) are Marcellus age shales present in Kentucky? (b) Which of the 4 bentonites found in the Scott County (VA) well marks the top of the Needmore (of Onondaga age) in Virginia?

Agreement on the basic procedure of transmitting data to the EGSP Data Bank having been arrived at, the flow of the data is commencing.

2.0 CONTRACT OBJECTIVES

Redrafted cross-sections are expected to be ready for comment at Poster Session of EGSS #2, including correlation tables. Objectives fairly current; but data sets submitted might fall below objective rate.

3.0 TECHNICAL PROGRESS

- 3.1 Stratigraphic Characterization. Revision of the Extended Rome Trough and the Big Stone Gap Tie sections (revisions in the hands of the draftsman) have not solved the Marcellus-Olentangy-Needmore questions. The correlation tables prepared merely document the problems.

Both Wilson and Zafar visited the Virginia outcrops, and drillers logs or well completion reports for most Virginia wells in the Middlesboro Syncline were obtained. Some Tennessee wireline logs and commercial sample studies were purchased.

- 3.2 Middlesboro Syncline Characterization. The Middlesboro Syncline has oil and gas production and stratigraphy muddled by structure: it appears to have potential for additional production. It is also the locus of the central part of the complex Eastern Longitudinal Regional Cross-Section. The longitudinal section has been laid out, the transverse section (Big Stone Gap Tie) has been revised, an indepth surface stratigraphic study has been collaboratively commenced by Paul E. Potter (University of Cincinnati) and Roy C. Kepferle (USGS-Cincinnati) which will be supplemented with a structure and Chattanooga isopach, chiefly by Wilson and Zafar.

- 3.3 Data Handling. The basic mode of transfer of data from the KRG Data Bank to the EGSP Data Bank via encoded standard EGSP formats has been accepted. Hang-ups have not been edited out of the procedures, yet.

Source documents from Letcher, Harlan, and Bell Counties, Kentucky, have been selected and partially prepared for coding. Wells from Tennessee and Virginia have also been selected. Completion of coding for all datum points on regional cross-sections is the present detailed task chosen. Outcrops are converted to synthetic boreholes for coding.

We received a tape of Kentucky wells from WHCS and EGSP Data Bank, with which we have run listings, which we are sure we can augment safely. Geologic queries can be addressed to the tape and good results obtained.

The tape on which we loaded the Lewis County and certain other data have been set aside for present: it can later be processed to be compatible with the WHCS data and EGSP-generated tape.