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GEOLOGIC AND GEOCHEMICAL STUDIES OF THE NEW ALBANY GROUP
(DEVONIAN BLACK SHALE) IN ILLINOIS TO EVALUATE ITS
CHARACTERISTICS AS A SOURCE OF HYDROCARBONS

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GEOLOGICAL EVALUATION

Introduction

This project is a detailed analysis of the lithology, stratigraphy, and structure of the New Albany Group in Illinois to determine those characteristics of lithology, thickness, regional distribution, vertical and lateral variability, and deformation that are most relevant to the occurrence of hydrocarbons.

This study will result in the preparation of cross sections, facies maps, and geologic structure maps based on subsurface data available in the Illinois Survey files. Previous work in Illinois is being re-evaluated and updated. New data on the physical, chemical, and mineralogic characteristics of the New Albany will be derived from the studies of new cores in Illinois and will be incorporated into the stratigraphic and structural investigations of existing data.

Advise DOE on Coring in Illinois

Progress

In early October, 1979, the Illinois Geological Survey obtained approximately 275 feet of oriented core (13IL) from the Gordon T. Jenkins #1 Simpson well in Wayne County, Illinois. A detailed description of that core was included in the November monthly report. Analysis of off-gas samples from this core has been completed and the data are being studied. Preliminary results indicate that these samples produced more off-gas than previous samples of the New Albany taken in Illinois. This supports the contention that a 19-county area in southeastern Illinois (including Wayne County) has the best potential of having gas resources in the New Albany. In the core, more gas was released from black shale samples from the Grassy Creek Shale and the middle black shale unit of the Selmier Shale than other parts of the section.

This core completes the program of coring for this project in Illinois.

Coordination of Stratigraphic Maps

Progress

Cluff, Lineback, and Reinbold visited the Indiana Geological Survey October 30 to November 1, 1979. Along with workers from the Indiana Survey, they undertook a field examination of several important outcrops. After the field examination, office discussions were held, and most outstanding stratigraphic problems were resolved.

The Indiana Survey, at the urging of Illinois workers, agreed to cease using the term Hannibal Shale as a unit equivalent to the Hannibal-Saverton Shale interval in Illinois. However, the Indiana workers did not wish to extend the term Hannibal-Saverton into Indiana, and instead they agreed to return to using the Michigan Basin term, Ellsworth Shale, for the Hannibal-Saverton equivalent interval. With this understanding, thickness maps of the equivalent units can now be easily coordinated at the state line.

It was also resolved to formally adopt the Indiana term, Selmier Shale (Lineback, 1968) to replace the term Sweetland Creek Shale in southeastern Illinois. This change has now been accepted by the Illinois State Geological Survey. Although the Sweetland Creek Shale of western and central Illinois appears to be mostly in a higher stratigraphic position than the Selmier, there is partial physical and temporal equivalence. In Illinois the two formations are separated by an arbitrary vertical cutoff, and are, therefore, never both recognized in the same stratigraphic section (fig. 1).

In the interest of basin-wide uniformity of recognition, the Blocher Shale-Selmier Shale contact has been redefined from that of Lineback (1968, 1970). Lineback originally placed this contact at the break between underlying black shale and overlying greenish-gray shale in outcrop sections. However, in the subsurface, based on geophysical logs, cores, and sample studies, the most consistently recognizable horizon is the break between calcareous black shale (underlying) and noncalcareous black to gray shale (overlying). In order to make the outcrop definition of the Blocher-Selmier contact consistent with the regional subsurface definition, Lineback, Cluff, and Reinbold, in early December, visited the Indiana type sections of the Blocher and Selmier for the purpose of redescribing the sections and redefining the units. In both outcrop sections a sharp break was noted within the black shale between the calcareous and dolomitic (noncalcareous) portions. We believe that this sharp break correlates with the geophysical log break in the subsurface of the deep basin, and we have redefined the contact at this horizon in the outcrops.

PUBLICATIONS

In late November, M. L. Reinbold submitted a manuscript entitled "Facies, Formation Boundaries, and Time-Rock Stratigraphy in the Upper Part of the New Albany Shale Group (Devonian-Mississippian) in the Illinois Basin, U.S.A." for publication in the Proceedings (Compte Rendu) of the Ninth International Congress of Carboniferous Stratigraphy and Geology.

A manuscript by R. M. Cluff, M. L. Reinbold, and J. A. Lineback entitled "The New Albany Shale Group in Illinois" is currently in review at the Illinois Survey. This manuscript has undergone considerable revision recently in order to reflect revisions in stratigraphic nomenclature.

REFERENCES CITED

- Lineback, J. A., 1968, Subdivisions and depositional environments of the New Albany Shale (Devonian-Mississippian) in Indiana: American Association Petroleum Geologists Bull., v. 52, p. 1291-1303.
- Lineback, J. A., 1970, Stratigraphy of the New Albany Shale in Indiana: Indiana Geological Survey Bull. 44, 73 p.

Figure 1: Approximate location of vertical cut-off between Sweetland Creek Shale and Selmier Shale in the subsurface.

MINERALOGIC AND PETROGRAPHIC CHARACTERIZATION

Introduction

This project is directed at characterizing in detail the mineralogic and petrographic properties of the New Albany Shale in Illinois. This includes the quantitative and qualitative characterization, by optical and x-ray techniques, of the inorganic mineral constituents, the dispersed organic matter, and the fabric of the shale. The data generated will provide a fundamental basis for the regional and local correlations of geologic data, for interpretation of the sedimentology, depositional environment, diagenetic history, and for evaluation of hydrocarbon potentials based on the degree of thermal maturation of organic matter in the New Albany Shale.

Microscopic Characterization

Progress

Presently, samples are being examined with the SEM-EDS (scanning electron microscope equipped with an energy dispersive spectrometer) to determine whether we can recognize changes in the forms of organic matter that might be related to chemical changes imposed during maturation. The EDS detects x-ray responses from elements present in samples heavier than neon, detecting none from carbon atoms.

Two maceral-rich acid-concentrated organic matter samples (NAS-433 and NAS-478) were mixed with epoxy, mounted on copper stubs and allowed to harden. The samples were polished and then coated with gold prior to SEM-EDS analysis. With the SEM, the macerals (vitrinite, inertinite) are sometimes difficult to distinguish from mounting medium (epoxy). Vitrinite particles about 30 to 100 μm in size have been identified and no EDS response was observed. This is consistent with data collected from the suspected organic material observed within chips of shale previously examined. As reported in the abstract, "Preliminary Results of Scanning Electron Microscope Studies Samples from the New Albany Shale Group," (see monthly report to DOE, November 1, 1979), organic matter is presently identified by morphology and low level EDS response. The low level response for organic material within the shale matrix is probably due to responses from underlying or adjacent minerals.

These examinations also show that medium silt to fine sand-sized grains of quartz, pyrite, and rutile are included in the acid-concentrated organic matter samples despite the sample preparation procedures designed to eliminate most of the minerals (Quarterly Report to DOE, October 9, 1979). This procedure permits traces of some carbonates, silicates, and heavy minerals to remain in the organic concentrate. Nevertheless, the presence of these grains suggests a close association between these particles and the organic matter.

Problems

Because of the anticipation of some difficulty in distinguishing organic matter from the epoxy, a particle mount of the concentrated organic matter was attempted.

Dried organic material was lightly dusted on to a copper stub coated with a thin film of Duco cement. The sample (NAS 433) was allowed to dry and then was coated with gold prior to examination with the SEM. Because the sample had a good deal of relief, obtaining an even coating was difficult, and, as a result, charging was a problem.

Other mounting, coating and/or staining techniques will be experimented with to determine the best method for examining these organic matter concentrates.

Lithologic and Radiographic Characterization

Preparation of the thin sections for the Hardin County, Illinois, (11IL) core was completed this quarter.

Seven Wayne County, Illinois, (13IL) core samples were cut, crushed, and distributed for x-ray and vitrinite reflectance analyses. The preparation of slabs for radiography for seven samples from this core is in progress.

X-Ray Diffraction and Clay Orientation

D. A. Burke, R. M. Cluff, and M. H. Barrows met with John Hower, clay mineralogist and Head of the Geology Department at the University of Illinois, to discuss the x-ray diffraction data. Some questions were raised at that time about the methods used in calculating the clay mineralogy from the raw data. The questions raised are being investigated.

Twelve feldspar samples were analysed by x-ray diffraction this quarter. The samples are being used as standards for Mossbauer spectroscopic studies of the New Albany Shale being undertaken by the Chemistry Group. In connection with these studies, the shift in the major dolomite peak was measured for 32 samples from the Christian County, Kentucky, (1KY) core and the Sangamon County, Illinois, (1IL) core. The measurements were made to obtain a rough idea of the iron content of the dolomites.

The Wayne County, Illinois, (13IL) core samples are being prepared for x-ray diffraction analyses.

Vitrinite Reflectance

Progress

Vitrinite reflectance analysis was completed for the Peoria County, Illinois, (8IL) core, Fayette County, Illinois, (10IL) core and the Bullitt County, Kentucky, (2KY) core samples. Vitrinite reflectance analysis was also completed for 24 supplementary drill cutting samples. Analysis of all samples chosen for studies of the regional variations in vitrinite reflectance have now been completed. Only 61 samples, selected from various stratigraphic units in four deep wells in Illinois, remain to be analyzed. These samples were selected to evaluate the rate of increase in reflectance with depth (an index of the geothermal gradient) as it relates to the maturity of the New Albany Shale in Illinois.

Papers

A paper by R. M. Cluff, "Organism-sediment Relationships in the New Albany Shale Group (Devonian-Mississippian) of Illinois," has been accepted for publication by the Journal of Sedimentary Petrology. Revisions of the paper are now in progress. The abstract of the paper appeared in the Geological Society of American Abstracts with Programs, v. 10, no. 7, p. 381.

"Relationship of Depositional Facies and History to Hydrocarbon Generation in the New Albany Shale Group (Devonian-Mississippian) of Illinois," by R. M. Cluff, M. H. Barrows, and M. L. Reinbold was submitted as an invited paper for the 1980 AAPG-SEPM annual meeting in Denver, Colorado. The abstract appeared in the monthly report to DOE, November 1, 1979.

A paper summarizing our scanning electron microscope work has been completed and is now being reviewed. The paper is being submitted for inclusion in the session dealing with characterization of geological materials at the SEM, Inc., sponsored meeting to be held in Chicago, Illinois, April 21-25. An abstract of this paper appeared in the monthly report to DOE, November 1, 1979.

PHYSICAL PROPERTIES

Introduction

This project is a study of the index properties, directional properties, and strength of the oriented core of Devonian black shale from the Illinois Basin.

Results

The core (13IL) from Wayne County, Illinois, has arrived and is being logged and oriented. Several sections could not be oriented due to abundant fractures or missing fragments. Several high angle, vertical to subvertical, fractures were also recorded.

All data are being filed in the MINERS program. Formation tops for approximately two thousand wells have been filed, all according to AAPG codes. This system will allow for eventual expansion of the data base to include formations not included in the New Albany. Additional data have also been prepared and entered on the first seven Illinois wells. These data include moisture content, specific gravity, drilling rate, tensile strength, sonic velocity, shore hardness, sharpness, mineralogy, lithologic characteristics, and vitrinite reflectance.

GEOCHEMICAL CHARACTERIZATION

QUANTITATIVE DETERMINATION OF MAJOR, MINOR, AND TRACE ELEMENTS IN SHALES

Introduction

Determine not less than 49 major, minor, and trace elements in 300-500 shale samples, which are representative cross sections of the cores taken. Include organic and mineral carbon; total hydrogen; total sulfur and when that exceeds 0.5%, pyritic and sulfate sulfur. Also, report other elements observed during normal routine analysis. The data generated will be used to evaluate: 1) the potential economic importance of trace element concentrations in organic-rich shales, 2) new geochemical exploration techniques for natural gas, 3) trace element enrichment in shale organic matter, 4) the occurrence of heavy metal sulfides in shales, 5) potential catalytic effects of trace elements on shale pyrolysis yields, and 6) potential disposal problems.

Elemental Analysis

Progress

Twenty-four samples from the Wayne Co., Illinois core (13IL) received in December to be ground in preparation for chemical analysis mark the end of the acquisition of a total of 392 shale samples for analysis for major, minor and trace elements. Another 26 samples were received for determination of certain elements only, usually total and inorganic carbon.

Analyses of the samples, excluding the last 24, have been completed or nearly so by most methods. This includes determination of the major and minor elements by X-ray fluorescence spectroscopy, determination of 32 elements by neutron activation analysis, determination of total carbon and hydrogen, total sulfur, inorganic carbon and varieties of sulfur. Determination of 15 elements by optical emission spectroscopy on 150 shale samples remaining to be analyzed by that method was resumed in December. One area of delay in the compilation of all the data for statistical analysis is the tabulation of the extensive data from neutron activation analysis.

INORGANIC/ORGANIC ASSOCIATIONS OF TRACE ELEMENTS IN BLACK SHALES

Introduction

Develop chemical and/or physical methods for the separation of the organic and inorganic phases of shales, and determine the trace elements that are associated with each phase. Methods tested include float-sink gravity separations, mechanical separations (Humphrey Spiral), acid extractions, and zonal centrifugation. Compare results of analyses for ten shales, their gravity fractions, and their separated organic phases to determine the elements closely associated with organic matter. Separation procedures that are most promising will be used to study further the organically combined trace elements in additional shale samples. This research is designed to yield new information concerning chemical variations in shale organic matter, which is the shale component about which little is known and which may be the most characteristic feature of gas bearing shales.

Progress

Several additional runs using various techniques of density gradient separations were made to isolate the kerogen material from the clay matrix. No kerogen separation was observed. However, a separation of a clay material in the light density gradient took place during several of the runs. These clays are being analyzed by neutron activation analysis.

MODE OF OCCURRENCE AND RELATIVE DISTRIBUTION OF HYDROCARBON PHASES IN SHALE

Introduction

Determine the character of off-gases from approximately 10-foot intervals in cores collected in the Illinois Basin. In addition, determine the relative distribution of hydrocarbons in ten specially prepared core samples, which are the same as those in previous unit. Preserve the samples in airtight containers and subsequently analyze them for evolved gases; highly volatile, low-molecular weight liquids; medium-volatile hydrocarbons; and solvent-extracted, low volatile hydrocarbons using GC-MS methods. Determine non-volatile, high-molecular weight hydrocarbons by GC analysis of shale pyrolytic products.

Determine the carbon isotopic composition of methane in off-gases from core samples whenever sufficient methane can be collected. Compare this data to other pertinent data such as gas composition and vitrinite reflectance for the purpose of making interpretations as to the origin and maturity of the gas. Perform laboratory experiments to study the relative effects and significance of chemical and isotopic fractionation that occurs as gas is released from core samples.

Data accumulated can be evaluated to gain a better understanding of the origin, migration, and location of natural gas associated with the shales.

Progress

Released Gas Analysis

During the first week of October, 1979, a total of 66 black-shale core samples were collected from a well (1311) drilled in Wayne County, Illinois. The samples were sealed in aluminum canisters, taken to the laboratory and stored in a constant temperature (20°C) room. The pressure inside the cans was monitored at least once every week and twice in some weeks.

The largest gain in pressure inside the canisters appeared to take place within the first 2 or 3 days and began to level off steadily over the remainder of the test period. This indicates a very early release of gas from the shale; therefore, a considerable loss of gas could have occurred during the nearly 2-hour period of time the core was exposed prior to sealing the samples in canisters.

The percent total and individual hydrocarbons in the head-space atmosphere of the sealed canisters was determined by gas chromatography. Released gases (and air) were separated in an Alltech Associates CTR Column and a Perkin-Elmer Sigma I gas chromatographic system with a hot-wire detector. Under the conditions used for GC the lower limit of detection for iso-butane and isopentane is about 0.2 percent.

Twenty-two of the 66 samples released an equivalent of more than one Standard Cubic Foot (SCF) of hydrocarbons per cubic foot of shale. Thirty of the remainder released an equivalent of 0.5 to 1.0 SCF hydrocarbons per cubic foot of shale.

The methane content in most samples is about average for "natural gas". However, the ethane and to some extent the propane contents are much higher than expected, and the butane and higher hydrocarbon content is lower than normally expected for "natural gas".

Twenty-four of the above samples (one from approximately each ten-foot interval of the core) were selected and submitted for further chemical and geological analyses. The results of the released gas analyses for these 24 samples are given in Tables III-C-1 and III-C-2. No corrections for possible losses prior to sealing or because of oxygen depletion were made. Also no provision was made for "free-gas" still trapped in the internal pores of shale. Therefore, in all probability, the hydrocarbon estimates per cubic foot of shale are low.

Sample 13IL10C1 was selected for further geological and chemical analyses because the gamma-ray log shows it to have a high organic carbon content. This was in spite of the fact that the amount of released-gas could not be determined because of an unfortunate leak in the canister valve.

The mean wetness of the released gas is between 30-35 percent; the gas contains a relatively high percentage of ethane and propane. Neither isobutane nor isopentane were detected in every case with the hot wire detector used in the gas chromatographic analyses. Hexanes and higher were never detected. However, selected samples analyzed using a flame ionization detector showed the latter hydrocarbons to be present in amounts up to 0.2 percent.

The attached paper on Volatile Hydrocarbon Analysis by Chou and Dickerson was submitted for publications in the proceedings of the October 1-3 meeting in Morgantown.

TABLE III-C-1 Wayne County, Illinois (13IL)
Core and Head Space Characteristics

Sample	Depth to Top (Ft.)	Bulk Density g/cm ³	Head Space Vol. CM ³	Head Space Press. (Torr)	Time Interval Days	Head Space CO ₂	Head Space O ₂	Gas Composition N ₂	Gas Composition H.C.	SCF H.C. Cu.Ft.Shale
04C1	5046.3	2.68	2200	820.1	34	0.01	17.29	73.87	8.74	0.33
05C1	5054.6	2.51	2048	911.8	34	0.12	8.80	50.66	40.48	1.24
06C2	5069.6	2.44	2225	1027.0	34	0.22	13.89	59.14	26.77	1.26
07C2 ^a	5078.1	2.44	2051	1385.1	34	2.66	5.85	41.42	50.07	2.40
08C1	5082.2	2.44	2113	1056.2	34	0.26	13.13	57.42	29.20	1.19
09C1 ^b	5090.3	2.41	2326	947.0	34	1.13	13.69	63.99	21.19	1.20
10C1 ^b	5100.3	2.43	2166	779.0	34	0.28	18.93	75.25	5.53	N.D.
11C2	5115.4	2.48	2152	897.1	34	0.21	15.10	64.51	20.18	0.75
12C3	5128.6	2.53	2115	927.6	34	0.20	14.30	62.22	23.27	0.85
13C2	5135.3	2.46	2278	922.5	34	0.23	15.45	63.90	20.43	1.04
14C3 ^c	5148.4	2.44	2069	894.4	33	0.32	8.34	50.31	41.03	1.26
15C2	5154.3	2.40	2012	1204.7	34	0.19	5.11	47.14	47.56	1.83
16C2	5164.1	2.48	1988	990.0	34	0.28	12.59	59.14	27.98	0.84
17C4	5178.2	2.63	2085	1049.7	34	0.44	11.03	57.33	31.23	1.19
18C2	5184.1	2.58	2226	1018.5	33	1.30	8.89	59.03	30.79	1.50
19C1	5190.2	2.62	2149	972.8	33	0.42	13.52	62.03	24.02	0.96
20C1	5202.1	2.59	2119	944.9	33	0.56	8.66	54.99	35.79	1.31
21C2	5214.0	2.55	2052	1124.1	34	0.41	9.85	53.92	35.80	1.38
22C2	5224.5	2.79	2200	938.7	34	0.11	12.36	63.78	23.74	1.07
23C4	5239.6	2.51	2093	1228.0	32	0.39	9.09	49.62	40.91	1.86
24C2	5245.5	2.60	2008	1008.3	32	0.12	13.97	61.13	24.79	0.78
25C3	5258.4	2.58	2176	785.6	33	0.08	18.13	72.06	9.73	0.32
26C3	5267.2	2.60	2170	776.7	33	0.14	16.07	65.97	17.82	0.58
27C1	5270.5	2.58	2269	860.5	33	0.02	18.53	72.26	9.19	0.42

HC = Hydrocarbons

a.) The head-space gas was bled off to atmospheric pressure after 23 days.

b.) The valve in the canister containing this sample leaked.

c.) Canister developed a slow leak past the rubber septum.

TABLE III-C-2 Wayne County, Illinois (13IL)
Composition of Hydrocarbons in Released Gas

Sample	% Methane	% Ethane	% Propane	% Butanes	% Pentanes	% Wetness
04C1	71.78	19.15	7.04	1.71	.32	28.22
05C1	67.84	20.00	8.77	2.85	.55	32.16
06C2	74.89	17.43	5.78	1.56	.33	25.11
07C2	67.33	21.53	8.42	2.30	.43	32.67
08C1	70.96	18.75	7.26	2.47	.56	29.04
09C1	77.11	17.15	5.00	.58	.17	22.89
10C1	75.34	17.72	4.91	1.67	.36	24.66
11C2	76.87	17.17	4.80	1.00	.17	23.13
12C3	70.47	18.68	7.68	2.46	.71	29.53
13C2	69.46	18.95	7.67	2.51	1.40	30.54
14C3	67.83	20.87	8.42	2.30	.58	32.17
15C2	63.45	24.06	9.86	2.34	.29	36.55
16C2	72.61	17.95	6.84	1.72	.87	27.39
17C4	66.72	20.74	8.82	2.63	1.09	33.28
18C2	60.63	22.44	11.48	4.12	1.33	39.37
19C1	67.43	19.99	9.20	3.02	.36	32.57
20C1	64.04	21.61	9.78	3.12	1.45	35.96
21C2	66.52	21.34	8.66	2.49	.98	33.48
22C2	67.03	20.97	8.82	2.59	.58	32.97
23C4	65.41	21.69	9.65	2.87	.38	34.59
24C2	70.81	18.91	7.63	2.16	.48	29.19
25C3	77.19	16.18	5.12	1.50		22.81
26C3	71.77	18.36	7.28	2.17	.41	28.23
27C1	75.84	16.26	5.98	1.66	.26	24.16

Volatile Hydrocarbon Analysis

PYROLYSIS OF EASTERN GAS SHALE: EFFECTS OF TEMPERATURE
AND ATMOSPHERE ON THE PRODUCTION OF LIGHT HYDROCARBONS

by

Mei-In Melissa Chou and Donald R. Dickerson

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United States Department of Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

PYROLYSIS OF EASTERN GAS SHALES—EFFECTS OF TEMPERATURE AND ATMOSPHERE

ABSTRACT

Samples of black shale from four cores of the New Albany Shale Group (Devonian-Mississippian) from the Illinois Basin in Kentucky and Illinois were used in this study. Sections measuring 4 inches (9 cm) in length were taken from the 4-inch (9-cm) diameter cores and were sealed in canisters for study of released gas. Following the study of released gas, the shale was crushed to <100 mesh for use in the study of the effects of temperature and atmosphere on the pyrolysis of shale.

The correlation coefficients between the quantity of gas released at room temperature from the "canistered" core sections and the organic carbon content, and between the gas released and the total porosity of the shale samples were calculated for the individual cores. The coefficients for the quantity of gas released and the organic carbon content of the four cores were 0.7018(06IL), 0.0023(02IL), 0.8034(04IL), and 0.7531(01KY).

A study was made of the gaseous hydrocarbons produced by pyrolysis of shale at 600°C. Two regression lines could be drawn on the graph of the hydrocarbon gas produced versus the original organic carbon content, one ($r^2=0.96$) fitting data points for the Illinois cores and the other ($r^2=0.92$) fitting data points for the Kentucky core.

The composition of the noncondensable hydrocarbon gases produced by heating selected black shale samples at four different temperatures was studied. The formation of alkanes was favored over that of alkenes, particularly at low temperature. Methane, ethane, and ethylene from thermal cracking and higher carbon number alkenes were positively identified in the gases from shale heated to above 120°C.

A study was made of the effect of the pyrolysis atmosphere on the yield of light hydrocarbons (C_1 to C_8), carbon dioxide, carbon monoxide, acetaldehyde, and acetone during thermal degradation of a gram amount of selected shale samples. The effect of various amounts of oxygen in the pyrolysis atmosphere was monitored. The yield of an individual hydrocarbon generally increased with the increase in the oxygen content of the pyrolysis atmosphere until the oxygen content reached the 10 percent level; when the oxygen content was increased above 10 percent, there was a decrease in yield. The yield of carbon dioxide and carbon monoxide increased with the increase in oxygen content of the pyrolysis atmosphere.

Results reported in this study may increase the ability to predict the potential for production of gas from the black shale in the New Albany Group. The study may also provide information useful for improving the quality of the gas produced by pyrolysis of shale.

INTRODUCTION

As part of the Eastern Gas Shale Project of the U.S. Department of Energy, the Illinois State Geological Survey (ISGS) is conducting a number of geologic and geochemical studies¹ of the New Albany Shale Group (Devonian-Mississippian) in the Illinois Basin to evaluate its potential as a source of hydrocarbons. The amount of volatile materials in the shale, their origin, and their continuous formation are of considerable interest with regard to the history and current alteration of shale formation. The present study was undertaken in order to determine the relationships between the light hydrocarbons (C_1 to C_5) released from the shale and the organic carbon content, the pyrolysis temperature, and the molecular oxygen content of the pyrolysis atmosphere. Through observation of the changes—changes that occur when conditions for pyrolysis are changed—in the amounts of CO_2 , CO , CH_3CHO , CH_3COCH_3 , alkanes, alkenes, and in the alkane to alkene ratios, an insight may be gained into the oxidative processes taking place in the shale during pyrolysis.

EXPERIMENTAL PROCEDURE

Gas released from shale at room temperature

The quantity and composition of gas released at room temperature from specially canned core sections were measured. Ten of the core sections were from drill holes in Christian County, Kentucky (01KY); nine from Effingham County, Illinois (02IL), twenty-nine from Henderson County, Illinois (04IL), and twenty-five from Tazewell County, Illinois (06IL). The locations of these holes are shown in figure 1.

The shale core sample (approximately 4 inches (9 cm) in height and 4 inches (9 cm) in diameter) was sealed in a 2800-mL aluminum resealable canister as soon as possible after the core had been brought to the surface and the sample cut. Each canister was equipped with a rubber septum-sealed valve. The canistered samples were stored in a room with a constant temperature of 21°C for approxi-

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mately 3 to 4 months. Hydrocarbons that had been formed by natural processes, e.g., by microbial degradation of organic matter, and had remained trapped in the shale until the core was cut were released to the headspace of the canister. The pressure inside the canisters was monitored periodically with a mercury manometer. The gas yield was calculated from the volume of the canister headspace and the pressure of the gas. The composition of the gases was determined with a Beckman GC-4 gas chromatograph equipped with a hot wire detector and a flame ionization detector. A CTR column (Alltech Associates, Inc.), with the injector at 100°C and temperature programmed from 60°C to 180°C at 16°C/min was used with the hot-wire detector at 185°C. A Chromosorb 102 column with the injector at 100°C and temperature programmed from 50°C to 150°C at 16°C/min was used with the flame-ionization detector at 175°C.

Yield of gaseous hydrocarbons (C_1 to C_5) from pyrolysis of shale

Thirty shale samples were studied. Eight of the samples were from the core from Christian County, Kentucky, six were from Effingham County, eight were from Henderson County, and eight were from Tazewell County, Illinois.

A 250-mg sample of pulverized shale (<100 mesh) was weighed into a custom-made pyrex tube (7 in. x 0.7 in. ID). The tube was sealed with a rubber serum cap secured with a wire band. The sample was degassed with a small hypodermic needle, and the tube was then placed in a pre-heated (600°C) electric tube furnace for 5 minutes. A known amount of pure cyclopropane was injected into each sample tube for use as an internal standard. The gases that were noncondensable at $29 \pm 1^\circ\text{C}$ were sampled from the headspace and analyzed on a Perkin-Elmer 3920B gas chromatograph equipped with a flame ionization detector and interfaced with a Perkin-Elmer Sigma 10 data system. A stainless steel column (6 ft x .125 in. [2M x 3 mm ID]) packed with Chromosorb 102 (80/100 mesh) was used. The inlet and detector temperatures were 200°C and 250°C, respectively, and the column temperature was programmed from 40°C to 180°C at 8°C/min and was held at the upper temperature for 8 minutes. The flow of helium carrier gas was 20 mL/min.

A blank was run to be certain that all the gas in the tube came from the shale. A small amount, however, may have come from indigenous gas trapped in the pore structure of the shale. Figure 2 shows the gas chromatogram of a representative gas sample separated on the Chromosorb 102 column. The yield of pyrolysis products was determined by integration of the chromatograms and was calculated by using the Sigma 10 data system.

Effect of temperature on the pyrolysis of shale

A shale sample taken from a section of the drill hole in Christian County, Kentucky, which was 2182 to 2249 ft below the surface, was used in this study.

The temperatures selected for pyrolysis were 60°, 145°, 300°, and 450°C. Small portions (0.5 to 1 g) of pulverized shale sample (<100 mesh) were weighed into pyrex tubes. Each tube was sealed with a rubber serum cap secured with a wire band as previously described.

A silicon oil bath was used to heat the samples to 60° and 145°C, and an electric furnace was employed for higher temperatures. The heating time was always 18 hours. The gas compositions were analyzed by gas chromatography using a Chromosorb 102 column and were checked with a Carbowack C/ 0.2 percent CW 1500 column; operating conditions were the same as described in the preceding section. Figure 3 shows a typical GC trace of a gas sample separated on the Carbowack C/ 0.2 percent CW 1500 column.

Effect of molecular oxygen on the pyrolysis of shales

A shale sample taken from the core from the drill hole in Effingham County, Illinois, at 3,053 ft below the surface was used in this study.

One-gram amounts of samples of pulverized shale were weighed into pyrex tubes and sealed as described above. The bulk of the air in the sample tube was exchanged for a gas mixture of known composition by evacuating the tube and filling it with oxygen and nitrogen in the desired proportions. The percentage of oxygen in the sample tube was checked by gas chromatography before pyrolysis.

All samples were pyrolyzed at 450°C for 15 minutes. The headspace gases, with an added internal standard, were measured by gas chromatography on both a Chromosorb 102 and a Carbowack C/

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0.2 percent CW 1500 column. The operating conditions were as described previously. A 5A Molecular Sieve column was also used for separation of the hydrocarbons and the products of oxidation. Conditions for the chromatography were: injection port at 200°C; column oven with initial hold of 3 minutes at 40°C and then programmed from 40°C to 260°C at 20°C/min and held at 260°C for 10 minutes; hot wire detector at 300°C; helium carrier gas at 30 mL/min flow rate. The identification of the components of the gas was confirmed by GC-MS analysis.

RESULTS AND DISCUSSION

Gas released from shale at room temperature

For the four cores studied, correlation coefficients were calculated for the relationship of the quantity of gas released from the "canistered" core sections at room temperature to the organic carbon content and total porosity of the shale. The correlation coefficients (r^2) of the organic carbon content with the quantity of gas released, for the four cores, were 0.70(06IL), 0.002(02IL), 0.80(04IL), and 0.75(01KY). The Illinois State Geological Survey made porosity measurements (at 100°C) on some of the 77 samples, and the results have been reported elsewhere (see table 1). The correlation coefficients between the porosity and the released gas for the four cores were 0.19, 0.30, 0.16, and 0.02, respectively. The amount of gas released from shale at room temperature did not appear to be related to the porosity of the shale.

For the Effingham County core (02IL), there is considerable scatter to the points in the plot of the data for the released gas yield versus the organic carbon content (fig. 4). This may be explained in part by the fact that in this area the black shale overlies an oil pool. The composition of the gas released from the shale was essentially identical to that of the gas released from a producing oil well nearby. This indicates that most of the gas migrated into the shale rather than being indigenous to it.

There was good correlation between the amount of gas released and the organic carbon content for the other three cores; however, the correlation was not as good as that between the organic carbon content and the gas released upon pyrolysis of the shales, as established in the next section of results. The poorer correlation between indigenous volatile material and organic carbon content may be due, in part, to the fact that the amount of gas in the core is a function not only of the amount of gas formed over geologic time periods, but also of the amount that remained trapped in the shale. It is also possible that the trapped gases may have originated elsewhere and migrated into the shale in question. Other geologic factors may be operative as well.

The correlation of the gas released with the organic carbon content and the lack of correlation between the gas released and the porosity is in agreement with the findings of Kalyoncu et al.³ and Snyder et al.⁴

Yield of gaseous hydrocarbons (C_1 to C_5) from pyrolysis of shales

The relationship of the gas yield from the pyrolysis of shale at 600°C with the organic carbon content of shales is shown in figure 5. There is a direct correlation between the gaseous hydrocarbon yield and the organic carbon content. Despite some scatter of data points, two regression lines can be drawn through the points in figure 5. One ($r^2=0.96$) closely fits data points for Illinois drilling hole cores and the other ($r^2=0.92$) follows data points for the Kentucky drill hole core only. For all data points the correlation coefficient (r^2) is 0.86. The reason that the Kentucky core produced more hydrocarbon gas than the Illinois cores per unit of organic carbon content has not been accounted for. A difference in the nature of the organic matter or the existence of a special mineral-surface catalytic reaction may be the cause. Of these four drilling holes, only the one in Kentucky appeared to have the potential to be an economical gas-producing well.

Effect of temperature on the pyrolysis of shale

Samples of shale from the core from a drilling hole in Christian County, Kentucky, were pyrolyzed at 60°, 145°, 300°, and 450°C for 18 hours. The long pyrolysis time was chosen in order to accumulate a sufficient amount of gas for analysis at a comparatively low temperature (60°C). Pyrolyses over an eighteen-hour period could not be carried out at temperatures higher than 450°C because of possible damage to the rubber septum seal. The average values of the relative hydrocarbon yields from several determinations at each temperature are presented in table 2. Typical GC traces obtained at 60° and at 300°C are shown in figure 6. At 60°C the hydrocarbon products were mostly alkanes; alkenes were in trace amounts only. The yields of C_1 and C_2 hydrocarbons from thermal cracking and of higher carbon number alkenes are substantially increased as the temperature of

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pyrolysis is raised to 300°C. The alkane/alkene ratios for C₂ to C₅ hydrocarbons as a function of pyrolysis temperature are shown in figure 7. The ratios for C₂, C₃, C₄, and C₅ hydrocarbons show that conditions for the formation of these alkenes are more favorable at high temperatures³.

The total yield of gases (C₁ to C₅) increases fairly rapidly as the temperature of pyrolysis is increased (fig. 8). The increase in yield is dramatic at a pyrolysis temperature of 450°C.

The trends observed in this study can be related to the trends observed in the study of the effects of molecular oxygen on pyrolysis (see fig. 9). The data may also provide information on the type of hydrocarbons that exist in the shale.

Effect of molecular oxygen on the pyrolysis of shale

The yields of products obtained from heating shale at 450°C for 15 minutes with various percentages of oxygen in the pyrolysis atmosphere are presented in table 3. The products are comprised of C₁ to C₈ hydrocarbons and include CH₃COCH₃, CH₃CHO, CO, and CO₂. The yield of each hydrocarbon generally increases with an increase in oxygen content of the pyrolysis atmosphere until the oxygen content reaches 10 percent.

Figure 9 shows the ratio of alkanes to alkenes produced for carbon numbers 2 through 6, as a function of the oxygen content in the pyrolysis atmosphere. The plot of the alkane to alkene ratio for C₂ shows that the alkene formation becomes relatively more favorable as the oxygen content increases. For C₃, C₄, C₅, and C₆, alkene formation becomes only slightly more favorable relatively, as the oxygen content becomes higher in the pyrolysis atmosphere.

The higher oxygen levels will result in higher surface temperature because of oxidation. Thus an effect of oxygen is to lower the pyrolysis temperature at which the maximum level of evolution of organic gases occurs. Whether the trends in yields observed are the same at different temperatures is under investigation. Information concerning the effect of controlling both the temperature and the quantity of molecular oxygen on the pyrolysis of shale should prove very helpful for optimizing shale retorting operations.

The yields of CO₂, CO, CH₃CHO, and CH₃COCH₃ as a function of the oxygen content of the pyrolysis atmosphere are given in figure 10. The yields of CO₂, CO, and CH₃COCH₃ increase significantly as the percentage of oxygen increases in the pyrolysis atmosphere.

Many details of the complex reaction involved in the oxidation of hydrocarbons by molecular oxygen have not yet been elucidated. It is commonly accepted that a chain mechanism is operative^{5,6} and that one of the first products formed is a hydroperoxide that may be oxidized further or decomposed thermally, thereby to initiate new chains. It is also known that these intermediates are responsible for the increased yield of oxygenated compounds in the thermolysis of hydrocarbons in higher oxygen concentrations.^{5,6} Most likely, oxidation proceeds by the pathways shown on the diagram at the top of the next page. In the initial reaction hydroperoxide radicals are formed by combination of the organic free radicals (formed by thermolysis from shale hydrocarbons) and molecular oxygen, and further thermolysis reactions produce aldehyde and ketone molecules.

CONCLUSIONS

Our study of the gas released from shale at ambient temperature shows that the amount of gas released is highly dependent on the organic carbon content and is not limited by the porosity of the shale. For the shales studied, the organic carbon content of a given shale appears to be a much better indicator of the potential for gas production from shale than does porosity data. There may be other geological factors, however, that play an important role in the production of gas from shale.

About twenty times more gas was produced from the shale by high temperature pyrolysis than was obtained by natural release at ambient temperature. The yield of hydrocarbons in pyrolysis showed a higher degree of dependence on the organic carbon content of a given shale than was found for ambient temperature gas release. This may be true, in part, because the gas produced by pyrolysis was not affected by geologically controlled factors.

In the study of the effects of temperature on pyrolysis, data showed that the yield of the total quantity of light hydrocarbons (C₁ to C₅) was increased the most for pyrolysis temperatures above 300°C, and the relative proportion of alkene to alkane produced for a given carbon number increased as the pyrolysis temperature was increased. The same trend was observed in the study of

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the effect of the presence of molecular oxygen on the pyrolysis of shale. The proportion of alkenes to alkanes that were produced for a given carbon number increased as the oxygen content of the atmosphere was increased; however, except for C_2 , the increase in the relative production of alkene to alkane was not very significant. The quantity of any individual hydrocarbon that was produced generally increased as the oxygen content increased in pyrolysis atmosphere until the oxygen content reached 10 percent; thereafter there was a decrease in yield as the process of combustion became more significant. A plot of the effect of oxygen on the formation of CO and CO_2 had a point of inflection at about the 10 percent oxygen level. Possibly, the presence of some molecular oxygen could lower the pyrolysis temperature needed to produce a gas of desired composition. The study of the effect of molecular oxygen at different temperatures of pyrolysis and the determination of gases other than hydrocarbons formed in pyrolysis of shale at different temperatures would be helpful in order to test this conclusion. Moreover this additional study could be used to determine the changes that occur in the composition of the light gases produced from the organic matter in shales as temperature and atmosphere of pyrolysis are varied.

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TABLE 1

Linear regression analysis on the amount of gas released from shale at room temperature and the porosity of shale.

Core and sample #	Depth to top of sample (ft)	y Gas released, cu ft/cu ft shale	x Porosity (%)	$y = a + bx$ r^{2*}
06IL-16C1	1053.15	0.0067	11.8	0.19
19C1	1083.20	0.0321	11.3	
20C1	1093.35	0.0277	6.8	
02IL-01C1	3011.4	0.30	7.0	0.30
04C1	3033.0	0.29	4.6	
07C1	3085.5	0.57	7.0	
08C1	3096.5	0.51	6.66	
04IL-10C1	413.5	0.0089	15.7	0.16
20C1	513.4	0.0329	13.4	
29C1	604.5	0.0013	9.1	
01KY-01C1	2182.25	1.47	3.6	0.02
04C1	2230.20	0.39	4.2	
05C1	2240.10	0.76	2.7	
06C1	2250.00	0.09	2.9	
Overall				0.35

* r^2 = the correlation coefficient

TABLE 2

Relative percentages of hydrocarbons (C_1 to C_5) produced in the pyrolysis of shale from a drill hole at Christian County, Kentucky, at selected temperatures for 18 hours.

Composition	Pyrolysis temperature ($^{\circ}C$)			
	60 $^{\circ}$ (%)	145 $^{\circ}$ (%)	300 $^{\circ}$ (%)	450 $^{\circ}$ (%)
methane	1.7	1.8	20.2	18.8
ethylene	-	1.1	7.0	6.6
ethane	0.1	2.0	13.8	15.8
propylene	0.1	1.7	10.7	11.7
propane	12.7	12.9	15.6	15.9
i-butane	5.0	8.7	6.4	3.5
1-butene	-	0.7	3.0	8.0
n-butane	51.0	40.9	16.9	18.2
1-pentene	-	0.3	0.5	0.5
n-pentane	29.4	29.8	6.0	1.4

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TABLE 3

Composition of product obtained from heating shale at 450°C for 15 minutes with various percentages of oxygen in the pyrolysis atmosphere.

Constituent	Yield of hydrocarbons (X 10 ⁻⁵ g/g shale)				
	O ₂ in pyrolysis atmosphere				
	1.48%	5.1%	10.11%	15.16%	20.0%
methane	78.93	91.60	119.56	81.76	86.29
ethylene	17.96	21.01	27.97	21.66	23.80
ethane	68.20	75.94	92.61	67.42	68.03
propylene	35.86	40.89	50.19	38.73	38.87
propane	47.77	50.84	60.04	45.92	44.77
butenes	22.97	24.77	29.26	23.25	22.15
i-butane	4.00	4.29	5.01	3.86	3.66
n-butane	24.19	26.00	30.04	23.08	21.76
cyclopentane	0.56	0.63	0.65	0.55	0.43
pentenes	11.54	12.72	14.70	10.97	9.90
i-pentane	7.82	8.67	10.40	7.58	6.95
neo-pentane					
n-pentane	7.45	7.73	8.33	6.44	5.78
cyclohexane					
methyl-cyclohexane	0.70	0.73	0.62	0.56	0.44
hexenes	3.73	4.00	4.05	3.25	3.05
i-hexane & isomers	3.67	3.81	3.71	3.19	2.93
n-hexane	2.41	2.45	2.44	1.96	1.86
benzene	1.72	1.72	1.71	1.44	1.37
C ₇ 's	5.70	5.62	4.59	6.48	3.75
C ₈ 's	1.98	1.54	0.73	1.05	0.89
acetone	0.41	0.59	1.27	1.57	2.27
CH ₃ CHO	11.17	14.13	15.86	37.70	33.49
CO	6.03	9.77	37.29	70.09	84.27
CO ₂	14.16	21.78	84.05	140.23	161.96
Total	378.93	431.23	605.08	598.74	628.67

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Figure 1. Location of wells.

Figure 2. GC trace of light hydrocarbon gases from shale pyrolysis. Column: stainless steel 2m x 3mm I.D. Chromasorb 102. Temperature programmed from 40°C to 180°C (held at 180°C for 8 minutes). Hydrocarbon gases: (1) Methane, (2) Ethylene, (3) Ethane, (4) Propylene, (5) Propane, (6) Cyclopropane (std.), (7) iso-Butane, (8) 1-Butene, (9) Butane, (10) 2-Butenes, (11) Acetone, (12) 1-Pentene, and (13) Pentane.

Figure 3. GC trace of light hydrocarbon gases from shale pyrolysis. Column: stainless steel 2m x 3mm I.D. Carboxack C/O.2 percent CW 1500. Temperature programmed from 40°C to 180°C (held at 180°C for 10 minutes). Hydrocarbon gases: (1) Methane, (2) Ethane and Ethylene, (3) Cyclopropane (std.), (4) Propane and propylene, (5) iso-Butane, (6) 1-Butene, (7) n-Butane, (8) Neopentane, (9) Cyclopentane, (10) saturated C₅, (11) iso-Pentane, (12) 1-Pentene, (13) cis-2-Pentene, (14) trans-2-Pentene, (15) n-Pentane, (16) iso-Pentene, (17) Cyclohexane, (18) Methyl-Cyclopentane, (19), (20) saturated iso-Hexane isomers, (21) iso-Hexane, (22) Benzene, (23) 1-Hexene, (24) trans-2-Hexene, (25) n-Hexane, (26) n-Heptane, and (27) n-Octane.

Figure 4. The organic carbon content versus the volume of gas released at room temperature from shale samples taken at 10-foot intervals from the core at Effingham County, Illinois.

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Figure 6. Typical GC trace of gaseous products from shale pyrolysis at 60°C (C, D) and at 300°C (A, B). A and C—Chromasorb 102 column; B and D—Carbowack C/0.2 percent C/W 1500 column.

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Figure 7. The alkane/alkene ratio of the hydrocarbons produced by pyrolysis of shale as a function of temperature.

Figure 8. The total yield of hydrocarbons (C₁-C₅) produced from shale as a function of pyrolysis temperature.

Figure 9. The alkane/alkene ratio of hydrocarbons produced by the pyrolysis of shale as a function of the percentage of oxygen in the pyrolysis atmosphere.

Figure 10. The yield (x10⁻⁴) of CO₂, CO, CH₃CHO, and the yield (x10⁻⁴) of CH₃COCH₃ produced by the pyrolysis of shale as a function of the percentage of oxygen in the pyrolysis atmosphere.

Medium Volatile Hydrocarbon Analysis

No new data for volatile hydrocarbons has been developed this quarter

Solvent Extraction

Four black shale samples have been extracted with benzene soxhlet extraction. Each sample was extracted for 40 hrs.

The soxhlet extracts were further separated by column chromatography into three fractions - aliphatic, aromatic, and asphaltene. The samples extracted, the percent of total shale extracted, and the percent of each fraction from the chromatography separation are given in Table III-C-3. The 01KY samples are from Christian County, Kentucky, the 01IN04C1 sample is from Sullivan County, Indiana, the 13IL17C3(S00406) sample is from Wayne County, Illinois.

Elemental analyses were made on the total extracts and the chromatographic fractions. The hydrogen to carbon ratios were calculated from the analytical results. The elemental analysis and H/C ratios are given in Table III-C-4. Asphaltene fractions were predominate in the benzene-methanol extraction of shale samples 04IL14C1, 01KY07C1, composite 06IL18-20C1, 06IL10C1, 06IL25C1 and composite 01KY01L1 and 01KY05L1, (See quarterly report Jan. 8, 1978). But in a benzene only extraction of shale, the aliphatic fraction appears to be the major chromatographic fraction (except sample 01KY10C1).

Further analyses on each aliphatic, aromatic and asphaltene fractions from the benzene extraction will be used for comparison to that from the benzene-methanol extraction.

A "neutral" aromatic fraction of core sample S00268 benzene-methanol extract was separated by using ion-exchange chromatography. Its GTC spectrum is shown on Fig. 1-5. The "neutral" fraction thus obtained was analyzed by GC-MS and this spectrum compared to the GC-MS spectrum obtained for this sample prior to ion-exchange separation. Only slight differences in the two spectra were detected.

Tentative identification was made for 46 compounds in the silica gel aromatic fraction and 48 compounds in the "neutral" fraction. Together, a total of 55 compound identifications have been made. The compounds are largely two- and three-ring condensed aromatic compounds substituted with one or more aliphatic side-chains. (See table III-C-5) Two phthalate ester contaminants were observed; they appeared only in the benzene-methanol sample, and were by far the largest peaks in this run. A very small and very late-eluting peak in the ion-exchange sample showed a significant ion at m/e 252. Subtraction of background indicated that this was very probably the molecular ion of a benzopyrene derivative.

TABLE III-C-3

Sample	Organic Carbon(%)	Benzene Extract(%)	% Recovery	Aliphatic	Aromatic	Asphaltene
01KY03C2	8.15	0.32	92.6	41.9	29.0	21.7
01KY10C1	9.23	0.87	103.3	14.8	25.2	63.3
01IN04C1	11.73	0.66	95.6	39.6	23.5	32.5
13IL17C3	8.4	0.53	93.2	40.6	25.3	27.3

TABLE III-C-4

Sample		Extract (benzene)	Aliphatic	Aromatic	Asphaltene
01KY03C2	C	86.10	87.03	88.12	79.83
	H	10.37	12.81	8.68	7.53
	N	0.71	0.00	0.64	1.73
	S	1.00	-	-	1.28
	H/C	1.44	1.75	1.17	1.12
S00010	C	85.53	86.03	88.10	84.72
	H	9.74	13.53	10.04	8.41
	N	1.34	0.00	0.00	1.82
	S	1.69	-	-	1.83
	H/C	1.36	1.87	1.36	1.18
01IN04C1	C	84.24	67.71	87.72	76.43
	H	11.22	11.10	9.99	8.70
	N	0.59	0.00	0.00	0.83
	S	1.20	-	-	1.15
	H/C	1.59	1.97	1.36	1.36
13IL17C3 (S00406)	C	86.73	86.68	89.16	85.66
	H	11.40	13.55	9.73	8.18
	N	0.42	0.00	0.00	1.41
	S	0.43	-	0.76	0.84
	H/C	1.57	1.86	1.30	1.14

Fig. 1

FIG. 2

** SPECTRUM DISPLAY/EDIT **
 01K70302 AROM. FRAC. (ION EXCH.) GEOLOGICAL SURVEY
 120-23003 SISO 2 OCTOBER 1979

FRN 7051
 1ST 50 PG: 755
 X= .50 Y= 1.00

Fig. 3

** SPECTRUM DISPLAY/EDIT **
01KY03C2 AROM. FRAC.(ION EXCH.) GEOLOGICAL SURVEY
120-22003 SISO 2 OCTOBER 1979

FPH 7051
1ST SC/PG:1117
X= .50 Y= 1.00

Fig. 4

FIG. 5

TABLE III-C-5 Shale Aromatic Fraction Summary

Ion Exchange		Benzene-MeOH		Key Ions	Tent. Identification
Scan #	Ret. Time	Scan #	Ret. Time		
186	9.2	184	9.2	142	A methylnaphthalene
203	9.7	199	9.6	"	"
277	11.8	274	11.8	154	Biphenyl ¹
300	12.3	296	12.3	141 156	A dimethylnaphthalene ²
312	12.8	326	13.2	" "	"
332	13.3	330	13.3	" "	"
354	14.0	350	13.8	" "	"
371	14.4	---	---	" "	"
409	15.5	405	15.4	141 168	A methylbiphenyl ¹ ?
439	16.3	434	16.2	155 170	A trimethylnaphthalene
451	16.7	447	16.5	205 220	BHT?
---	---	455	16.8	155 170	A trimethylnaphthalene
---	---	462	17.0	" "	"
472	17.3	468	17.1	" "	"
491	17.8	488	17.7	" "	"
---	---	493	17.8	" "	"
513	18.5	511	18.3	" "	"
541	19.2	537	19.0	" "	"
559	19.7	---	---	155 184	A tetramethylnaphthalene
584	20.4	---	---	169 "	"
624	21.6	625	21.5	" "	"
652	22.3	653	22.3	" "	"
665	22.8	666	22.7	165 180	A methylfluorene ³
671	22.9	672	22.8	155 184	A tetramethylnaphthalene
---	---	710	23.9	169 "	"
741	25.0	---	---	184	"
775	25.9	779	25.8	178	Phenanthrene ⁴
799	26.6	---	---	179 194	A dimethylfluorene ³
807	26.9	812	26.7	" "	"
832	27.6	837	27.4	" "	"
838	27.8	843	27.6	195 210	Tetramethylbiphenyl ¹
864	28.5	869	28.3	197 198	A pentamethylnaphthalene ⁵
888	29.2	894	29.0	" "	"

TABLE III-C-5 continued

Ion Exchange		Benzene-MeOH		Key Ions	Tent. Identification
Scan #	Ret. Time	Scan #	Ret. Time		
910	29.8	899	29.2	197 198	A. pentamethylnaphthalene ⁵
914	30.0	921	29.7	192	A monomethylphenanthrene ⁴
920	30.2	926	29.9	"	"
943	30.3	949	30.5	"	"
---	---	954	30.7	"	"
---	---	998	31.9	149	A phthalate ester
1005	32.6	1016	32.4	212	A hexamethylnaphthalene ⁶
1031	33.4	---	---	"	"
1074	34.5	1084	34.3	191 206	A dimethylphenanthrene ⁴
1079	34.8	1091	34.5	" "	"
1083	34.9	1095	34.6	" "	"
1095	35.2	1108	35.0	" "	"
1109	35.6	1123	35.4	" "	"
1125	36.0	1140	35.9	" "	"
1171	37.5	---	---	205 220	A trimethylphenanthrene ⁴
1193	38.1	1210	37.9	" "	"
1201	38.3	1219	38.1	" "	"
1218	38.8	1237	38.6	" "	"
1287	40.9	1305	40.6	" "	"
1383	43.7	---	---	219 234	A tetramethylphenanthrene ⁴
---	---	1413	43.6	149	A phthalate ester
2752	84.0	---	---	252	A benzopyrene?

¹Or acenaphthene. ²"Polymethyl" isomers may alternatively contain higher alkyl substituents.

³Or phenalene. ⁴Or anthracene. ⁵Or C₁₃H₁₀S: see text. ⁶Or C₁₄H₁₂S.

Isotopic Analysis of Off-Gases

A new mass-spectrometer was recently acquired at the Department of Geology of the University of Illinois. During the 2 months when this instrument was being installed and calibrated, we were unable to perform any isotopic analyses. The new instrument is now on-line (although some problems are still being encountered), and we have begun analyzing samples again.

Each of the 69 canned cores from the Wayne County drill site have been sampled for isotopic analysis at two different times, once on 10/11/79 and again on 11/12/79. The isotopic composition of methane has been determined for 26 of those gas samples taken on 10/11/79. The results of these analyses are tabulated below.

<u>Canister #</u>	<u>$\delta C^{13}CH_4$ o/oo</u>
4	-52.1
5	-53.0
6	-52.7
9	-52.2
10	-52.2
13	-53.0
22	-51.4
23	-52.1
24	-52.1
25	-50.8
26	-50.9
27	-50.2
28	-51.5
29	-52.1
30	-52.1
32	-51.8
34	-51.4
35	-50.9
36	-49.5
37	-50.4
38	-49.0
40	-49.8
41	-50.0
42	-50.1
63	-51.8
66	-50.2

Laboratory Study of Chemical and Isotopic Fractionation

The last of the pressurized vessels containing plugs of shale were scheduled to be bled off during December; however, because of the lack of a mass spectrometer to allow immediate analysis, it was decided to wait until January. Previous experience has shown that long term storage of samples frequently results in loss or contamination of the sample by leakage of the sample vial.

Adsorption/Desorption Studies of Gases Through Shales

Introduction

With nitrogen and carbon dioxide, determine internal surface area on shale core samples; on selected samples, use methane as the adsorbate (sorbate) at pressures within the range of 1 to 80 atmospheres. Comparison of these properties in gas-producing and non-gas-producing shales will be made to determine the relationship of shale physical properties to gas recovery.

Progress

Core samples from the Wayne County, Illinois core (13IL) have been received and sieved to the desired mesh size for gas adsorption studies. The internal surface area measurements with nitrogen and carbon dioxide have been made on 8 of the 24 samples to be studied. All of the samples will be completed in January and we will report the data in the next monthly report. Most of the samples selected for methane adsorption (sorption) at high pressures will be very compact with considerable ultramicroporosity (pores $< 5\text{\AA}$). Thus, long outgassing and adsorption periods will be required before equilibrium is reached. Therefore, high-pressure data will not be complete until the end of February.

CONTRACTOR FINANCIAL MANAGEMENT REPORT				REPORT FOR MONTH ENDING				
				November 30, 1979				
TO: U.S. Department of Energy Contract Division Research Contracts, Procedures and Reports Branch P.O. Box 5, Oak Ridge, Tennessee 37830			FROM: Robert E. Bergstrom Neil F. Shimp Illinois State Geological Survey Urbana, Illinois 61801			2. CONTRACT VALUE \$		
						3. FUND LIMITATION \$		
1a. TYPE 1. DESCRIP. Contract			b. NO. (US ERDA) ORO-DE- AC21-76-MC05203			4. INVOICE AMOUNTS BILLED \$		
2. SCOPE OF WORK CONTRACT Geology, Geochemistry Devonian Black Shale			c. AUTH. CONTRACT REPRESENTATIVE (Signature) Robert E. Bergstrom Neil F. Shimp 1/7/80			5. TOTAL PAYMENTS RECEIVED \$		
6. REPORTING CATEGORY			7. COSTS INCURRED		8. ESTIMATED COSTS/ \$		9. ESTIMATED FINAL COSTS	
			DURING MONTH a.		CUMULATIVE TO DATE b.		SUBSEQUENT MONTH a.	
					BALANCE OF FISCAL YEAR b.		TO COMPLETE BALANCE OF CONTRACT c.	
Salaries, wages			\$ 7,677.30		\$ 345,565.20		\$ 7,600.00 \$ 39,896.13	
Indirect cost			5,067.02		226,091.01		5,000.00 27,018.49	
Fringe benefits			511.50		28,498.28		600.00 44,726.24	
Commodities, materials, supplies			2,089.65		23,106.81		1,000.00 6,399.47	
Travel			1,088.09		14,279.47		500.00 1,664.45	
Equipment			540.00		56,225.86		200.00 679.64	
Laboratory preparation			---		1,011.30		--- 1,988.60	
Computer			31.98		26,352.16		--- - 886.94	
Contractual			---		5.10		--- 2,045.90	
Nuclear reactor			845.00		4,977.50		--- 4,287.50	
Mass spectrograph			1,867.00		6,467.00		--- 8,033.00	
Telecommunications			45.82		1,121.82		20.00 478.18	
Totals			\$19,763.36		\$733,701.51		\$14,920.00 \$136,330.66	