Geol Survey

Final Report

Geologic and Geochemical Studies of the New Albany Shale Group (Devonian-Mississippian) in Illinois

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R. E. Bergstrom and N. F. Shimp, Principal Invistigators
Robert M. Cluff, Project Coordinator

Illinois State Geological Survey
Open File Series 1980-2

June 30, 1980

Illinois State Geological Survey
Urbana, IL 61801

Prepared for
U.S. Department of Energy
Morgantown Energy Technology Center
Morgantown, WV 26505

Contract: U.S. Department of Energy DE-AC21-76ET12142

Note to readers: Printouts of the data contained on the computer file and copies of the structure map mentioned in this report can be obtained from the Illinois State Geological Survey upon written request.

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Studies of the New Albany Shale Group were under the general direction of Robert E. Bergstrom and Neil F. Shimp, Principal Investigators for geology and geochemistry. The investigators who conducted the scientific studies and produced the results in this report are listed as authors of the individual sections.

Robert M. Cluff coordinated and summarized the findings and conclusions from the various sections in the production of this final report. The Principal Investigators recognize his efforts as a major contribution.

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1. Stratigraphy and structure: Jerry A. Lineback, Mark L. Reinbold, David L. Stevenson, and Robert M. Cluff
2. Mineralogic and petrographic characterization: Robert M. Cluff, Richard D. Harvey, and W. Arthur White
3. Physical properties: Paul B. DuMontelle and Stephen R. Hunt
4. Mineral resources evaluation system: Lindell Van Dyke

Geochemical Projects

1. Major, minor, and trace elements: Joyce K. Frost and R. R. Ruch
2. Trace element distribution in organic and inorganic phases: Robert A. Keogh and John K. Kuhn
3. Hydrocarbon phases: Donald R. Dickerson and Dennis D. Coleman
4. Adsorption/desorption of gases through shale: Josephus Thomas and Robert R. Frost

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ENGLISH AND SI (METRIC) UNITS

Throughout this report both English and SI (metric) units are indicated for all measurements. In general, the units given first are those in which the data were originally collected or measured, and they are followed in parentheses by the calculated equivalent in the other system. In most cases English units will be given first because nearly all subsurface geologic data and drilling information in the United States are recorded using English units (feet). Many laboratory measurements, however, were made with apparatus calibrated in SI units (for example, sonic velocity determinations) and in those cases the SI units appear first.

I. PRINCIPAL RESULTS

This section summarizes the principal results of our study of the New Albany Shale Group in Illinois

GEOLOGY

The New Albany Shale Group in Illinois can roughly be divided into three regions:

1. The major depositional center in southeastern Illinois, where the New Albany reaches a maximum thickness of 460 feet (140 m), is predominantly laminated black shale, and is composed primarily of the Blocher, Selmier, and Grassy Creek Shales.
2. A second depositional center in southeastern Iowa and west central Illinois, where the New Albany is more than 300 feet (90 m) thick, is mostly bioturbated olive-gray and greenish-gray shale; it contains the Sweetland Creek Shale, Grassy Creek Shale, Saverton Shale, Louisiana Limestone, Horton Creek Formation, and Hannibal Shale.
3. A northeast-southwest trending area of thin New Albany Shale separating the two depocenters. This area of thin shale consists of interfingering gray and black shales. The Sweetland Creek, Grassy Creek, Saverton, and Hannibal Shales are the dominant formations.

The New Albany Group is middle Devonian at the base (Blocher Shale) and is early Mississippian (Kinderhookian) at the top (Hannibal Shale).

The main lithologic characteristics of the New Albany formations are as follows:

The *Blocher Shale* is a brownish-black to grayish-black, finely laminated, carbonaceous, calcareous and dolomitic shale.

The *Sylamore Sandstone* is a thin, time transgressive sandstone or sandy zone at the base of the New Albany.

The *Selmier Shale* contains alternating beds of laminated brownish-black to grayish-black shale and bioturbated olive-gray to olive-black shale.

The *Sweetland Creek Shale* consists of alternating beds of dark and light greenish-gray, indistinctly bedded, bioturbated shale.

The *Grassy Creek Shale* is dominantly brownish-black to grayish-black, laminated, pyritic, carbonaceous shale.

The *Saverton Shale* consists of interbedded greenish-gray, dark greenish-gray, and olive-gray bioturbated shale.

The *Louisiana Limestone* is a micritic carbonate present only at places in western Illinois.

The *Horton Creek Formation* contains limestone (including the Hamburg Oolite Bed), siltstone, sandstone, and shale at places in western Illinois.

The *Hannibal Shale* consists of greenish-gray, olive-green, and dusky yellow-green bioturbated mudstone and shale.

The New Albany apparently was deposited in a deep-water, stratified, *anoxic basin* centered in southeastern Illinois and adjacent western Kentucky. Fossiliferous carbonates were deposited in a very restricted aerobic zone. Bioturbated greenish-gray shales and indistinctly bedded shales were deposited in a transitional dysaerobic zone. Laminated brownish-black shales were deposited in the anaerobic zone. Anerobic conditions persisted throughout most of New Albany deposition in southeastern Illinois whereas dysaerobic conditions predominated in western Illinois. The area of thin New Albany between the main depocenters is characterized by the interbedding of dysaerobic and anaerobic shales.

Linear features on satellite images and air photographs proved to be related to glacial landforms. Few bedrock structures were detected by remote sensing.

Extensive fracturing and faulting occurs in southern and southeastern Illinois.

Petrographic studies have identified and characterized five major lithofacies in the New Albany Shale: (1) limestones and dolomites; (2) highly bioturbated mudstones; (3) indistinctly bedded shales; (4) thickly laminated shales; and (5) finely laminated shales.

The distribution of shale lithofacies was determined by the depositional environment of the shale, especially wave energy, bottom oxygenation, and bottom topography (water depth).

The mineralogy of the New Albany Shale is relatively uniform. The predominant silt-sized constituents are quartz, feldspar, and muscovite. Dolomite and pyrite are minor components of most samples. The predominant clay constituent is illite, with minor chlorite and mixed-layer illite-smectite in virtually all beds.

Reflected light studies of kerogen indicate that the organic matter in the brownish-black shales is predominantly Type II kerogen (oil-prone), whereas the organic matter in the greenish-gray shales is Type III kerogen (gas-prone). The differences in kerogen types are believed due to selective preservation rather than to variations in the type of organic matter deposited.

Vitrinite reflectance and liptinite fluorescence studies reveal increasing thermal maturation of organic matter to the southeast and can be related to the structure of the basin.

Studies of the amount and type of organic matter, thermal maturation, and the occurrence of solid hydrocarbons strongly suggest that active petroleum generation and expulsion occurred in southern and southeastern Illinois and western Kentucky. Nowhere in the Illinois Basin is the shale known to have reached the principal zone of gas generation.

Preferred weakness (planes) in shale cores was not found with use of acoustic compressional wave velocity determinations, nor were weakness directions found by x-ray particle orientation techniques.

Mechanical testing by the point-load method proved to be a good way of showing the preferred plane of weakness in cores; these directions of weakness matched results shown by indirect tensile strength testing at 30° intervals of azimuth.

GEOCHEMISTRY

No single method or combination of methods *used to isolate organic matter* from black shale yielded an ash-free organic fraction. The most successful method proved to be a series of acid treatments with dilute HNO_3, HF, and HCL. Ash contents of the isolated organic fractions ranged from 0.15 to 4.09 percent.

The zonal centrifuge techniques using aqueous sucrose densities were ineffective for separating small amounts of finely disseminated organic matter from the mineral matrix of whole shales.

Residual mineral matter in the isolated organic fraction prevented conclusive assignment of trace elements to the organic or inorganic phases. However, data for Ni, U, Se, Sb, Mo, and V indicate that at least a portion of their concentrations in the isolated organic fraction is due to their association with the organic matter.

The elements U, Mo, Sb, and Cs in the organic fraction show a positive correlation with the gas content of the whole shale; however, there is no significant difference in their enrichments between the gas-bearing and non-gas-bearing shales examined.

The amount of gas released from core samples correlated closely with gamma-ray intensity determined from borehole logs.

Combined pyrolysis-gas chromatography provides a simple, direct method for qualitatively characterizing the non-volatile organic matter contained in the shale. The composition of the pyrolysis products is influenced by both the pyrolysis temperature and the organic content of the shale.

Degradation of the organic matter takes place at temperatures above 550°C.

The quantity of non-condensable gases produced by pyrolysis of shale increased with increasing organic content of the shale and with increasing temperature. The increase in yield of gas was not linear, even for shale samples from the same core. Both saturated and unsaturated paraffins were produced.

The oxygen content of the atmosphere within the retort affects the composition of the pyrolysis products.

Results of pyrolysis studies may have important implications for the design of in situ retorting of shale for gas production.

Organic compounds evolved by heating shale are dependent on the pyrolysis temperature and on the organic content of the shale. Volatile indigenous compounds are evolved at low temperatures. These compounds can also be extracted by benzene-methanol solvent. The organic matter is degraded to highly volatile hydrocarbons by moderately high (about 550°C) pyrolysis temperatures.

Pyrolysis of the asphaltene fraction of the organic matter extracted from shale gives results similar to those obtained for the whole shale. Pyrolysis of shales of widely different stages of maturation yields results that are unique for each shale. The temperature of the initial fragmentation can be related to the interactions of the molecules or to the strength of the bonds in the large molecules making up the organic matter in the shale.

Isotopic fractionation occurs during outgassing of a core. Experiments show that with proper sampling techniques the fractionation is probably not sufficient to cause errors in interpretations based on analysis of off-gases.

Gases analyzed in this study all appear to be of *low-grade thermal origin,* with no significant contribution of bacterial gas.

Gases obtained from core 02IL have chemical and isotopic compositions similar to solution gases from oil deposits directly beneath the shale. The data suggest a common origin for the gas in the shale and for the gas in the oil. Caution is advised when interpreting the gas content of Devonian shales in the immediate vicinity of oil reservoirs.

The isotopic composition of methane appears to correlate with the vitrinite reflectance value of the shale. The methane is isotopically lighter, however, than would be predicted by the gas-source rock pairs reported by Stahl (1977).

Porosity of a shale depends upon three major factors—depth of burial, carbonate content, and organic content.

Shales can hold appreciably more methane at their burial depths than is typically found in gas-bearing cores.

Methane not only occupies pore space but is also pressure-solubilized in the organic portion of the matrix in the more deeply buried shales of high-organic content.

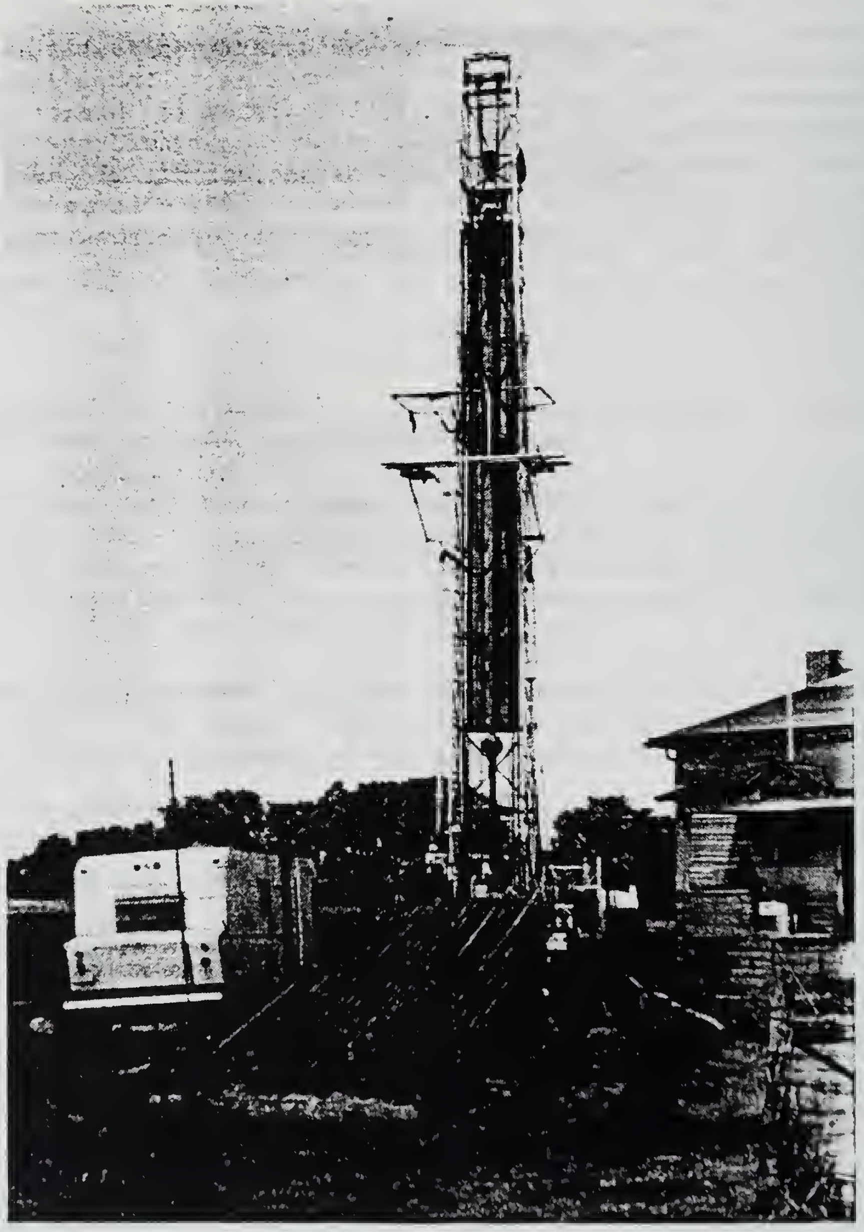
Shales with molecular sieve characteristics are produced with increasing depth of burial combined with increasing organic content. Much of the total pore volume is associated with ultramicropores, or passageways, with diameters less than 5 angstrom units.

The release-rate of methane from shale is a function of the degree of ultra-microporosity present in the shale, and is also a function of shale "particle" size and orientation.

The two desirable factors which apparently contribute the most to methane generation—increased burial depth (for thermal degradation) and increased organic content—also produce a very low-permeability structure detrimental to rapid gas release.

NATURAL GAS PRODUCTION

The best potential for gas production was determined to lie in a 19-county area in southeastern Illinois corresponding to the main depocenter of the New Albany. In this area the New Albany is thickest, and contains the greatest percentage of brownish-black, organic-rich shale. This area also corresponds to the area of deepest burial and greatest thermal maturity of organic matter in the shale. Adjacent parts of Indiana and Kentucky may also be included in this area of highest potential.



Henderson County core site (July, 1977).

II. INTRODUCTION

In September 1976 the Illinois State Geological Survey began geologic and geochemical studies of the New Albany Group in Illinois to evaluate its potential for yielding hydrocarbons, particularly natural gas. The Survey also performed chemical and physical analyses of Devonian shale samples from other states, submitted by agencies participating in the United States Department of Energy (DOE) research program on the Devonian gas shales of the eastern United States.

The DOE-sponsored program is keyed to the national goal of developing increased self-sufficiency in energy resources in the United States. Devonian shale formations in the Appalachian Basin, from eastern Tennessee to southern New York, have yielded significant quantities of natural gas. Currently, about 9,600 wells produce gas from Devonian shales in the Appalachian Basin. One giant gas field alone, the Big Sandy Field in eastern Kentucky, has produced over 2 trillion cubic feet (5.6×10^{10} cu m) of natural gas from Devonian shale.

The Devonian black shale in the Appalachian Basin attains a maximum thickness of about 1,500 feet in parts of Pennsylvania. It also occurs in the Illinois Basin, underlying the southern parts of Illinois and Indiana and the western part of Kentucky. In Illinois the black shale is called the New Albany Group (Devonian and Mississippian age) and attains a maximum thickness of about 460 feet (140 m).

Although lithologically similar to the Devonian shales of the Appalachian Basin, the New Albany has produced gas in only a few small areas of Indiana and western Kentucky. There has been no known gas production from the New Albany in Illinois, and few oil and gas operators in the Illinois Basin have even considered the shales a viable exploration target. Because of the great lateral extent and thickness of the shales, however, resource estimates of the total gas trapped within them are vast. If suitable technologies can be developed to recover the gas from these low permeability reservoirs and thereby increase the productive capacity of wells, the Devonian shales might become an important source of natural gas in the near future.

On the basis of proven large volumes of natural gas in the Devonian black shale in the Appalachian Basin and indications of significant hydrocarbon content in the equivalent New Albany Group in the Illinois Basin, the Illinois State Geological Survey conducted geological and geochemical investigations in Illinois to determine the character and magnitude of this potential resource.

The objectives of the ISGS investigation were:

1. To compile available drill-hole and outcrop data on the New Albany Group in Illinois. Six oriented cores of the New Albany Group obtained through contractual drilling arranged by DOE provided an important new source of data.

2. To study the stratigraphy and structure of the New Albany Group (along with overlying and underlying rocks) in Illinois to determine the relationship of stratigraphy and structure to the occurrence of hydrocarbons (especially natural gas).

3. To obtain selected data for comparison with geophysical logs to facilitate appraisal of the New Albany Group.

4. To characterize in detail the New Albany Group in Illinois with respect to physical, mineralogical, and chemical properties and hydrocarbon content in order to determine the most favorable targets for production of hydrocarbons under more sophisticated techniques of extraction.

5. To encode geologic and chemical data obtained in the investigation in a computer format (MINERS) designed for rapid retrieval and graphic presentation.

6. To characterize chemically the Devonian shales to facilitate (1) evaluation of their economic importance; (2) exploration for natural gas; and (3) environmental assessment of the possible effects of exploitation of this resource.

Bob Keogh and Dave Stevenson sample Henderson County core for off-gas analysis (July, 1977).

III. BASIC DATA FILE, CORING OPERATIONS, AND SAMPLE ACQUISITION

BASIC DATA FILE OF DEVONIAN AND DEEPER TESTS IN ILLINOIS

More than 20 years ago the Oil and Gas Section of the Illinois State Geological Survey began to keep a separate set of records for tests drilled through the base of the New Albany Shale Group (Middle Devonian-Kinderhookian). These records became known as the "Devonian and deeper file." The data in the records range from basic items such as well name, location, elevation, and total depth to detailed geologic information such as formation tops and partial sample studies. This file has been used a great deal by Survey staff members and by visitors to the Survey because it expedites the acquisition of deep subsurface data in Illinois.

As part of the present study, the ISGS has updated, revised, and encoded the data in the Devonian and deeper files for computer processing. Approximately 12,900 Devonian tests in southern and central Illinois were entered into the computer data base. The data in the computer file includes:

Unique well number (composed of state and county code and county number)

Company name, drill hole number, and farm name

Legal location (including section, township, range, and location within section)

Elevation of logging reference

Total depth

Deepest formation penetrated

Illinois State Geological Survey sample set number

Date drilled

Availability of geophysical logs

The Survey has published a 2-volume, computer-generated listing of this data (Stevenson, D. L., J. N. Keys, and R. M. Cluff, 1980a, 1980b) to facilitate exploration for deep oil and gas in Illinois and to encourage the investigation of unconventional energy resources, such as gas in Devonian shales.

CORING OPERATIONS AND SAMPLE ACQUISITION

Samples for physical, lithologic, mineralogic, and geochemical analysis were obtained from five sources:

DOE-sponsored core drilling. Six cores through the New Albany Shale Group in Illinois and western Kentucky were drilled as part of the Eastern Gas Shales

Project. This group of oriented cores was the principal source of samples for lithologic, mineralogic, and geochemical analyses and the sole source of samples for destructive testing of physical properties. During the drilling of the wells Survey personnel collected, described, and sampled 1,232 feet of shale core. The DOE-sponsored cores are summarized as:

1. Orbit Gas #1 Ray Clark (core 01KY)
   Location: 650 feet NL 90 feet EL of Kentucky grid Section 12-G-25,
   Christian County, Kentucky
   Drilled: September, 1976
   Elevation: 548 feet above mean sea level (kelly bushing)
   Recovery: 129 feet oriented core

2. Tri-Star Production #1-D Lancaster (core 02IL)
   Location: SE 1/4 SW 1/4 NW 1/4 Sec. 31, T. 9 N. R. 4 E. Effingham
   County, Illinois
   Drilled: February, 1977
   Elevation: 612 feet above mean sea level (ground level)
   Recovery: 88 feet oriented core

3. Northern Illinois Gas #1 RAR (core 04IL)
   Location: SW 1/4 SW 1/4 NE 1/4 Sec. 32, T. 8N. R. 4W. Henderson
   County, Illinois
   Drilled: July, 1977
   Elevation: 722 feet above mean sea level (ground level)
   Recovery: 303 feet oriented core

4. Northern Illinois Gas #1 MAK (core 06IL)
   Location: NE 1/4 NE 1/4 NW 1/4 Sec. 8, T. 23N. R. 2W., Tazewell
   County, Illinois
   Drilled: August, 1977
   Elevation: 641 feet above mean sea level (ground level)
   Recovery: 259 feet oriented core

5. Rector and Stone Drlg. #1 Missouri Portland Cement (core 11IL)
   Location: NE 1/4 NE 1/4 NE 1/4 Sec. 36, T. 11S. R 7E., Hardin
   County, Illinois
   Drilled: November, 1978
   Elevation: 578 feet above mean sea level (ground level)
   Recovery: 178 feet partially oriented core

6. Cordon T. Jenkins #1 Simpson (core 13IL)
   Location: SW 1/4 SE 1/4 SW 1/4 Sec. 17, T. 3S., R. 8E., Wayne
   County, Illinois
   Drilled: October, 1979
   Elevation: 387 feet above mean sea level (kelly bushing)
   Recovery: 275 feet oriented core

The locations of these six cores are shown on figure III-1.

Cores from ISGS files. Two cores through the entire New Albany Shale Group and three cores through a portion of the New Albany were obtained from the ISGS permanent core collection. Oil and gas operators donated three additional cores through part of the New Albany Shale to the Survey during the course of this study. All these cores were examined and sampled for lithologic, mineralogic, and geochemical analysis as part of the present study. (The locations of these wells are shown on figure III-1, and the well names and locations are listed in table III-1.) Detailed information on each of these cores can be obtained by request from the Illinois Geological Survey.

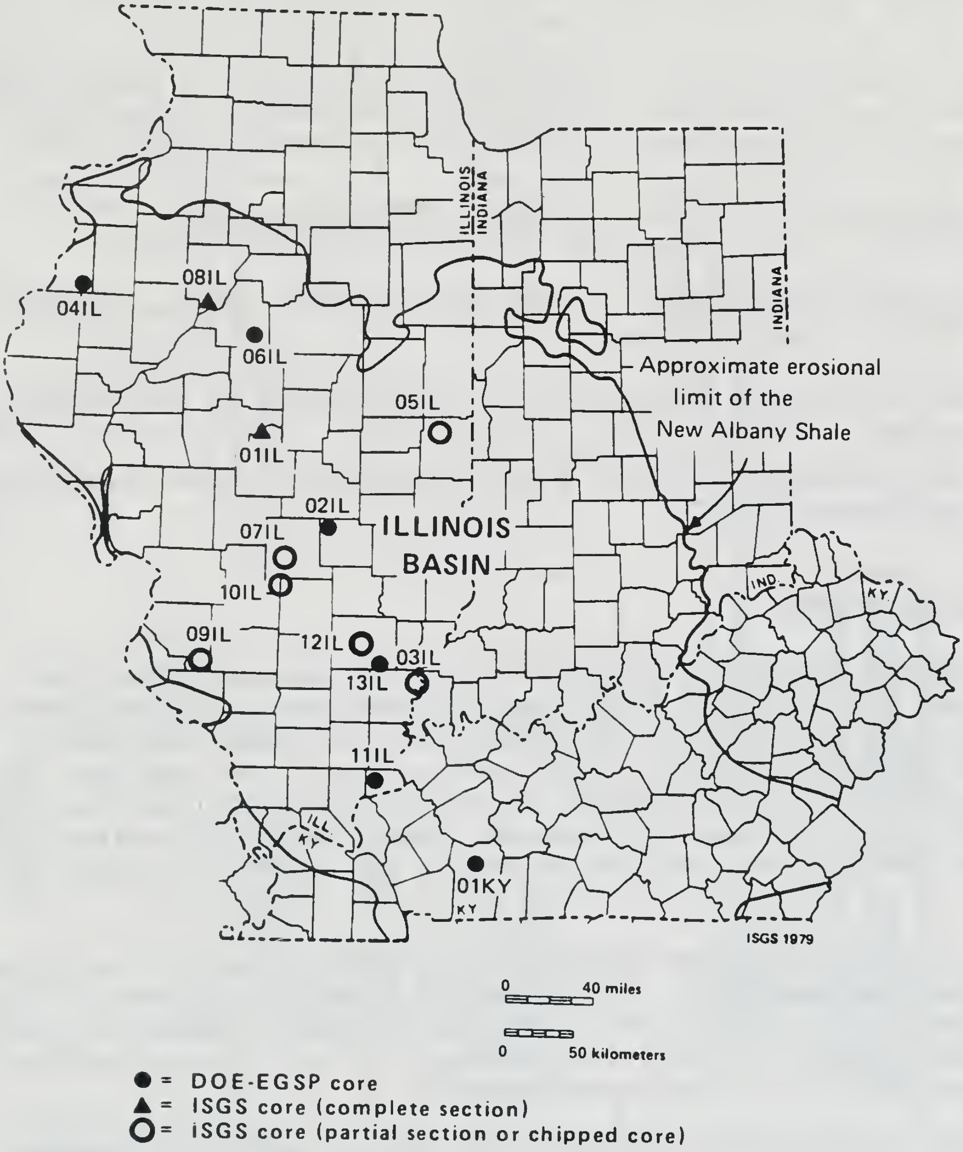


Figure III-1. Locations of the six DOE-sponsored cores through the New Albany Shale Group and of eight cores from the ISGS files.

Samples of drill cutting from ISGS files. From the ISGS Samples Library, Survey personnel handpicked 482 samples of rotary and cable tool drill cuttings from 123 wells penetrating the New Albany Shale. These samples were used for vitrinite reflectance, x-ray mineralogy, and trace element studies. The samples are serially numbered and are all preceded by the prefix NAS (for New Albany Shale). Table III-2 lists the well names and locations of these samples.

Miscellaneous samples from Illinois and other areas. A suite of 26 drill cutting samples was supplied by the Indiana Geological Survey for vitrinite reflectance analysis (table III-3). Samples of the New Albany Shale and adjacent strata were also collected from several outcrops in Illinois, Indiana, and western Kentucky for lithologic study. A few drill cutting samples from western Kentucky and Virginia were collected for comparison to the Illinois and Indiana data. All of the above samples were included in the NAS series.

A few samples of New Albany Shale from DOE-sponsored cores in Indiana and western Kentucky were provided by the Indiana and Kentucky Geological Surveys for comparison to Illinois. Most of these samples came from two cores:

Energy Resources of Indiana #1 Pheghly Farms (Core 01IN): NW 1/4 NW 1/4 NE 1/4 Sec. 14, T. 6 N., R. 10 W., Sullivan County Indiana

Norm #1 Knievim (Core 02KY): 17950 feet NL 13550 feet WL of Brooks Quadrangle, Bullitt County, Kentucky.

Sample numbers for samples from these cores are prefixed by the 4-digit codes shown above.

Processing and preparation procedures for the New Albany Shale samples are illustrated in figure III-2.

SAMPLE NUMBERING SYSTEM

A system of sample numbering devised at the Survey especially for this project is used in this report. The sample number consists of 8 ciphers. The first 4 ciphers identify the core from which the sample was taken: the first two indicate the order of the core by state; the third and fourth are the abbreviations for the name of the state. The fifth and sixth ciphers of the sample number indicate the data set. Each 10-foot interval of the New Albany in the core is identified by a data set numbered in order starting at the top.

The seventh cipher is a letter designating the main purpose for which the sample was taken and analyzed. "L" stands for lithologic studies; "C" for chemical analyses of off-gases and constituent elements (sealed in canisters at the drilling site); "S" for sonic testing; "T" for indirect tensile strength tests; and "P" for point-load tests.

The last cipher in the number indicates the specific number of the sample—lithologic or chemical—taken from that data set interval of the core. In the case of lithologic samples, L1 samples are selected by a geologist during examination of the core to be representative of the predominant lithology in that data set, and L2, L3, etc. are taken of accessory lithologies as needed. Thus, for example, the sample number 01IL02L2 identifies the second or accessory lithologic sample taken from the second data set down into the New Albany from the 01IL core. In a fully computerized system, the first four ciphers can be keyed to the 9-digit API identification to identify the specific location of the core.

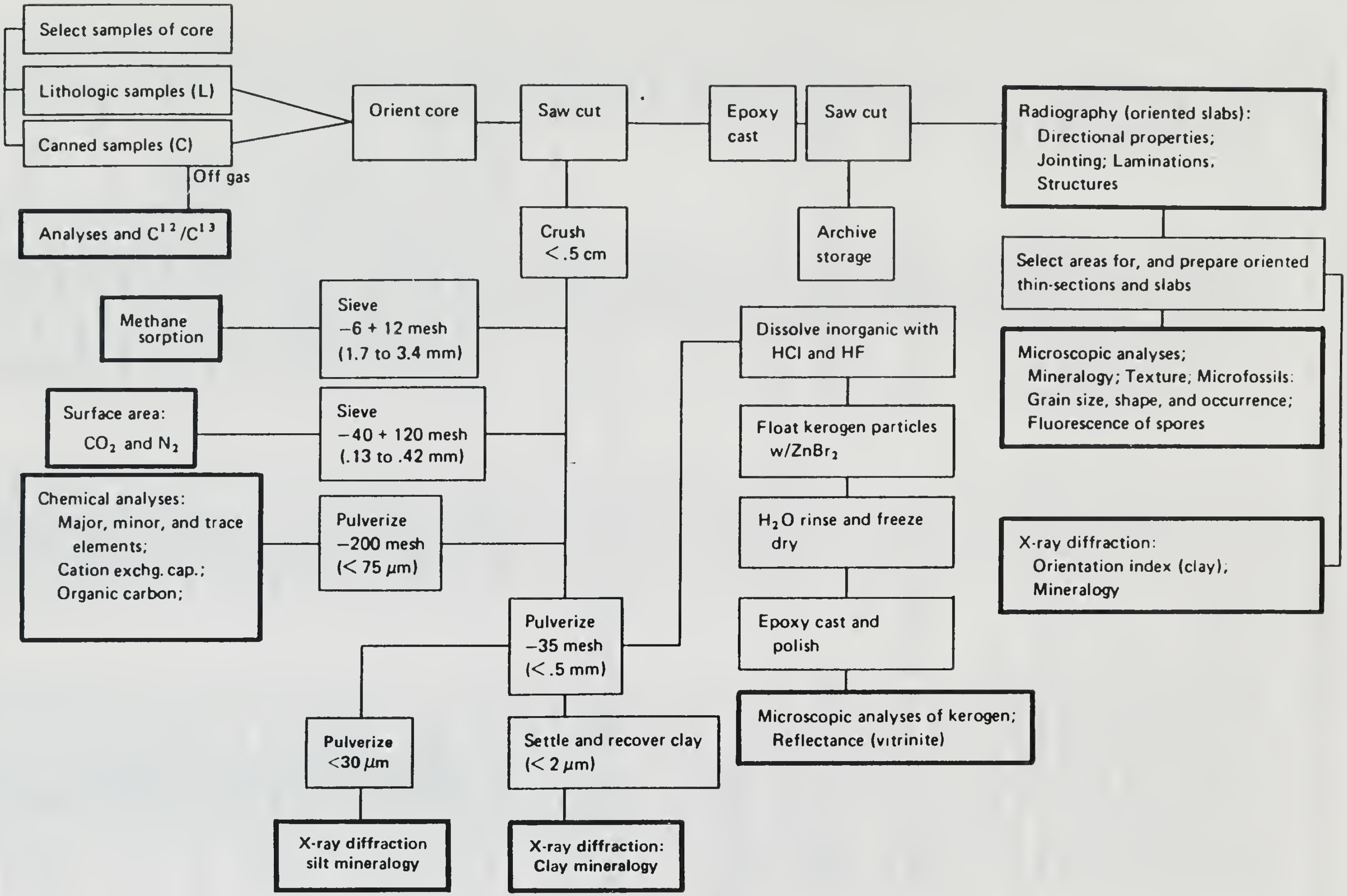


Figure III-2. Processing and preparation of samples of New Albany shales for mineralogic, petrographic, and geochemical analyses at the Illinois State Geological Survey. Sample preparation steps are in thin line boxes and analyses are in wide line boxes.

TABLE III-1. New Albany Shale cores used in this study.

Core designation	Well name	Location	County	
Illinois				
01IL	Miller #1 G. W. Sample	SW SW NE 11-15N-3W	Sangamon	▲
02IL	Tri Star Prod. #1D Lancaster	SE SW NW 31-9N-4E	Effingham	●
03IL	Superior Oil #C-17 H. C. Ford	C SW SE 27-4S-14W	White	○
04IL	No. Illinois Gas #1 RAR	SW SW NE 32-8N-4W	Henderson	●
05IL	Peoples Gas #1 Witt	SE SE SW 19-16N-13W	Edgar	○
06IL	No. Illinois Gas #1 MAK	NE NE NW 8-23N-2W	Tazewell	●
07IL	Benedum Trees #1 Van Zant	SW/C 24-6N-1W	Fayette	○
08IL	Midland Electric Coal #1 Peters	SW SW NE 11-7N-6E	Peoria	▲
09IL	Coral Oil #1 Schroeder	SE NW SE 6-3S-6W	St. Clair	○
10IL	Helm Petroleum #1 Ballance	SW NE SW 12-4N-1W	Fayette	○
11IL	Rector & Stone #1 Missouri Portland Cement	NE NE NE 36-11S-7E	Hardin	●
12IL	Hobson Oil #2 Taylor	SE NE NW 34-1S-7E	Wayne	○
13IL	G. T. Jenkins #1 Simpson	SW SE SW 17-3S-8E	Wayne	●
Indiana				
01IN	Energy Res. Indiana #1 Pheghly Farms	NW NW NE 14-6N-10W	Sullivan	●
Kentucky				
01KY	Orbit Gas #1 Ray Clark	650'NL 90'EL 12-G-25	Christian	●
02KY	Norm #1 Knievim		Bullitt	●

● = DOE-EGSP core
▲ = ISGS core (complete section)
○ = ISGS core (partial section)

TABLE III-2. Location of New Albany Shale (NAS) samples taken from well cuttings in Illinois[a].

Sample numbers (NAS-)	County	Sec-T-R	Well name
028-029	Clay	16-3N-6E	So. Ill. Oil #1 Mearns
030-032	Effingham	32-6N-5E	Juniper Petrl. 12x-32 Gerth
033-034	Jefferson	18-3S-1E	Dunnill #1 Kujawa
035-039	Madison	35-5N-7W	B. Hall #1 Wehling
040-043	Mason	3-19N-10W	Pinkston #1 Blessman
044-045	Washington	30-2S-3W	Amoco Prod. #1 Kolweier
046-047	Washington	27-3S-1W	Juniper Petrl. #24x-27 Kubiak
048-051	Washington	1-3S-4W	Anschutz #1 Eigenrauch
052-055	Wayne	27-1N-7E	Pure Oil #3 Billington
056-059	Wayne	14-1N-8E	Nation Oil #1 Van Fossan-Brown
060-063	Wayne	28-1S-6E	Texaco #5 Fuhrer
064-068	Wayne	29-2S-9E	Collins Bros. #1 Hill
069-074	Wayne	4-3S-7E	Savage/Zephyr #1 Sprague
083-088	Christian	28-13N-1W	Union Oil #1 Cleveland
089-092	Gallatin	11-8S-10E	Humble Oil #33 Busiek-Crawford
093-097	Gallatin	29-9S-9E	Texaco #1 Walters
098-102	Greene	32-11N-11W	Kewanee Oil #1 Eula
103-105	Lawrence	29-4N-12W	Atlantic Richfield #77 Lewis
106-107	Logan	7-19N-3W	Allspach #1 Park
108-112	Macon	33-18N-2E	Hill #1 Haynes
113-117	Pope	10-13S-6E	Williams #1 Austin Roberts
118-121	Saline	34-10S-6E	Texas Pacific #1 Wells
122-126	Saline	32-10S-7E	Texota Oil #1 King

[a] Note that several samples were taken from some wells.

TABLE III-2. *Continued*

Sample numbers (NAS-)	County	Sec-T-R	Well name
127-133	Wabash	9-1S-12W	So. Triangle Oil #D2 Zimmerman
134-135	Woodford	28-27N-3W	Centrl. Ill. Light #C18 Cilco
136-138	Champaign	12-22N-11E	Peoples Gas #1 Condit
139-141	Christian	25-11N-1E	Franks Petrl. #1 Wagner
142-146	Clay	11-2N-5E	Keystone Oil #1 Woomer-Campbell
147-149	Clark	4-10N-11W	Corley #1 Miller
150-151	Coles	27-12N-7E	Energy Prod. #G-1 Arterburn
152-155	Coles 20-14N-7E	20-14N-7E	Brehm #1 Lambert
156-157	Crawford	2-5N-11W	Bell #1 Miller
158-161	Crawford	12-5N-14W	Doheny #1 Arnold
162	Crawford	36-6N-11W	Slape Drilling #1 Kincaid
163	Crawford	6-7N-11W	K Oil #1 Mehler
164-165	Crawford	12-7N-11W	West Drilling #1 Brown
166-167	Crawford	31-7N-13W	Ill Oil Invest #1 Mallory et al.
168-170	Cumberland	4-10N-9E	Texaco #1 McCandlish
171-174	De Witt	1-20N-4E	Peoples Gas #1 Lamb
175-176	Edgar	4-14N-11W	Jones-Simpson Drill. #1 Steele-Moss
177-178	Edgar	1-14N-14W	Wauson Petrl. #1 Sims
179-181	Effingham	3-7N-7E	Energy Res. of Ind. #1 Niemerg
182-186	Hamilton	1-4S-5E	Kewanee Oil #1 Wellen
187-190	Hamilton	13-6S-5E	Shell Oil #4 Nohava
191-193	Hamilton	6-6S-7E	Texaco #1 Cuppy
194-196	Iroquois	21-24N-13W	Peoples Gas #1 Mumm
197-199	Iroquois	13-25N-11W	Peoples Gas #1 Keen
200-203	Jasper	1-8N-8E	Total Leonard #1 Theoele
204-206	Jefferson	32-4S-3E	Juniper Petrl. #33x-32 Hayse
207-208	Lawrence	9-3N-11W	Schlensker Drill. #1 Seward
209	Madison	23-4N-5W	Stocker & Sitler #1 Suess
210-212	Marion	35-3N-2E	Brehm Drill. #1 Behnke
213-215	Lawrence	25-3N-13W	Highland Oil #1 Hobbs
216-217	McDonough	23-4N-2W	Bur-Kan Petrl. #1 Chipman
218-220	McLean	33-23N-2E	Zimmerman #1 McLean Co.
221-225	McLean	31-23N-3E	Union Hill Gas #1 Bozarth
226-227	McLean	26-23N-6E	Garland & Hoover #1 Green
228-230	Piatt	13-21N-6E	Union Hill Gas #1 Buchan
231-233	Sangamon	11-15N-3W	Corley #1 Anderson
234-235	Sangamon	1-16N-6W	Caney Oil #1 Eugene Schlitt
236-238	Vermilion	12-19N-11W	Allied Chem. #1 Allied Chem.
239-240	Vermilion	10-23N-11W	Peoples Gas #1 Layden
241-243	Vermilion	15-23N-14W	Peoples Gas #1 Swanson
244-250	White	23-6S-9E	Haley Prod. #1 Trainor
251-253	Williamson	25-8S-3E	Brehm Drill. #1 Harris Unit
291-294	Bond	12-5N-4W	Texas Co. #1 Sybert
295	Champaign	33-17N-9E	Douglas Oil & Gas Bozdeck
296-299	Champaign	23-19N-10E	Peoples Gas #1 Tracy
300-303	Champaign	19-19N-8E	Vickery Drilling Co. B-0-1
304-307	Clark	33-11N-14W	Fanchot #A-1 Elliott
308-309	Clay	16-3N-5E	Southern Ill. Oil Prod. #1 Fatheree
310	Clay	15-2N-7E	Steele #1 Leak
311-314	Coles	16-13N-9E	Union Oil of Calif. #1 Moler
315-318	DeWitt	16-21N-3E	Harris #1 Lewin
319-321	Douglas	31-16N-8E	Cabot Corp. #2 Cabot-Tuscola
322	Douglas	2-14N-10E	Joe Beckner Drill. #1 Jividen
323-327	Fayette	21-6N-2E	Brehm #1 Ireland
328-331	Fayette	31-5N-3E	Shell Oil #1 Ford
332-335	Franklin	36-6S-2E	Shell Oil #19 C.W.&F. Coal
336-339	Franklin	19-7S-2E	Gallagher #1 Zeigler Coal & Coke
340-343	Franklin	20-6S-4E	Texaco #1 U.S. Steel
344-346	Jackson	36-9S-2W	Grammer #1 Dickerson
347-348	Jackson	11-7S-2W	Texaco #1 Harsha
349-352	Jackson	21-10S-3W	National Assoc. Pet. Co. #1 Hays

TABLE III-2. *Continued*

Sample numbers (NAS-)	County	Sec-T-R	Well name
353-356	Jefferson	28-3S-3E	Crystal Oil Co. #1 Story
357	Montgomery	8-7N-2W	Calvert Drill. #1 Blackburn
358-360	Johnson	34-13S-3E	Texas Pacific Oil #1 Farley
361-363	Knox	2-11N-2E	Illinois Power G-2
364-366	Macon	36-16N-1E	Corley #1 Hill
367-369	Macoupin	19-12N-6W	Wright #1 Thoron
370-372	Marion	25-4N-3E	Total Leonad #1-25 Lane
373-377	Montgomery	11-9N-3W	Mobil Oil Co. #1 Dewerff
378-380	Montgomery	33-12N-5W	Phillips Pet. Co. #5 Farmersville
381-383	Morgan	15-13W-8W	Panhandle E. Pipeline Co. #7-15 Whitlock
384	Moultrie	7-15N-6E	Felmont Oil Corp. #1 Ware
385-386	Perry	19-5S-2W	Total Leonard Inc. #1 Pick
387-390	Piatt	5-19N-5E	Texaco #1 Trenchard
391-397	Saline	8-10S-5E	Parker #1 Parker
398-404	Saline	9-9S-5E	Brehm Drill. & Prod. #1 Ozment
405-407	Shelby	17-9N-3E	Energy Resources #1 Gregg
408-411	Shelby	3-10N-5E	Total Leonard Inc. #1 Engel
412-414	Tazewelll	36-24N-7W	Central Light #1 Rutherford
415	Shelby	3-10N-5E	Total Leonard Inc. #1 Engel
416-418	Union	12-12S-1W	Fry #1 Hill
419-425	Wayne	21-1S-9E	Luttrell #1 Fetherling
426-432	White	21-3S-9E	National Oil Co. #1 Granger
441-444	Clinton	6-2N-4W	Anschurtz #1 Schroder
445-451	Jasper	17-5N-10E	Pure Oil Co. #A-5 Honey
452-454	Mason	9-22N-7W	Engelke #1 Woodrow
455-459	Montgomery	11-8N-5W	Calif. Co. #1 Schmidt
460-462	Peoria	25-11N-8E	Prentiss #1 Coon
463-465	Pike	32-3S-4W	A. W. Neal Co. #1 Crump
466-468	Pike	23-6S-3W	Texaco #1 Scott
469-471	Schuyler	11-1N-3W	Kerwin #1 Wrench
472-477	White	15-5S-9E	Brehm #1 Reinwald
478-486	Effingham	15-6N-6E	Kingwood Oil #1 McWhorter
487-504	Hamilton	6-6S-7E	Texaco #1 Cuppy
505-521	Pope	2-11S-6E	Texas Pacific #1 Streich Comm.
522-536	Gallatin	29-9S-9E	Texaco #1 Walters
537-547	Shelby	19-14N-2E	NEA YES Inc. #1 Stoggsdill
548-552	Fulton	10-6N-1E	New Jersey Zinc #H-16 Thompson
553-556	Fulton	13-8N-2E	New Jersey Zinc #H-23 Williams
557-562	Knox	31-11N-2E	New Jersey Zinc #J-16 Gumm

TABLE III-3. Location of New Albany Shale (NAS) samples obtained from well cuttings in Indiana (courtesy of the Indiana Geological Survey).

Sample numbers (NAS-)	County	Sec-T-R	Box numbers
265	Daviess	16-3N-7W	9806
266	Spencer	3-6S-4W	9684
267	Foutain	33-22N-7W	4754
268	Lawrence	20-5N-2E	6088
269	Martin	5-3N-4W	3577
270	Sullivan	14-8N-8W	7029
271	Posey	18-5S-13W	9339
272	Sullivan	36-7N-10W	8080
273	Harrison	2-6S-4E	7358
274	Crawford	18-3S-1W	10437
275	Putnam	12-12N-3W	5411
276-281	Elkhart		
282	Warrick	36-4S-9W	3951
283	Montgomery	14-17N-3W	4969
284	Vermilion	27-14N-9W	10060
285	DeKalb	8-35N-14E	7177
286	Sullivan	32-8N-8W	3274
287	Owen	14-9N-5W	6561
288	Morgan	3-12N-1W	6752
289	Hendricks	12-14N-1E	6069
290	Washington	17-2N-5E	10021

Survey personnel describe and sample Hardin County core (December, 1978).

IV. STRATIGRAPHY

Mark L. Reinbold, Jerry A. Lineback, and Jerry T. Wickham

ABSTRACT

The New Albany Shale Group in the Illinois Basin can be classified into five main lithologies: black or brownish-black shale, gray to greenish-gray shale, calcareous or dolomitic shale, siltstone, and limestone. Detailed stratigraphic correlations based on cores, geophysical logs, and sample studies indicate that these lithologies grade vertically and laterally into one another, with complex intertonguing relationships.

Black shales in the New Albany Group (including the Grassy Creek, middle Selmier, and Blocher Shales) predominate in the center of the basin in southeastern Illinois and adjacent western Kentucky. The black shales thin northward and westward and grade laterally into a dominantly olive-black to greenish-gray shale succession in western Illinois (Sweetland Creek, Grassy Creek, and Saverton Shales). A thick wedge of greenish-gray shale and siltstone (Hannibal and Saverton Shales) dominates the upper portion of the New Albany Group in western Illinois and thins rapidly southward.

INTRODUCTION

The New Albany Shale Group and equivalent strata (Middle Devonian-Kinderhookian) occur widely in the subsurface of the Illinois Basin in Illinois, southwestern Indiana, and western Kentucky. Natural gas has been produced from the New Albany on a limited commercial basis in southern Indiana and western Kentucky. Although gas shows have been reported in the Illinois black shales, there has been no commercial production to date.

We have investigated in detail the lithology, stratigraphy, and structure of the New Albany in Illinois to obtain basic geologic information needed for geotechnical and geochemical studies evaluating any potential natural gas resource. Data from the geological evaluation have been used to construct numerous stratigraphic cross sections of the New Albany (fig. IV-1) and to develop a series of thickness maps of the major stratigraphic units within the New Albany. From this data and from lithologic studies (Section VI), a depositional model has been developed to explain the distribution of various lithofacies in the New Albany. Data on geological aspects of the New Albany have been used in conjunction with other data to (1) identify a 19-county area in southeastern Illinois as the highest resource potential; (2) to essentially eliminate the rest of the New Albany in Illinois as too thin or too lacking in source beds to yield commercial quantities of natural gas (See Section XVI).

The geological study was based on examination of cuttings and geophysical logs from several hundred oil test wells in Illinois. Examination of existing cores (and the six cores taken specifically for this project) allowed for detailed study of lithology (see Section VI) and provided the basis for subdivision of the shale into different lithologic types. Geo-

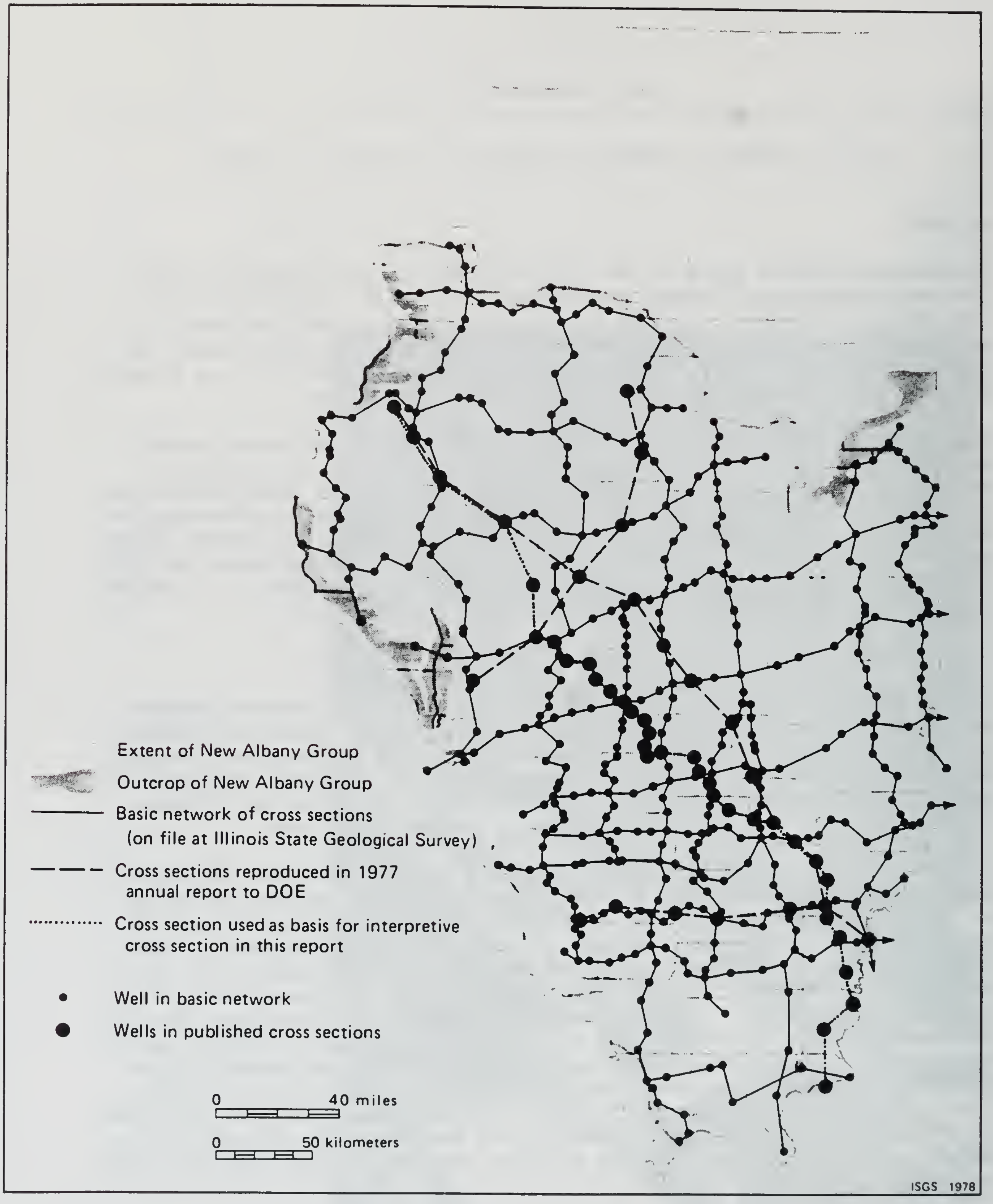


Figure IV-1. Locations of cross sections of the New Albany Shale Group and adjacent strata in Illinois. All cross sections are on open file at the Illinois Geological Survey in Urbana.

physical log characteristics were directly compared to lithologic types in the cores and well cuttings. The logs were then used to trace geologic units through the subsurface.

This final report presents the stratigraphic summary of the New Albany Shale Group. A geological report providing complete details on stratigraphy (including thickness maps and cross sections) is now in preparation (Cluff, Reinbold, and Lineback).

THE NEW ALBANY SHALE: AN OVERVIEW

The New Albany Shale, originally designated a formation, is named for New Albany, Floyd County, Indiana (Borden, 1874). In Illinois, the New Albany Shale has been assigned group status (Collinson and Atherton, 1975). Previous important studies in Illinois were conducted by Workman and Gillette (1956), Collinson et al. (1967), and North (1969).

The New Albany Group reaches a maximum thickness of more than 460 feet (140 m) in Hardin County in southeastern Illinois and in adjacent western Kentucky (figure IV-2). Laminated black shale is the predominant lithology in southeastern Illinois, which was apparently the depositional center of the ancestral Illinois Basin during the middle and late Devonian.

A second depositional center lies in southeastern Iowa and adjacent west central Illinois, where the shales are Upper Devonian and Kinderhookian. Thicknesses of more than 300 feet (90 m) are attained in Henderson and Hancock Counties, Illinois, and extend northwestward into Iowa. Bioturbated olive-gray and greenish-gray shales are the predominant lithologies in this region.

The two depositional centers are separated by a northeast-southwest trending area of thin New Albany strata consisting of interfingering gray and black shales.

The New Albany Shale conformably overlies Middle Devonian limestones belonging to the Hunton Limestone Megagroup in southern and eastern Illinois; the lowest unit, the Blocher Shale, grades laterally westward into the Lingle Limestone of the Hunton. Beyond the limit of the Blocher Shale, the Sylamore Sandstone marks the base of the New Albany, and the basal New Albany strata unconformably overlap the Hunton Limestone Megagroup toward the north and west.

The New Albany is conformably overlain by the Chouteau Limestone (Kinderhookian) over most of southern, central, and eastern Illinois. In extreme western Illinois, the McCraney Limestone partially occupies the position of the Chouteau. Across most of western Illinois, an erosional unconformity separates the New Albany from younger Valmeyeran strata.

Blocher Shale

The Blocher Shale (Campbell, 1946; Lineback, 1968, 1970; Cluff, Reinbold, and Lineback, in preparation) is named for the town of Blocher, Scott County, Indiana.

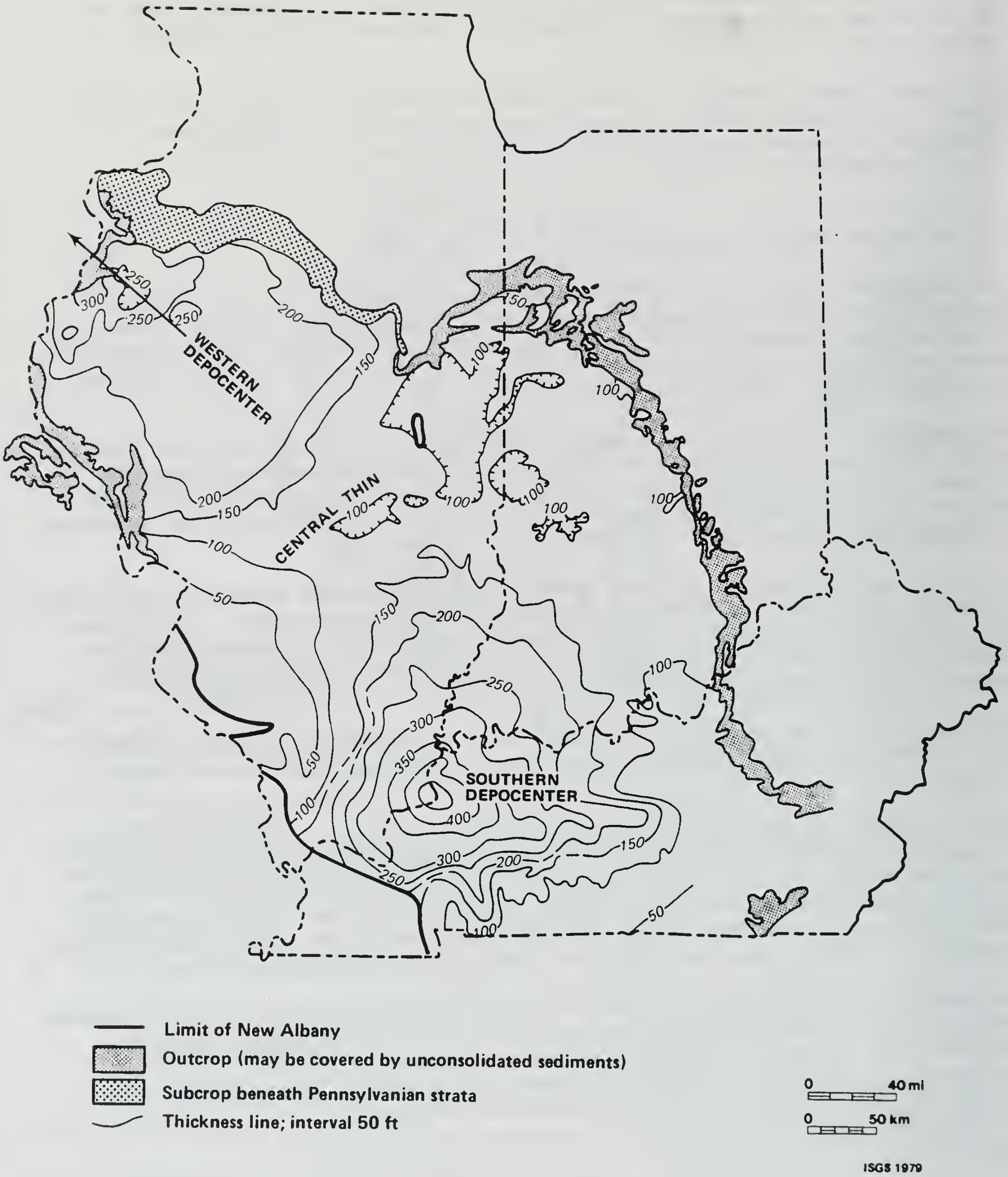


Figure IV-2. Total thickness of the New Albany Shale Group in the Illinois Basin.

The Blocher Shale, as used in this study, is distinguishable on the basis of its calcareous and dolomitic black shale; it is the only shale unit in the New Albany to contain much calcite. The high carbonate content of the Blocher imparts distinctive geophysical characteristics that permit it to be traced throughout the basin. Lineback (1968, 1970) however, included some dolomitic black shale above the calcareous shale in the Blocher on the Indiana outcrop. As a result of correlations between the outcrop and the subsurface of the Illinois Basin, Cluff, Reinbold, and Lineback (in preparation) revised the outcrop Blocher by restricting it to calcareous shale, thus making the definition and identification consistent between the subsurface and the surface outcrops.

The Blocher is a brownish-black to grayish-black, finely-laminated, carbonaceous, calcareous and dolomitic shale. Thin beds of fine-grained limestone, dolomite, calcareous sandstone, and phosphatic sandstone are also present in the Blocher. The Blocher reaches 80 feet (24 m) in eastern Hardin County, Illinois and adjacent Kentucky (fig. IV-3). Eastward, it thins to less than 3 feet (1 m) on the Indiana outcrop. The Blocher grades westward into limestone along a line that forms an arbitrary vertical cutoff where the base of the New Albany is stepped up to units overlying the Blocher.

Sylamore Sandstone

The Sylamore Sandstone (Penrose, 1891) is the basal Upper Devonian formation in parts of central and western Illinois (Workman and Gillette, 1956) and is named for Sylamore Creek, Stone County, Arkansas. The Sylamore is rarely more than 3 feet (1 m) thick (more commonly only a few centimeters thick) and sometimes is only a thin, sandy, or pyritic layer at the base of the Sweetland Creek or Grassy Creek Shales. The formation is typically a thin bed of rounded to subrounded, medium- to fine-grained quartz sand cemented by calcite, dolomite, or pyrite. The bed may be silty or shaly and is very commonly phosphatized. Although thin, the Sylamore marks the basal unconformity of the New Albany over a wide area (fig. IV-4) and rests on rocks of different ages. The Sylamore itself is time transgressing, becoming younger westward in Illinois.

Selmier Shale

The Selmier Member of the New Albany Shale was named by Lineback (1968, 1970) for an exposure in a quarry at North Vernon, Jennings County, Indiana. Cluff, Reinbold, and Lineback (in preparation) lowered the base of the Selmier in the type section to the top of the calcareous Blocher Shale. In so doing, they restricted the Blocher to black calcareous shale and placed the black dolomitic shale between the restricted Blocher and the greenish-gray shale of the original Selmier. Subsurface correlation by means of well cuttings and geophysical logs shows that the dolomitic black shale at the base of the outcrop Selmier extends westward and forms the middle black shale unit in a succession dominated by greenish-gray shale that was called Sweetland Creek Shale in Illinois by Collinson et al. (1967), and North (1969). Cluff, Reinbold, and Lineback (in preparation), however, show that the type Sweetland Creek is largely a younger unit than the Sweetland Creek in the deeper part of the Illinois Basin. Therefore the interbedded greenish-gray and black shales in southeastern Illinois that correlate with the expanded outcrop Selmier

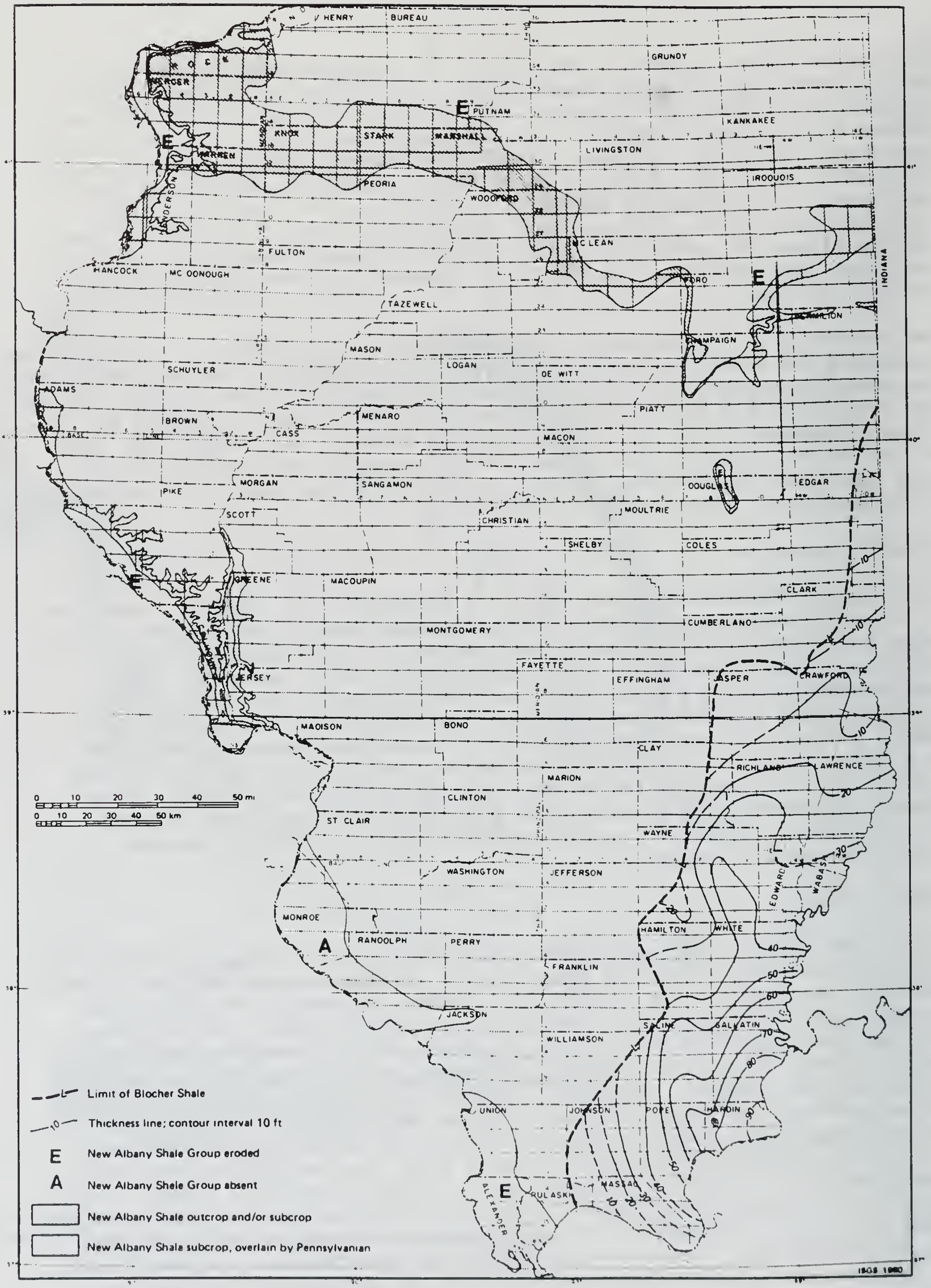


Figure IV-3. Thickness of the Blocher Shale in the Illinois Basin.

were referred to the Selmier Shale, used as a formation in Illinois. The Selmier is separated from the Sweetland Creek by an arbitrary vertical cutoff that precludes the two formations from occurring at the same location.

The Selmier Shale consists of alternating beds of brownish-black, grayish-black, and olive-gray to olive-black shales and mudstones. The dark-colored shales of the Selmier are generally thickly or poorly laminated. The greenish-gray shales are generally intensly bioturbated. Silt beds and beds of micritic dolomite are present at places. The Selmier extends throughout much of the southern and eastern portions of the Illinois Basin, exceeding 200 feet (60 m) in eastern Hardin County and adjacent parts of Kentucky and thinning rapidly westward (fig. IV-5). The shale also thins gradually eastward across Indiana to 27 feet (8 m) at the type location and less at some other Indiana outcrops. In southeastern Illinois, the Selmier generally overlies the Blocher Shale and underlies the Grassy Creek Shale.

Sweetland Creek Shale

The Sweetland Creek Shale (Udden, 1899) is named for Sweetland Creek in Muscatine County, Iowa. Collinson et al. (1967) indicated that the Sweetland Creek included olive-gray and green shales underlying the Grassy Creek Shale in western Illinois. They also extended the term Sweetland Creek eastward into the Illinois Basin. Cluff, Reinbold, and Lineback restrict the use of Sweetland Creek to areas west and north of the deeper parts of the basin. Only the uppermost part of the Selmier Shale is equivalent to the Sweetland Creek, and most of the Sweetland Creek is a lateral facies of the lower part of the Grassy Creek Shale.

The Sweetland Creek Shale consists of alternating beds of dark greenish-gray, greenish-gray, and grayish-green shales with minor amounts of olive-gray or olive-black shale. The dominant lithofacies is indistinctly bedded, moderately bioturbated shale. Pronounced interbedding of this lithofacies with thickly laminated olive-black shales is common.

The Sweetland Creek in the subsurface is distinguished principally in central Illinois and parts of southwestern Illinois. Because equivalent strata in western Illinois grade into the overlying Grassy Creek and cannot be distinguished reliably from the Grassy Creek they are mapped with the Grassy Creek (fig. IV-6). The Sweetland Creek Shale is separated from the Selmier Shale by an arbitrary vertical cutoff (fig. IV-5).

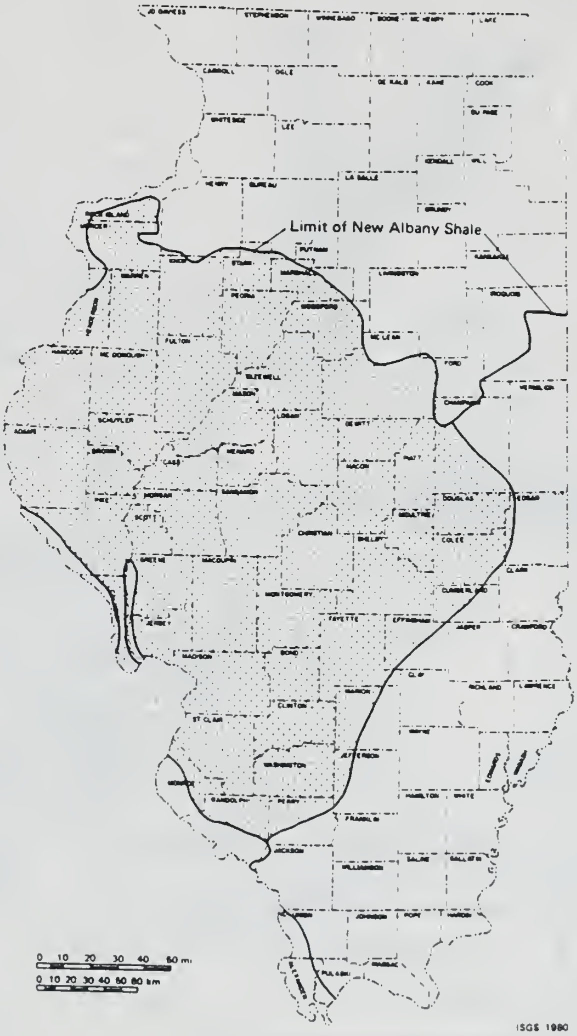


Figure IV-4. Approximate extent of the Sylamore Sandstone. (After Workman and Gillette, 1956; W. F. Meents, personal communication, 1979; and core descriptions in ISGS files.)

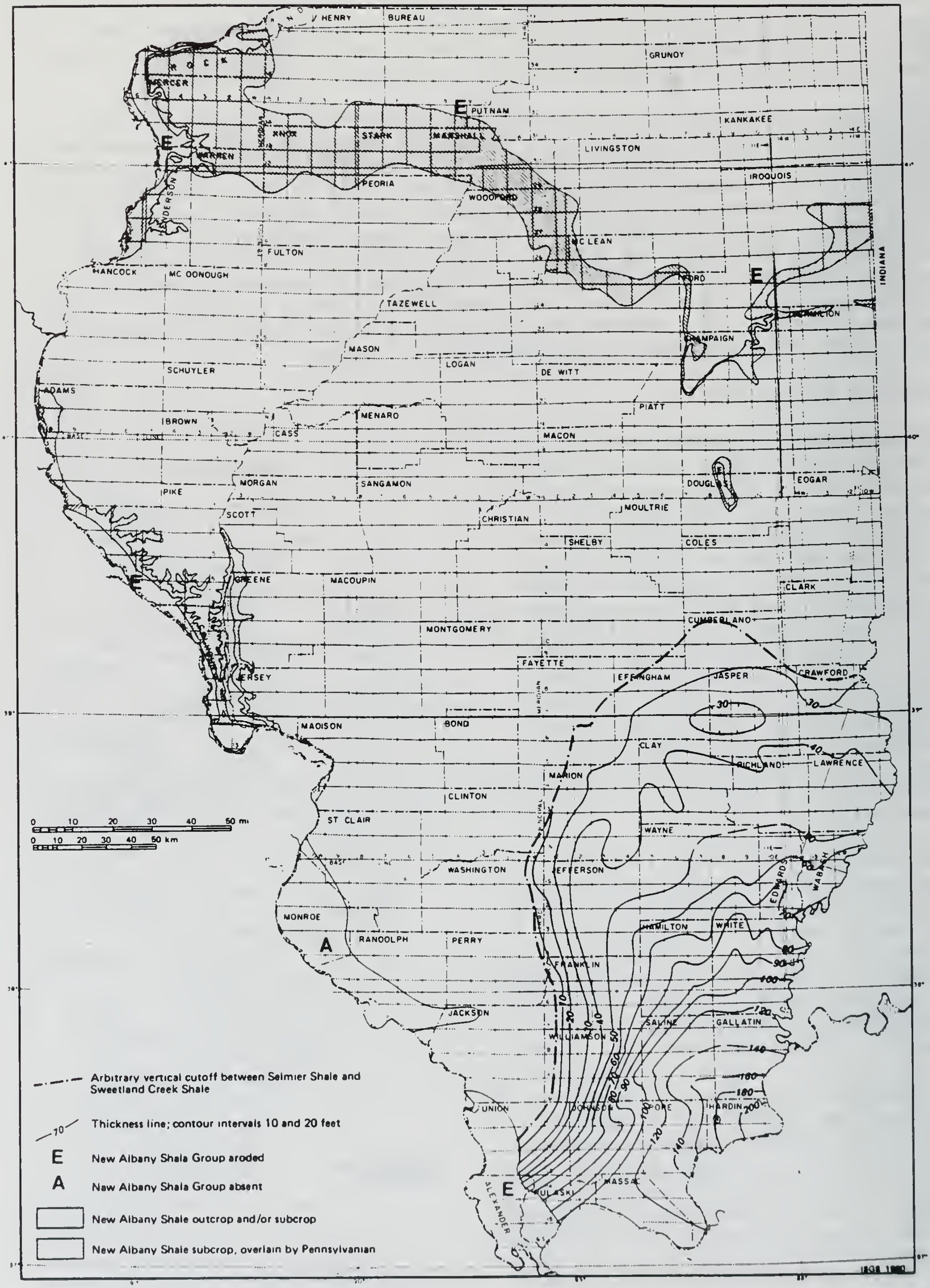


Figure IV-5. Thickness of the Selmier Shale in the Illinois Basin.

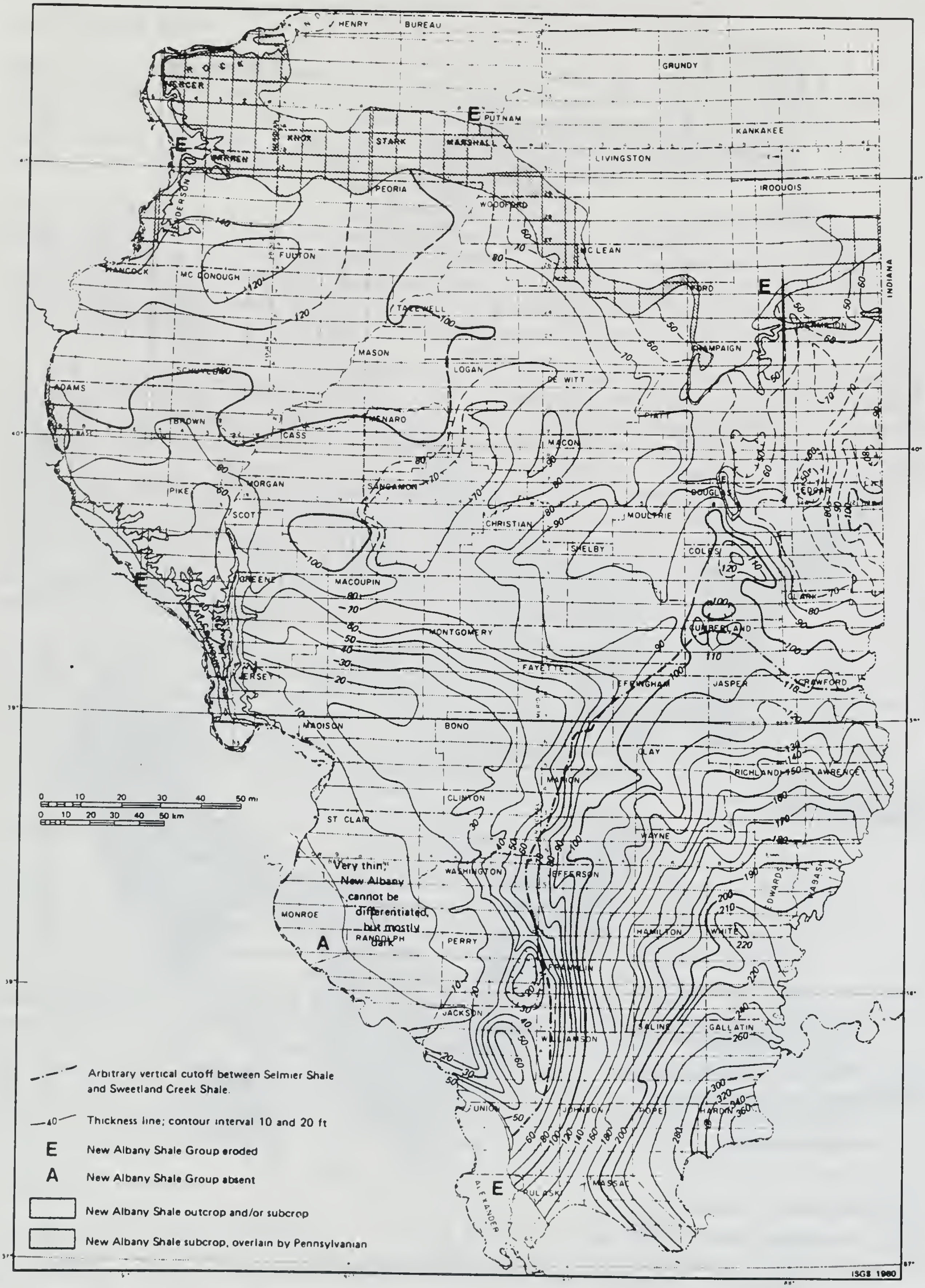


Figure IV-6. Thickness of the Sweetland Creek/Selmier/Grassy Creek Shales.

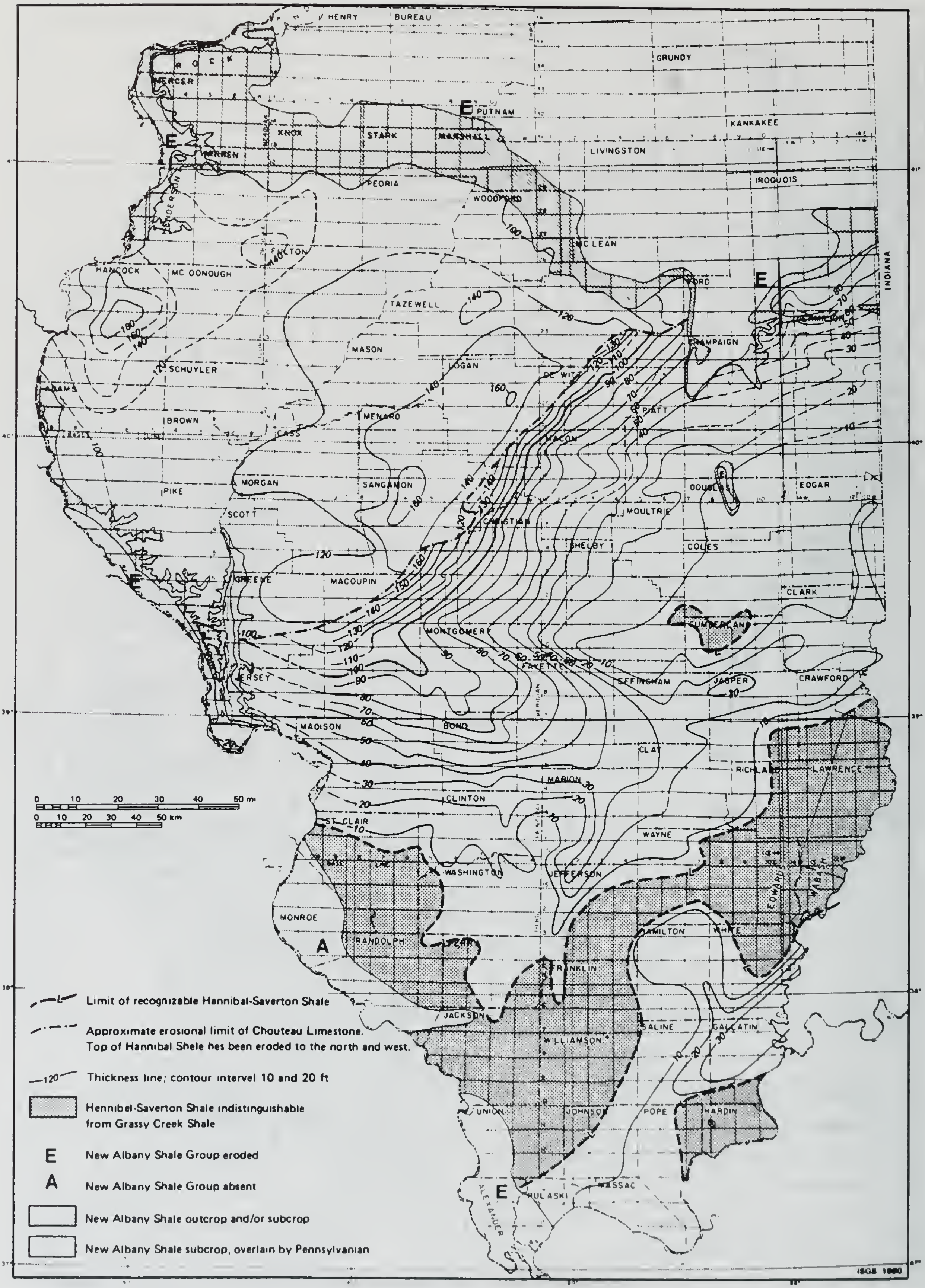


Figure IV-7. Thickness of the Saverton/Louisiana/Horton Creek/Hannibal interval (undifferentiated).

Grassy Creek Shale

The Grassy Creek Shale (Keyes, 1898, 1912) is named for Grassy Creek, a stream in Pike County, Missouri. Collinson et al. (1967) differentiated the Sweetland Creek Shale from the Grassy Creek. Workman and Gillette (1956), Collinson et al. (1967), and North (1969) extended the name Grassy Creek to southeastern Illinois.

The Grassy Creek Shale includes the dominantly black shale interval of the middle and upper part of the New Albany Group. It is mostly brownish-black to grayish-black, finely laminated, pyritic, carbonaceous shale. The organic carbon content of these shales is among the highest in the New Albany. The Grassy Creek grades northwestward into less carbonaceous olive-black to olive-gray shale with interbeds of olive-green to grayish-green mudstone.

The thick, dominantly black shales which characterize the Grassy Creek Shale are found primarily in the central part of the Illinois Basin in southeastern Illinois. To the north and west, the black shale interfingers with gray shales and becomes difficult to distinguish from the underlying Sweetland Creek Shale. The upper part of the Grassy Creek grades laterally northwestward into a thickening wedge of greenish-gray shale and siltstone, the Saverton and Hannibal Shales. The Grassy Creek attains its maximum thickness, about 160 feet (50 m), in eastern Hardin County, Illinois, and adjacent Kentucky (fig. IV-6). It is also more than 130 feet (40 m) thick in Wayne, Edwards, and Wabash Counties. Undifferentiated Grassy Creek-Sweetland Creek Shale attains a thickness of 140 feet (43 m) in western Illinois.

The Grassy Creek overlies the Selmier Shale in southeastern Illinois and southwestern Indiana with a sharp contact between black and greenish-gray shale that forms one of the most widely traceable geophysical marker horizons in the basin. The contact with the Sweetland Creek Shale, however, is one of lateral gradation. The Grassy Creek in southeastern Illinois is equivalent to the Morgan Trail, Camp Run, and Clegg Creek Members of the New Albany in Indiana.

Saverton Shale

The Saverton Shale (Keyes, 1912), named for the town of Saverton, Ralls County, Missouri, consists of interbedded greenish-gray, dark greenish-gray and olive-black shales. The organic carbon content of these shales is low. The Saverton overlies and grades laterally southeastward into the Grassy Creek Shale; it is overlain by the Louisiana Limestone or Horton Creek Formation, and, where these distinctive units are absent, by the Hannibal Shale. The Hannibal is very similar lithologically to the Saverton and it is almost impossible to separate the two units. Therefore, we have mapped the combined thickness of the Saverton, Louisiana, Horton Creek, and Hannibal (fig. IV-7). Where separable from adjacent units, the Saverton reaches a maximum thickness of 120 feet (37 m) in northwestern Illinois and thins towards the south and east as it grades laterally into the Grassy Creek.

Louisiana Limestone

The Louisiana Limestone (Keyes, 1892) is named for the town of Louisiana, Pike County, Missouri. The Louisiana Limestone is a light-gray to tan, wavy-bedded, micritic limestone with thin shale and dolomite interbeds.

In surface exposures it is often very pure carbonate with little insoluble residue and is texturally very homogeneous (almost lithographic). Dolomite interbeds are often laminated, and in many areas the limestone appears faintly burrow-mottled. Subsurface samples of the Louisiana are also micritic limestone, but are often argillaceous and extensively bioturbated.

A wide variety of invertebrate fossils is found in the Louisiana, although fossils are not abundant. The fauna is dominated by small brachiopods and dwarf crinoids. Bryozoans, ostracods, sponges, corals, mollusks, trilobites, and conodonts are also found, but are rare (Williams, 1943). The Louisiana is thick (70 feet; 21 m) only in a small area near Hannibal and Louisiana, Missouri, and 30 feet (9 m) immediately east across the Mississippi River, in Illinois. An east-west elongated tongue of Louisiana, less than 10 feet (3 m) thick, extends across the southwest-central part of the state (fig. IV-8).

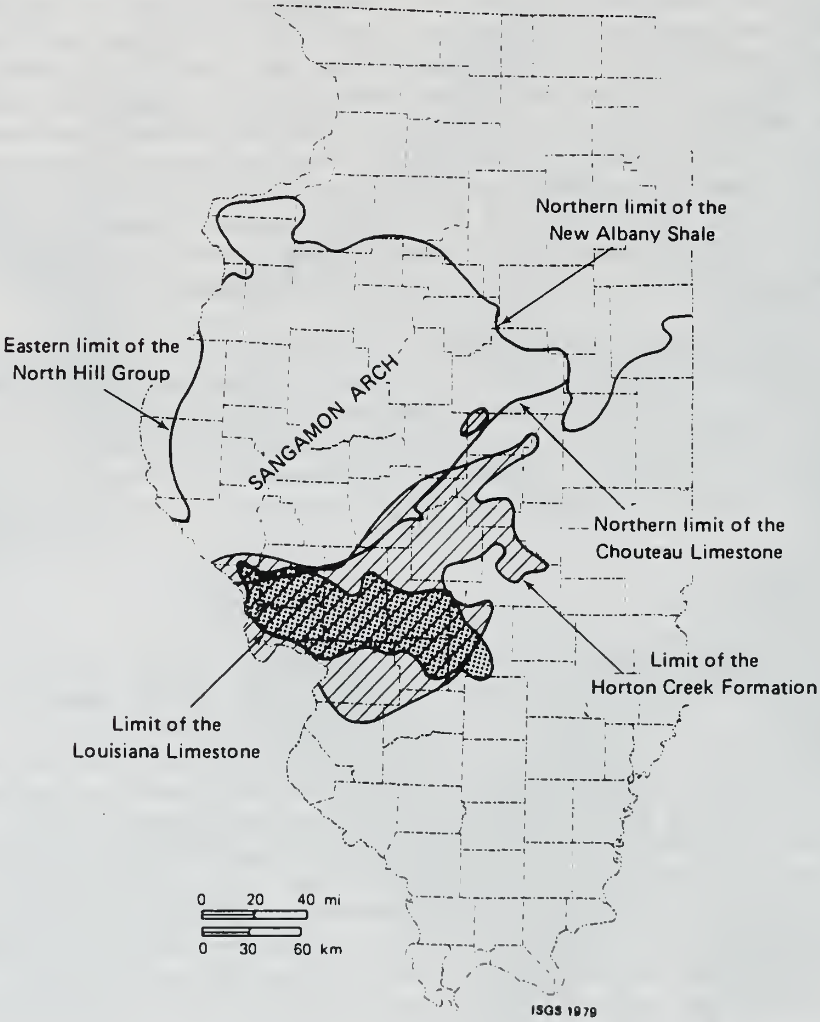


Figure IV-8. Extent of carbonate beds in the New Albany Shale of Illinois.

Horton Creek Formation

The name Horton Creek was proposed by Conkin and Conkin (1973) for the limestones, siltstones, sandstones, and shales previously included in the "Glen Park" Formation of Illinois. Conkin and Conkin designated the Horton Creek as the basal member of the Hannibal Shale in western Illinois. Collinson et al. (1979) designate the Horton Creek as a formation, essentially the same as the "Glen Park" Formation described by Atherton et al. (1975). The Hamburg Oolite Bed of the Horton Creek is a distinctive oolite that lies near the top of the Horton Creek Formation.

The Horton Creek is a complex unit consisting of siltstone, shale, sandy limestone, micritic limestone and dolomite, limestone conglomerates, and oolitic limestone. The most widespread carbonate lithology in the Horton Creek is gray to tan, argillaceous, sparsely fossiliferous, micritic limestone and dolomite similar to the Louisiana Limestone. These carbonate mudstones and wackestones are present throughout the extent of the Horton Creek and are the only carbonate lithologies observed towards the southern and eastern limits of the formation (fig. IV-8).

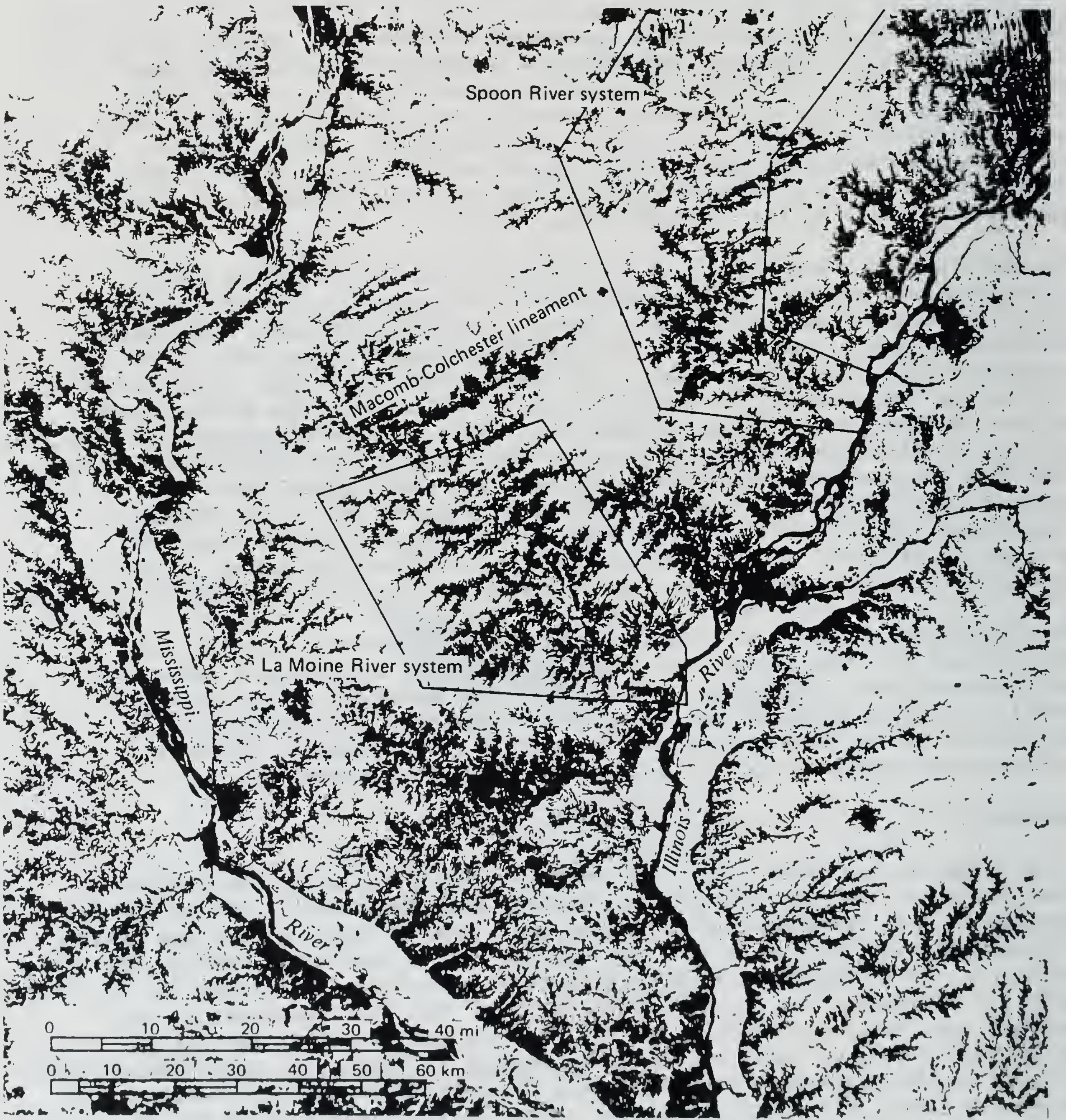
The Hamburg Oolite Bed lies in the upper part of the Horton Creek and is discontinuously present; it has been used to differentiate limestones in the Horton Creek from the Louisiana Limestone in the subsurface. The oolitic limestone is mainly present in a northeast-southwest trending belt across the northern part of the Horton Creek. The Horton Creek is 60 feet (18 m) thick in Macoupin County where it consists mostly of siltstone. The Horton Creek includes shales and siltstones between the thin tongues of the Hamburg Oolite Bed and Louisiana Limestone; the shale and siltstone is otherwise indistinguishable from the Hannibal and Saverton Shales. The shaly Horton Creek is included in the Saverton where the Louisiana is absent and in the Hannibal where limestone lithologies do not exist in the Horton Creek to separate it from the Hannibal. Where both distinctive Louisiana and Horton Creek carbonate lithologies are absent, the Hannibal and Saverton are undifferentiated.

The development of shoal and lagoonal carbonates in western Illinois and northeastern Missouri indicates a brief interlude in mud sediment deposition which allowed the development of shelf carbonate deposition. Calcareous fossils are found in black and greenish-gray shales at this stratigraphic position as far as southern Indiana (Campbell, 1946; Lineback, 1970) indicating the widespread nature of this brief depositional event.

Hannibal Shale

The Hannibal Shale (Keyes, 1892) is named for exposures in the Mississippi River bluffs at the city of Hannibal, Marion County, Missouri. The Hannibal consists of dark greenish-gray, greenish-gray, grayish olive-green, and dusky yellow-green mudstone and shale. Its organic carbon content is usually very low (<1%). Silty clay shales and argillaceous siltstones are present in places, particularly in the upper part of the formation. Mudstones of the Hannibal are highly bioturbated. A thin olive-black fissile shale called the Nutwood Member is locally present in western Illinois. In southeastern Illinois the Hannibal-Saverton is present in places between the Chouteau and Grassy Creek. In these localities a thin, black fissile shale may be present just below the Chouteau; this is believed to be the Henryville Bed of Indiana. Also present in cores and in outcrops in extreme southern Illinois are the very thin Jacobs Chapel Bed above the Henryville and the Falling Run Nodule Bed below. These names are used as beds in the Hannibal if greenish-gray shale is present below, or in the Grassy Creek if black shale underlies the beds.

The Hannibal is more than 110 feet (34 m) thick in west central Illinois (fig. IV-7); it is truncated by erosion below the Burlington Limestone in western Illinois and grades laterally into the Grassy Creek to the southeast.



LANDSAT image of western Illinois taken January 14, 1974. This snow-enhanced winter scene clearly shows the prominent linear features that cut across areas of shallow bedrock and areas of thick glacial drift.

V. STRUCTURE

D. L. Stevenson, R. M. Cluff, J. T. Wickham, J. A. Lineback

ABSTRACT

A revised geologic structure map on the base of the New Albany Shale Group shows few changes from previous maps. Other stratigraphic horizons were considered unsuitable for structural mapping. Linear features (revealed on images and photographs from earth-orbiting satellites and on air photographs) in the area of Illinois underlain by the New Albany, were examined. Most linear features proved to be related to glacial landforms and unrelated to structures in the underlying bedrock. Fracturing and faulting in the bedrock, similar to that present in the Cottage Grove and Wabash Valley Fault Systems in southern Illinois, have enhanced production of natural gas in other areas.

STRUCTURE ON BASE OF NEW ALBANY SHALE

The New Albany Group structure map (plate 1) is a revised version of the Hunton Limestone Megagroup map published by Stevenson and Whiting (1967). The top of the Hunton Megagroup is, in general, the same horizon as the base of the New Albany Shale and has been used previously in mapping the structure of Illinois. A study of Devonian and Silurian rocks in central and western Illinois by Whiting and Stevenson (1965) presents a structure map contoured on the top of the Hunton Megagroup; this map was subsequently expanded into their 1967 map.

The northern limit of the mapped area (plate 1) is the northern edge of the New Albany Shale. Although the Hunton Limestone extends some distance north of this line, its top is a surface beveled by pre-Pennsylvanian and pre-Pleistocene erosion, and, therefore, is unsuitable for structural mapping.

The eastern boundary of the mapped area is the Illinois-Indiana border. The contours have been matched to a similar structure map of Indiana (Bassett and Hasenmueller, in preparation). The western boundary follows the Mississippi River, except for the few places where the New Albany has been removed by erosion. In extreme southern Illinois, the map extends from a line formed by the Ste. Genevieve Fault and the eroded edge of the New Albany Shale Group to the Ohio River and eastward to the west edge of the Dixon Springs Graben. The southeasternmost portion of Illinois has not been mapped because of the complex faulting and the lack of drill holes penetrating the base of the New Albany Shale (only two exist). The location of these holes and the elevation of the base of the New Albany are shown on the map.

In the area of Hamilton, White, Saline, and Gallatin Counties, the control points are too sparse to provide adequate data for structural interpretation. In these counties, the elevation of the base of the New Albany was estimated by combining maps of the structure of the middle "massive" member (Scottsburg Member) of the Menard Limestone and the thickness map of the Menard to Hunton interval.

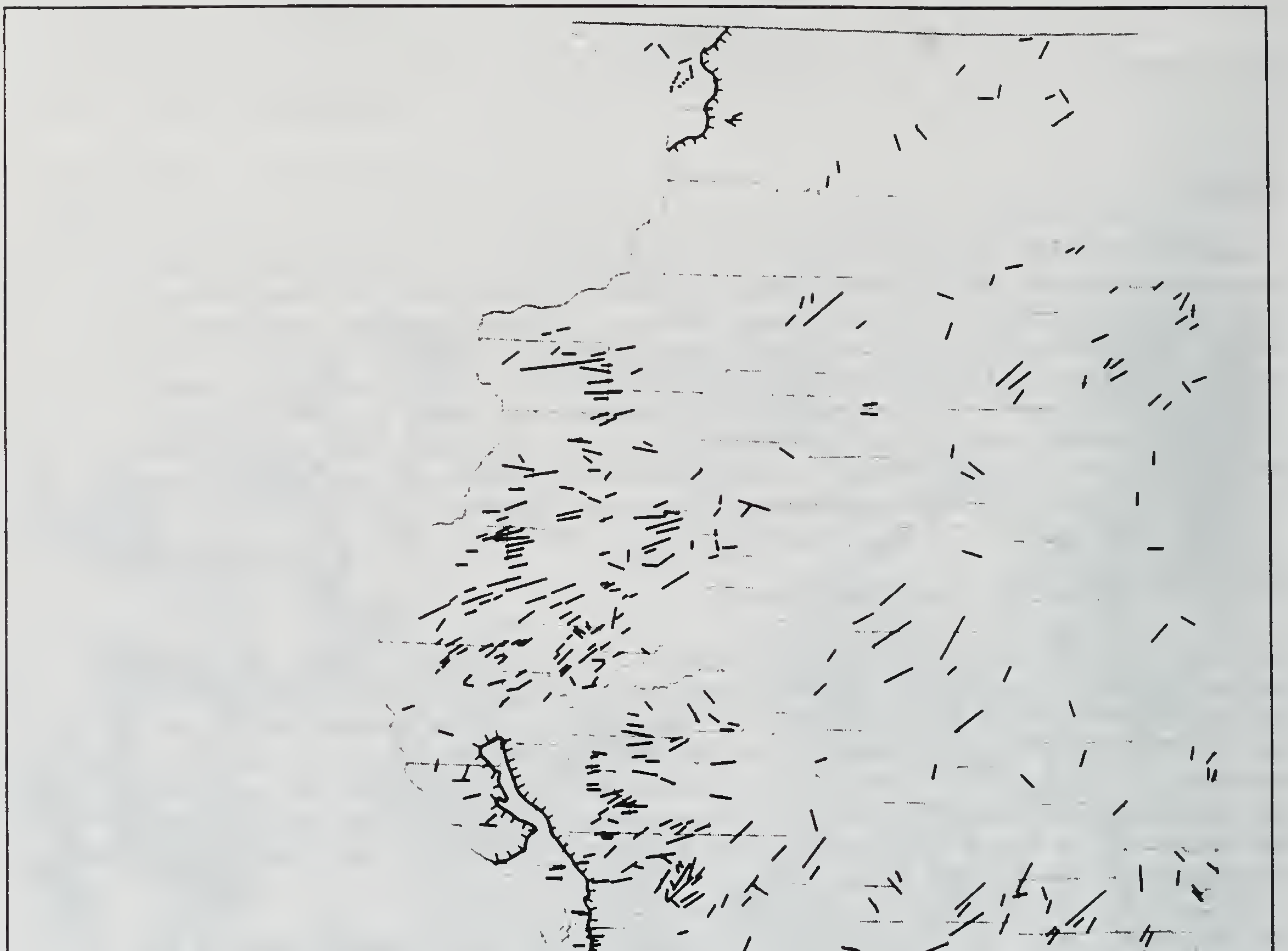


Figure V-11. LANDSAT-image surface linears in Illinois.

The sparsely drilled and complexly faulted area south of Township 10 South in extreme southern Illinois was mapped by relying heavily on structural mapping of shallower horizons. The faults shown in this area are essentially the same as those shown on the geological map of Illinois (Willman et al., 1967), with modifications based on work by Ross (1963) and Kolata, Treworgy, and Masters (in preparation).

Major revisions of previous mapping have been made in three areas. One is in Lawrence and Crawford Counties, where anticlinal axes along the La Salle Anticlinal Belt were inadvertently shown 6 miles east of their actual location on Stevenson's and Whiting's (1967) map. The second area is the Silurian reef area of southwestern Illinois, which Bristol (1974) mapped in detail, including additional data acquired by drilling since 1967. The third area of major revision is in White and Gallatin Counties. Here, detailed mapping of the Wabash Valley faults and Beech Creek (Barlow) structure in this area by Bristol and Treworgy (1979) resulted in the reinterpretation of the location and extent of several faults. A recent deep test on the Omaha Dome structure in T. 8 S., R. 8 E. also revealed that the shallow structure is largely the result of igneous intrusions in Mississippian sediments; apparently no structural high exists on the Devonian.

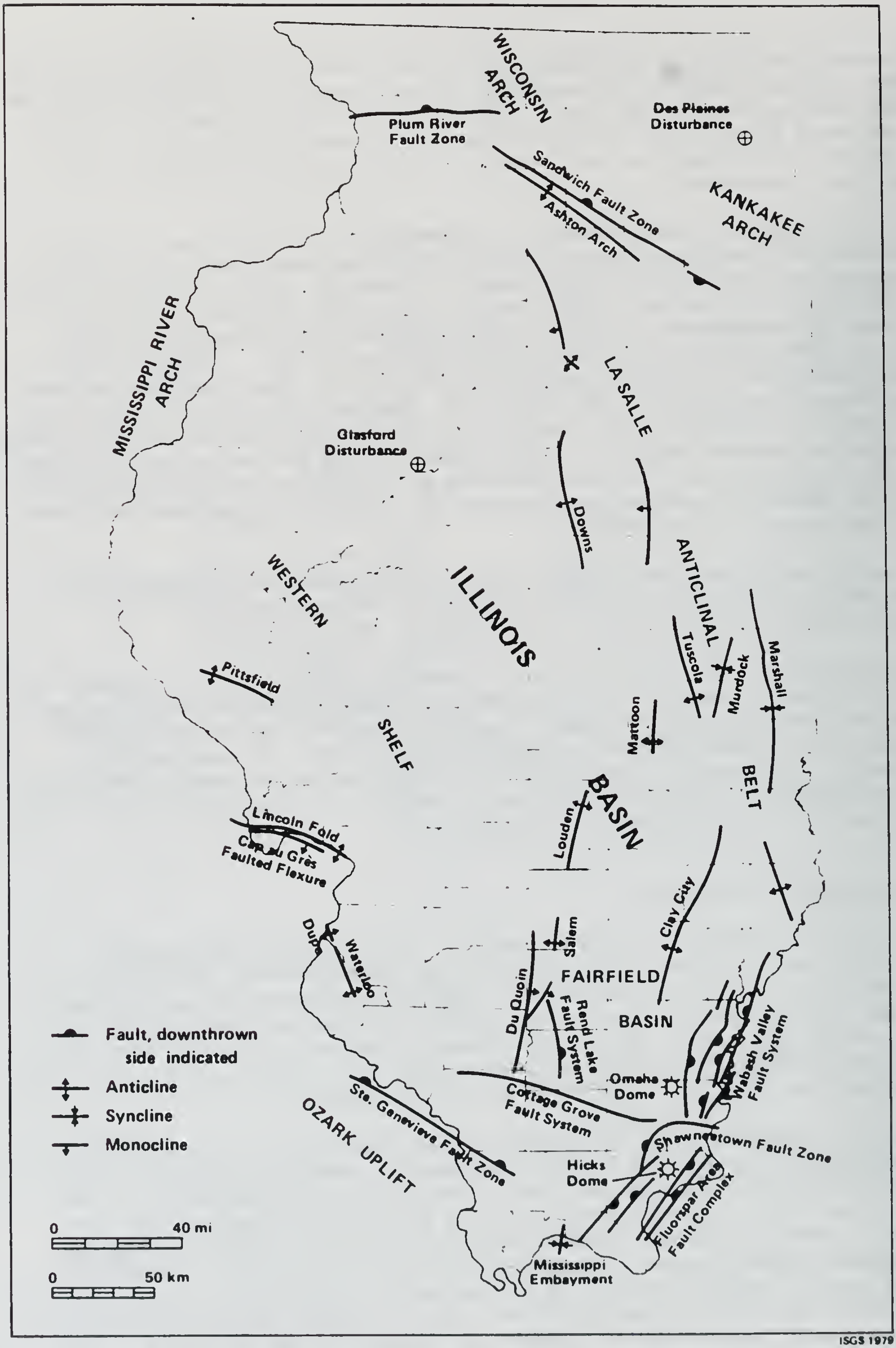
There are a few other minor changes based on scattered deep drilling done during the exploration for oil and gas and for gas storage sites (e.g., Brubaker Field in Section 31, T. 3 N., R. 3 E., Marion County).

A structure map of the top of the New Albany Shale Group was not prepared for the following reasons: (1) very few drill holes penetrate only the top of the New Albany and not the base; thus, no additional datum points could be used; (2) the structure of the top of the New Albany is essentially identical to the base; (3) the top of the New Albany is not easily identified where the overlying Chouteau Limestone is absent. The base of the New Albany is regionally a much superior mapping horizon.

LINEAR FEATURES OF ILLINOIS

Linear features visible on LANDSAT images of Illinois have been mapped (fig. V-1). Man-made linear features such as highways, railroads, pipelines and canals have been eliminated. Some short channelized stream segments may not have been eliminated and may be included as linear alluvial valleys on the lineaments map. In most cases, channelization occurred over a long enough distance that channelized streams were recognized by their lack of meanders and uniform stream width over long reaches.

The mapped lineaments (fig. V-1) include approximately 400 linear alluvial valleys, 9 fault traces, and 2 other lineaments. The 9 fault traces occur in southern Illinois, beyond the glacial boundary, and correspond to known zones of faulting. The two linear drainage divides occur in the Driftless Area of northwest Illinois. Linear alluvial valleys are present throughout Illinois and appear to have a variety of origins. From LANDSAT images and high altitude photography alone, it is impossible to discriminate between linears that are bedrock-controlled and linears formed by glacial processes. Determination of the origin of linears in a specific area of Illinois can be made only when the regional geology of the area is well understood and the linears



ISGS 1979

Figure V-2. Major geologic structures of Illinois. Compiled by Janis D. Treworgy, December, 1979.

in that specific area have been field investigated. Therefore, the origin of most linears in Illinois can only be tentatively defined on the basis of available evidence.

Almost all of Illinois, except for the southern and northwestern tips, is underlain by a variable thickness of glacial drift derived from multiple glaciations during the Pleistocene (Lineback, 1979). The drift is more than 50 feet (15 m) thick over large areas of the state and is more than 400 feet (122 m) thick in places. This cover of glacial drift and other Pleistocene deposits may effectively mask underlying bedrock structural features.

A number of linears in western Illinois have been investigated in the field. These linears are related to the last glaciation of the region. High-altitude aerial photography shows that linear glacial landforms such as drumlins and glacial flutes control the drainage patterns and, therefore, the orientation of linear alluvial valleys. Throughout much of western Illinois linear alluvial valleys parallel glacial flow directions.

Some linear alluvial valley segments in western Illinois may be bedrock controlled. Small linear valleys are present near the bluffs of the Illinois and Mississippi Rivers, where streams with high gradients have cut down into the bedrock. A small number of long linear alluvial valley segments in western Illinois are developed in bedrock and may follow some linear features within the bedrock. In southeastern Illinois, some linear features may also be controlled by bedrock jointing or fracturing.

Linear features can be useful when the types of linears being studied are recognized. The presence of linears and the direction of their orientation are important only when the particular causes of their development are understood.

FAULTING AND FRACTURING

Natural fractures have been major pathways for gas migration and accumulation in Appalachian gas fields (Hunter and Young, 1953). Although their exact nature and importance are debatable, it seems likely that extensive fracturing aids the flow of gas into wells and increases the volume of shale drained by any single well bore. Most of the major fault systems in Illinois (including the Wabash Valley, Cottage Grove, and Rend Lake Fault Systems and the Shawneetown Fault Zone) occur in southern and southeastern Illinois (fig. V-2). Extensive fracturing of rocks in these areas is known to exist, as indicated by observations in coal mines and by significant production of oil from fractured reservoirs in New Harmony Field, White County. Mineralization along fracture systems is common in the Fluorspar District in extreme southeastern Illinois.

Mary Barrows works at the Cambridge Stereoscan Scanning Electron Microscope used for petrographic studies of the New Albany Shale.

VI. PETROGRAPHY AND DEPOSITIONAL ENVIRONMENT

R. M. Cluff, R. D. Harvey, D. A. Burke, and M. H. Barrows

ABSTRACT

Petrographic studies of the New Albany Shale Group have identified and characterized five major lithofacies: (1) limestones and dolomites; (2) highly bioturbated mudstones; (3) indistinctly bedded shales; (4) thickly laminated shales; and (5) finely laminated shales. The distribution of these lithofacies—the basis for the major stratigraphic subdivisions of the New Albany Group—is shown to have been determined by the depositional environment of the shale, especially wave energy, bottom oxygenation, and bottom topography. A transect from the margin to the center of the Illinois Basin reveals a complete transition from high energy, aerobic, shallow-water environments to quiet, anaerobic, deep-water environments.

Shallow areas at the margin of the basin are characterized by rapid facies transitions over short distances. High energy, very shallow conditions are recorded by oolitic-skeletal grainstones and packstones with abundant calcified marine invertebrate fossils. Offshore, less agitated areas are represented by highly bioturbated carbonate wackestones, argillaceous quartz siltstones, and greenish-gray mudstones. Calcified invertebrates are generally rare in these facies, indicating deposition in dysaerobic conditions. Basinward, slope areas are characterized by olive-gray to black, weakly bioturbated shales commonly interbedded with thickly laminated black shales. Anaerobic conditions prevailed during most of New Albany time in the deepest areas of the basin, and finely laminated, undisturbed, pelagic black shales were deposited.

SCOPE AND PURPOSE

The major purpose of this project is to characterize in detail the petrographic properties of the New Albany Shale and relate those properties to the occurrence of hydrocarbons in the shale.

During these studies, we found that one of the most striking characteristics of the shales are the variation in distribution of benthic invertebrate fossils and biogenic sedimentary structures. Although many properties such as mineralogy and grain size vary only within relatively narrow limits, the bulk fabric of the rock varies considerably. These variations were caused primarily by the activity of benthic organisms, especially burrowers. Bioturbation destroys primary sedimentary structures, creates a distinctive swirling texture in the sediment, reduces the amount of organic matter preserved, changes composition of the organic matter preserved, and affects certain bulk physical properties of shale.

We have used data on bioturbation patterns and on the occurrence of invertebrate fossils to interpret the paleobathymetry, paleogeography, and depositional environments of the New Albany sea. The distribution of lithofacies in the New Albany Shale across Illinois is most consistent with deposition of the shale in a deep-water stratified anoxic basin centered in southeastern Illinois and adjacent western Kentucky. Because most hydrocarbons, including natural gas, originate from the thermal transformation (maturation) of sedimentary organic matter, the potential for commercial exploitation of gas from Devonian shales is greatest in the deep-basin area where organic-rich black shales are thickest.

Petrographic studies of shales may also contribute information useful in (1) predicting the behavior of shale when subjected to various types of fracture stimulation techniques and (2) in characterizing the flow of gas through shale reservoirs; we do believe, however, that the lithofacies classification outlined in this report will provide a useful and practical framework with which to evaluate the relationships between lithology, gas productivity, and fracture behavior when such data become available.

METHODS OF ANALYSIS

Field description of shale cores and outcrops

Megascopic descriptions were made in the field of all New Albany Shale cores used in this study and of numerous outcrops in Illinois, Indiana, and western Kentucky. The descriptions included such features as gross lithology; color (wet); thickness, spacing, continuity, and mineralogy of laminae; bioturbation; megafossils; occurrence of pyrite nodules and lenses; natural fracturing; unusual mineralization or other features; and visible gas shows. Field descriptions were made as quickly as practical without sacrificing detail. For the sake of consistency, nearly all field descriptions were made by the following four geologists: J. A. Lineback, R. M. Cluff, M. L. Reinbold, and J. T. Wickham.

Detailed characterization of selected samples

Samples were selected from each core for detailed petrographic study, usually at 10-foot (3 m) intervals or less. Radiographic analyses were made of oriented slabbed samples which were cut about 1/4 x 4 x 4 inches and x-rayed with a Picker Industrial Mini-Shot apparatus. A radiograph consists of a sheet of type M industrial x-ray film exposed to x-rays passing through the slabbed sample for 3 minutes at 38 kV. Different parts of the radiograph are exposed differently depending on the relative density, revealing variations of texture and structure of the slabbed sample. Each x-ray radiograph and matching core slab was examined and described at magnifications up to 50 x with a binocular microscope. Details on the preparation of core slabs for x-ray radiography are given by Harvey et al. (1978) and Bouma (1969).

Characterization of the microfabric of the shales and distribution of the clays, non-clay minerals, and organic matter was accomplished by microscopic examination of oriented thin sections cut perpendicular to bedding. In addition, an approximate measure of the degree of orientation of the clay minerals was determined for each sample by x-ray diffraction of a smoothed slab cut perpendicular to the bedding and mounted on a glass slide. This section was x-rayed from 2.5 to 22.5 degrees 2Θ and the areas of the peaks at 4, 8.8, 12.5, and 19.5 to 20.0 degrees 2Θ were determined. The orientation index is the ratio of the area of the 19.5-20.0° peak to the sum of the areas of the other peaks listed. Large orientation indexes indicate good preferred orientation of the clays parallel to bedding, while an index of 1.0 corresponds to completely random orientation. Depending on the intensity of the peaks (001 and hkl), adjustments for some samples had to be made for the particular clay minerals and micas present.

RESULTS

Lithofacies classification

Five general lithofacies are described in this and previous reports: (1) limestones and dolomites; (2) highly bioturbated mudstones; (3) indistinctly bedded shales; (4) thickly laminated shales; and (5) finely-laminated shales (Harvey et al., 1978; Cluff, in press).

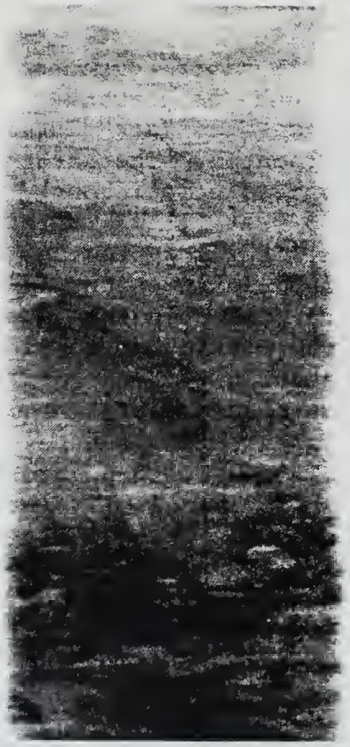
Limestones and dolomites. Carbonate rocks are a very minor component of the New Albany Shale Group; the Louisiana Limestone and portions of the Horton Creek Formation (formerly known as the "Glen Park" Formation in Illinois) are the only laterally persistent carbonates. The carbonate beds are usually thin (10 to 20 ft; 3-6 m) and may be discontinuous, although the Louisiana Limestone locally exceeds 35 feet (12 m) in thickness. The most common and widespread lithology is light gray to tan, wavy-bedded, bioturbated, and sparsely fossiliferous micritic limestone (fig. VI-1a). Thin shale partings and dolomitic beds are common in some areas. In most localities the limestones are faintly burrow mottled or completely homogeneous and have very probably (although not certainly) been totally bioturbated. One or more beds of oolitic limestone also are present in the New Albany. These are typically coarse-grained (calcarenites and calcirudites), cross-bedded, oolitic-skeletal grainstones and packstones with numerous rounded intraclasts of silty micrite. The bases of these beds are usually channeled erosional surfaces. These are the only rocks in the New Albany Shale Group that contain abundant or diverse calcified faunas.

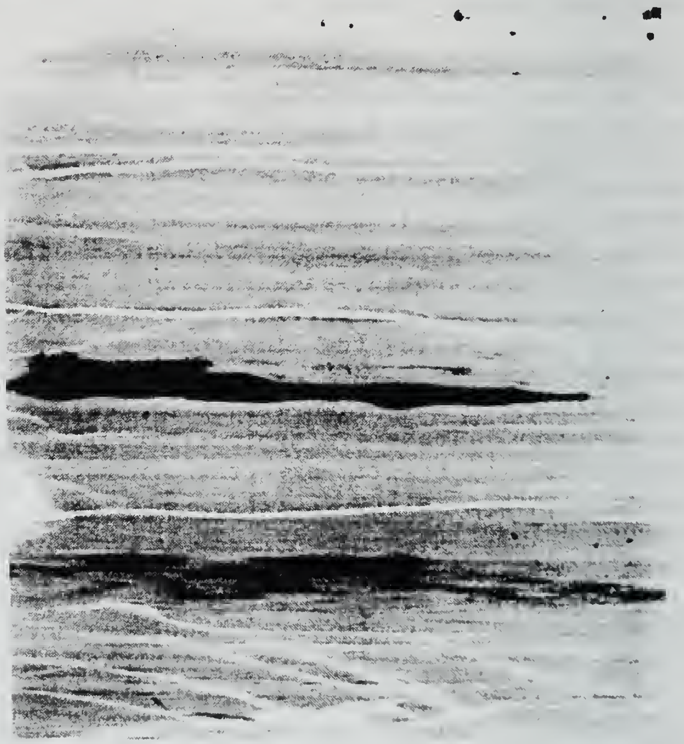
Lithofacies I. Bioturbated mudstones. Highly bioturbated mudstones form a major portion of the New Albany Shale Group and are the predominant facies in the broad area of thick sediments in west-central Illinois. Several thin tongues of bioturbated mudstone extend southward into southeastern Illinois. Highly bioturbated mudstones are typical of the Hannibal Shale, Saverton Shale, and portions of the Horton Creek Formation.

These mudstones vary widely in grain size, color, and organic content. The predominant lithology is moderately silty, dolomitic, greenish-gray shale grading locally into argillaceous siltstone, calcareous shale, or relatively silt-free olive-gray shale. They are typically unfossiliferous, although rare brachiopod or crinoid fragments are encountered. This lithofacies is characterized by the high degree of bioturbation, which has obliterated all traces of bedding and primary sedimentary structures (fig. VI-1b). When viewed under incident light these mudstones usually appear massive or only faintly mottled; however, x-ray radiography clearly reveals the swirling texture that results from extensive burrowing. Clay orientation analyses indicate a near-random or only slightly preferred orientation to the clays.

Figure VI-1. Lithofacies of the New Albany.

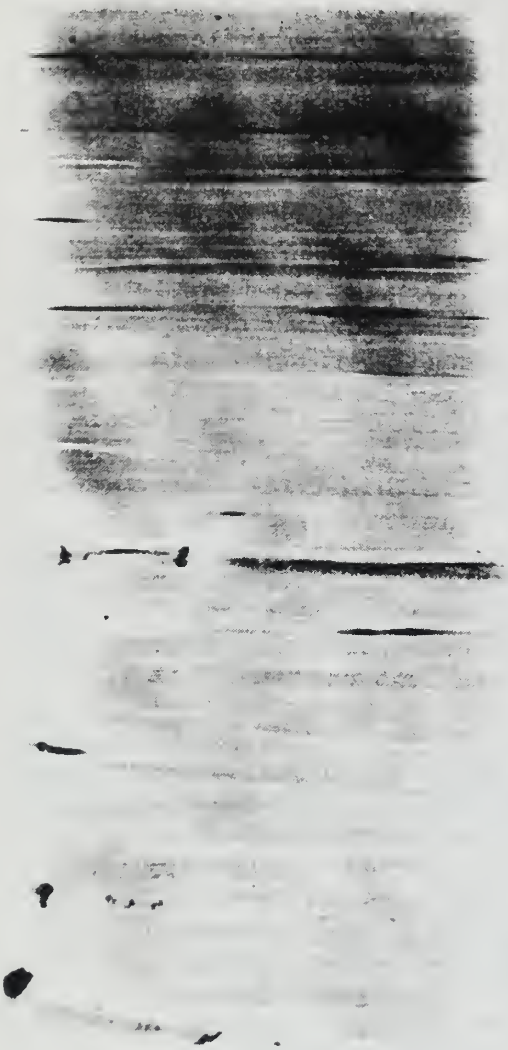
(a) Sparsely fossiliferous, bioturbated, micritic limestone. Characterized by homogeneous to faintly mottle texture and scattered brachiopod and pelmatozoan fragments in matrix. (Sample 7IL2L2, Fayette Co., IL)





(b) Lithofacies I: extensively bioturbated greenish-gray mudstone. The swirling texture is due to the mixing action of burrowing organisms. The short black specks and streaks are pyrite-filled burrows. (Sample IL3L1, Sangamon Co., IL)

(c) Lithofacies II: indistinctly bedded, olive-gray shale. Characterized by alternating light- and dark-colored bands, reflecting minor variations in organic content. Some of the high-organic layers are pyritic and appear black in this radiograph. The entire rock has been borrowed by small organisms, but few of the burrows have been pyritized. (Sample 4IL14C1, Henderson Co., IL)



(d) Lithofacies III: poorly laminated, brownish-black shale. Characterized by medium to thick, widely spaced laminations. Cut-and-fill structures or low-angle cross bedding are noted in some samples of this lithofacies. Sparse, widely spaced burrows are also common. (Sample 12IL3C1, Wayne Co., IL)

(e) Lithofacies IV: finely laminated, brownish-black shale. Characterized by fine, even, closely spaced, pyritic laminae; completely undisturbed by burrowing organisms. Most samples are characterized by numerous, small (1 to 2 mm) pyrite nodules and blebs aligned along bedding (black). (Sample 13IL10C1, Wayne Co., IL)

Lithofacies II. Indistinctly bedded shales. Indistinctly bedded shales are typical of the lower half of the Saverton Shale, the Sweetland Creek Shale, and the Selmier Shale. They are typically dark greenish-gray to olive-gray and are slightly higher in organic content than the bioturbated mudstones described above. They are generally unfossiliferous and contain little silt-sized or coarser material. They differ from the bioturbated mudstones in that burrowing is extensive but not total, as bedding is still preserved (fig. VI-1c). The burrows in these shales are mostly very small (less than 1 mm wide) *Chondrites* and *Planolites*. Irregular oblique burrows and flattened *Zoophycos* are common in some areas. Clay orientation indices are generally low (near random). Thin interbedding of burrowed, indistinctly bedded gray shales with laminated black shales is common in several portions of the New Albany Shale.

Lithofacies III. Thickly laminated shales. Thickly laminated shales occur throughout the Selmier Shale in southeastern Illinois, and, to a lesser extent, in the Sweetland Creek Shale and portions of the Grassy Creek Shale in western and west-central Illinois. They are often interbedded with indistinctly bedded greenish-gray shales. The thickly laminated shales are high in organic content and are olive-black to brownish-black. The laminations are thick, irregular, and widely spaced (fig. VI-1d), and pyrite nodules are common. Silt layers up to several centimeters thick (either rippled or cross laminated) occur in some areas. The thickly laminated shales have not been bioturbated except for sporadic burrows where they are interbedded with indistinctly bedded gray shales. Clay orientation indices are variable but are generally moderate to high. The thickly-laminated shales are also unfossiliferous except for occasional fragments of planktonic and nektonic taxa, chiefly phosphatic conodonts and fish debris.

Lithofacies IV. Finely laminated shales. Finely laminated shales comprise the bulk of the Grassy Creek and Blocher Shales and are the predominant lithofacies in southeastern Illinois. These shales are brownish-black to grayish-black, high in organic content, and pyritic. They are uniformly fine grained, and virtually no detrital material larger than 50 µm is present. The laminations are uniformly fine, even, and closely spaced (fig. VI-1e), and clay orientation indices are high, indicating strong orientation of the clay flakes parallel to bedding. In some samples, numerous small pyrite nodules are scattered along the laminae. Most of the sedimentation is pelagic, and no evidence of bottom disturbance by currents has been found.

Fossils in the finely laminated shales are predominantly planktonic and nektonic taxa, including *Tasmanites* (presumably spores of marine algae), fish debris, and pteropods. Occasionally, small calcareous brachiopods and linguloid brachiopods are found along bedding planes in the Blocher Shale. The sediments are completely undisturbed by burrowing organisms, and these shales are not interbedded with burrowed shales.

Depositional environment

The inferred depositional environments for each of the major lithofacies in the New Albany Shale (fig. VI-2) are summarized as follows:

Limestones and dolomites. Aerobic (>1.0 ml O_2/ℓ water), shallow-water (<150 ft; <50 m), locally high-energy environments (as shown by widespread oolites, local erosional unconformities, and limestone conglomerates). Because these are the only rocks in the New Albany Shale Group with abundant benthic invertebrate fossils, it is apparent that they represent the most highly-oxygenated areas of the New Albany sea. Burrowing organisms were unable to survive in the most highly agitated areas of carbonate deposition, and bioturbation is common only in the more quiet water carbonate wackestones and mudstones.

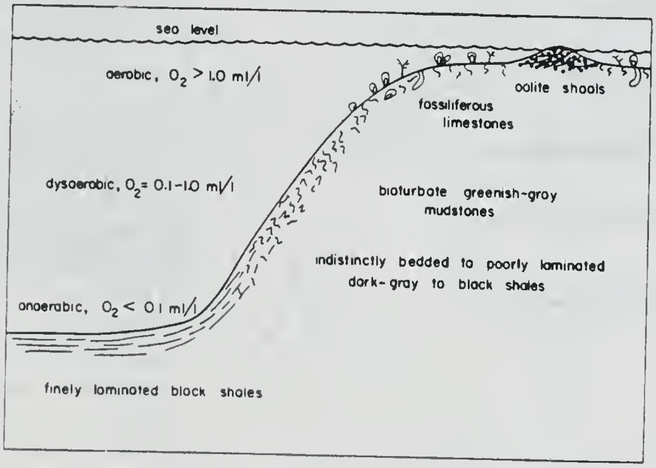
Bioturbated mudstones. Dysaerobic (0.1 to 1.0 ml O_2/ℓ water), moderate depth (150-500 ft; 50-150 m?), and quiet water environments. The extensive bioturbation and the absence of shelly benthos in these rocks indicate deposition in a poorly-oxygenated environment.

Indistinctly bedded shales. Marginal dysaerobic to anaerobic (<0.1 ml O_2/ℓ water), moderate to deep, quiet water environments. The less intense burrowing and preponderance of small burrows suggests that these shales were deposited in dysaerobic waters slightly less oxygenated and less favorable for benthic organisms than the highly bioturbated mudstones discussed above.

Thickly laminated shales. Anaerobic, deep (>500 ft; >150 m?), quiet water environments, broken only by occasional currents carrying terrigenous silt and other coarse-grained detritus.

Finely laminated shales. Anaerobic, deep, and very quiet water environments. The high organic content, rarity of burrows, absence of megafossils, and preservation of laminae in the laminated shales indicate deposition in a predominantly anoxic environment.

The distribution of these lithofacies across the Illinois Basin is best explained by deposition of the New Albany Shale in a stratified anoxic basin. Finely laminated shales (including the Blocher, middle Selmier, and Grassy Creek Shales) are predominant in and around the depositional



ILLINOIS STATE GEOLOGICAL SURVEY 1978

Figure VI-2. Stratified anoxic basin model, showing relationship of oxygenation to lithofacies. (After Rhoads and Morse, 1971)

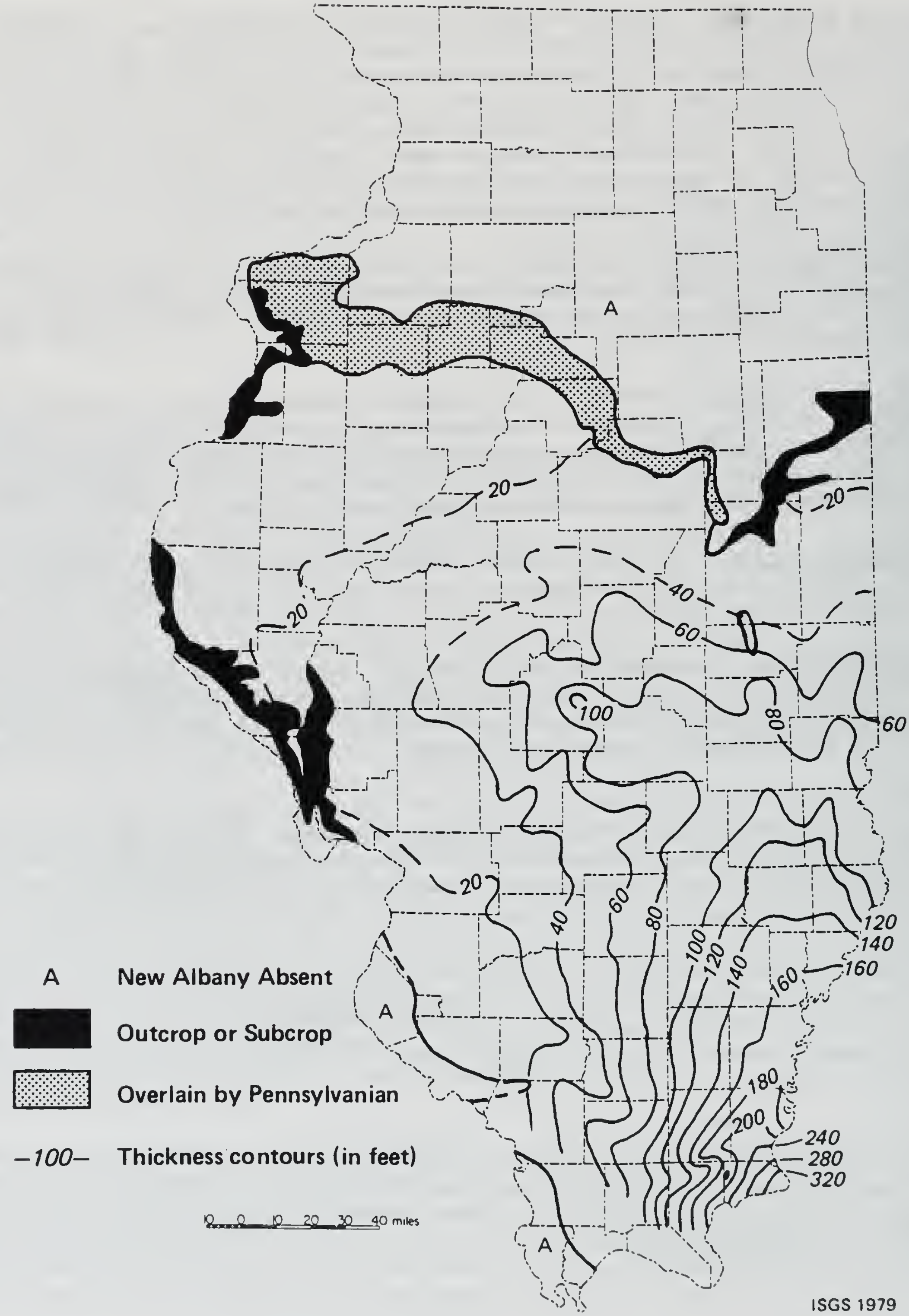


Figure VI-3. Cumulative thickness of radioactive shale within the New Albany Shale Group in Illinois. Radioactive shale is here defined as having a gamma ray log value >60 API units above a normal shale base line. (From Cluff, Reinbold, and Lineback, in prep.)

center of the basin in southeastern Illinois and western Kentucky (figs. IV-2, VI-3) and thin progressively in all directions away from there. Anaerobic conditions prevailed for long periods of time, and this was a relatively deep-water environment throughout New Albany deposition (fig. VI-4).

Bioturbated mudstones and indistinctly bedded shales (including most of the Sweetland Creek, Saverton, and Hannibal Shales) are the predominant facies in west-central Illinois, coinciding with the area of thick New Albany sediments shown in figure IV-2. Because poorly oxygenated conditions were maintained for a long period over a wide area of west-central Illinois, the broad region indicated on figure VI-4 was apparently a relatively flat shelf under 150 ft (50 m) or more of water during New Albany deposition.

The narrow region of thin New Albany sediments trending across central Illinois (fig. IV-2) is characterized by interbedding and intertonguing of indistinctly bedded shales, thickly laminated shales, and finely laminated shales (fig. VI-5). The interbedding and interfingering of these various lithologies (each representing different oxygenation conditions) are attributed to vertical movements of the anaerobic/dysaerobic boundary through the water column sweeping across a basin slope between the deep basin in southeastern Illinois and the broad shelf area of west-central Illinois (fig. VI-4).

The restricted distribution of carbonates in the New Albany is interpreted as the result of deposition along a shelf margin area—with the carbonates building near the slope break between the shelf area to the northwest and the narrow basin slope leading down into the ancestral Illinois Basin towards the southeast (figs. IV-8, VI-4, VI-5). Many areas of carbonates deposition coincided with locally emergent Devonian structures, such as the Lincoln Fold in extreme western Illinois. The shelf margin was apparently not a sharp break, but rather a northeast-southwest trending zone more than 30 miles (45 km) wide. In this shelf margin zone are found most of the carbonate beds in the New Albany, including the oolitic limestone belt in the Horton Creek Formation; however, thin carbonate beds also extend southeastward and down the basin slope for considerable distances. These slope beds are very argillaceous fine grained limestones and are distinctly basinal in character. The Hannibal-Saverton Shale thins very rapidly across the shelf margin (fig. IV-7), as does

Figure VI-4. Paleogeography of the New Albany Sea in Illinois. (From Cluff, in press) the Grassy Creek-Sweetland Creek undifferentiated interval (fig. IV-6) and the total New Albany thickness (fig. IV-2). The overlying Chouteau Limestone thins and pinches out, possibly grading laterally into Hannibal Shale, near the northwest limit of the shelf margin (fig. IV-8). These relationships suggest that the New Albany shelf margin was probably a gentle ramp rather than a sharp, steep break such as existed during deposition of the Burlington-Keokuk crinoidal bank (Lineback, 1966). The close similarity between the New Albany shelf margin area and the Burlington-Keokuk bank edge clearly indicates that the Valmeyeran paleogeography of the Illinois Basin was well established by late Devonian time.

The fact that many portions of the New Albany Shale are characterized by widespread lateral intertonguing and gradation of lithofacies, while other portions are characterized by thin interbedding of lithologies, indicates that depositional conditions were not static, but fluctuated on a local and regional scale. Tongues of laminated black shale extend out of the southern depocenter and far across western and central Illinois. The most notable of these tongues is the thin Grassy Creek Shale in those regions (fig. VI-5). Tongues of bioturbated greenish-gray shale also extend down off the western Illinois shelf region into the basin (i.e., gray shales in the Sweetland Creek and Selmier Shales).

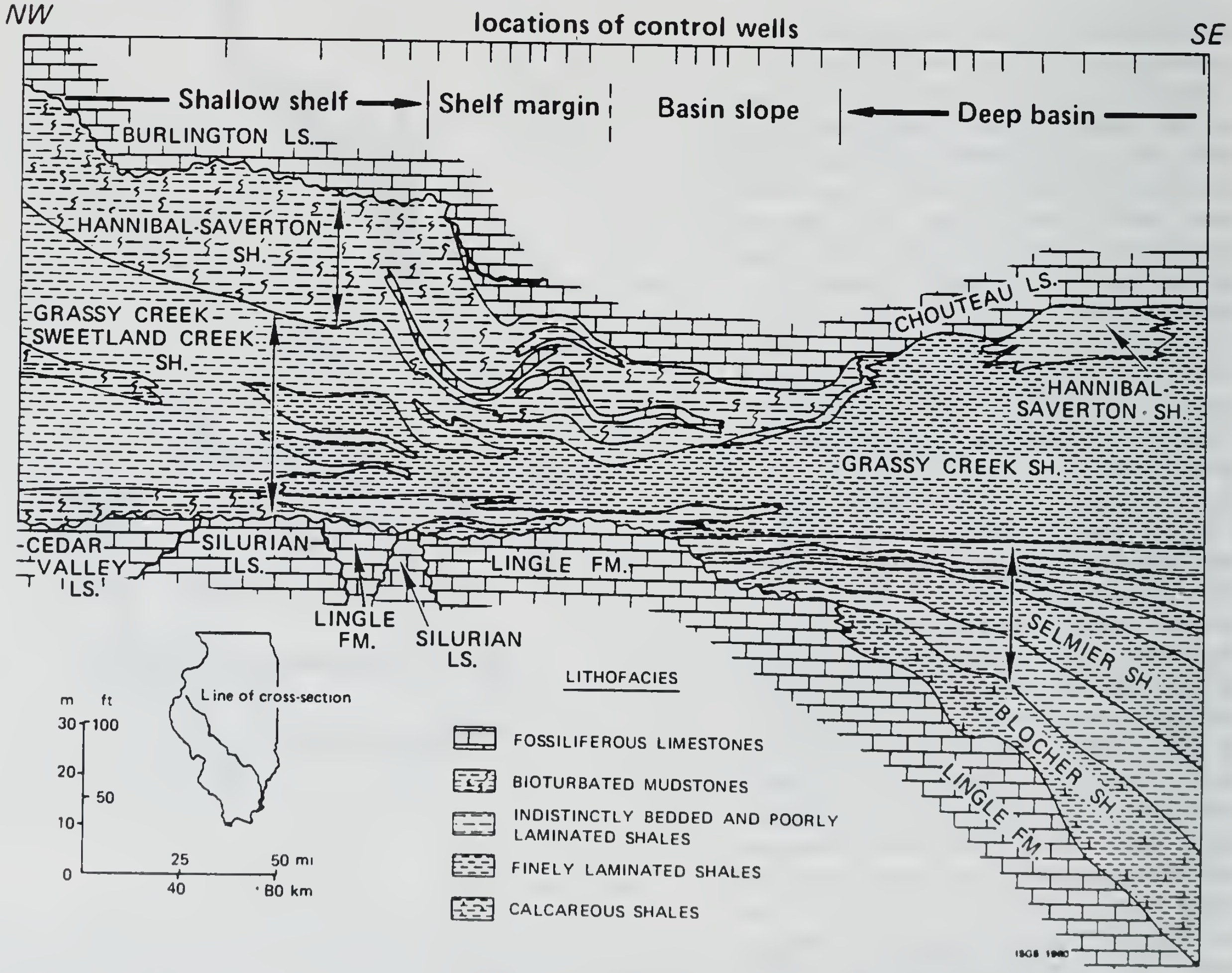


Figure VI-5. Diagrammatic cross section through the New Albany Shale Group in Illinois, illustrating broad lateral facies changes from shelf to slope to basin environments. (From Cluff, in press)

The regional interfingering of gray and black shales across Illinois is interpreted as the result of major vertical fluctuations in the position of the anaerobic/dysaerobic boundary. When the anaerobic/dysaerobic boundary rose in the water column, black shale transgressed across areas where gray shales had been deposited. Similarly, when the anaerobic/dysaerobic boundary fell in the water column, the area of black shale deposition was restricted and gray shales extended down into deeper areas of basin. Even during the maximum transgression of anaerobic conditions across the shelf area of western Illinois, however, less than 20 feet of black shale was deposited in this region. During most of New Albany deposition the fluctuations in oxygenation conditions were restricted to the deep-basin area, and most of the prominent facies changes occur on the basin slope and shelf margin.

David Burke examines an x-ray track on the Norelco x-ray diffractometer used for mineralogical studies.

VII. MINERALOGY

Richard D. Harvey, David A. Burke, M. H. Barrows, and R. M. Cluff

ABSTRACT

Mineralogic characteristics of the shales of the New Albany Group in Illinois revealed by x-ray diffraction and microscopic analyses indicate a relatively uniform composition for such a thick succession of rock strata. The silt-size constituents are predominately quartz with K-feldspar, plagioclase, and muscovite mica commonly present. Dolomite and pyrite are also minor components in most samples. The predominate clay mineral is illite in all strata of shale and mudstone. Chlorite and expandable clay minerals (mixed-layered illite-smectite) are minor constituents in virtually all beds. Apatite and marcasite are trace minerals in many samples.

The abundance of illite increases in an irregular pattern toward the area of thick accumulation of shale, the site of deepest submarine deposition in southeastern Illinois. The abundance of dolomite generally increases with depth within the brownish and dark-gray shales of the succession of the Grassy Creek, Sweetland Creek-Selmier (undifferentiated), and Blocher Shales. This relative increase is accompanied by a corresponding decrease in abundance of quartz. The abundance of calcite is quite variable in the Grassy Creek, Sweetland Creek, and Selmier Shales, while it is usually a major mineral in beds above and below. Pyrite is a major constituent in laminated shales high in organic content (i.e., most beds in the Grassy Creek and below in the deeper part of the Illinois Basin).

INTRODUCTION

Mineralogic identifications and characterizations of the cores and ISGS supplementary drill-cutting samples were made to evaluate the stratigraphic and areal distribution of the mineral constituents of the New Albany Shale Group. The evaluation of mineralogic properties in terms of their systematic changes in the rock, both vertically and areally, can help determine the sedimentology and paleoenvironments of deposition of the shales which are important aspects of potential occurrence and production of hydrocarbons.

The shales, largely comprised of clay-sized (<2 μm) material, were analyzed by x-ray diffraction (XRD) using two techniques: (1) analysis of powdered samples to determine the mineralogy of the silt constituents; and (2) separation of a <2 μm fraction of powdered samples and analysis of the clay minerals.

The textural distribution and occurrences of the minerals present and the identification of trace minerals were determined by thin-section petrography and a scanning electron microscope equipped with an energy dispersive spectrometer (SEM-EDS).

METHODS

The XRD analyses were made with a Norelco x-ray diffractometer equipped with a copper x-ray tube. The diffracted radiation passed through a monochromater to reduce fluorescent radiation from iron-rich samples; a scan rate of 2 degrees per minute was used.

Samples were crushed and split for the various purposes of the project (fig. III-2). The powdered samples for XRD were ground and packed into a standard rear-loaded powder sample holder to produce a randomly-oriented sample. The XRD scans were made from 25 to 65 degrees 2θ at a recording range of 500 counts full scale and a time constant of 2 seconds. Diagnostic peaks were chosen for individual minerals and the peak heights were recorded in counts/second. Although these data were not converted to percentage values, they are proportional to the abundance of the mineral in the sample insofar as the matrix effects for the shale samples were essentially constant (as were the instrumental and sample preparation effects). Thus the trends shown by these data provide the basis for mineralogic evaluations required for this study.

Sample splits for clay mineral analysis were dispersed in a blender with deionized water and allowed to settle. A few grains of sodium hexametaphosphate and sodium carbonate were added as needed to prevent flocculation. The <2 μm fraction was then siphoned off and flocculated with a few drops of 10 percent HCl, then centrifuged to form a paste. Oriented smear slides were made of the paste, allowed to dry in air, and placed in vapors of ethylene glycol held at a constant temperature of 28°C for at least five days prior to XRD analysis. The relative amounts of the various clay minerals present in the samples were determined according to their XRD intensities. The method of claculating their abundances in the samples, reported in table VII-1 and on the computer file, is based on XRD data of samples run after saturation in vapors of ethylene glycol (g) and run again after heating (h) to 375°C for one hour. The intensities used to calculate the expandables ratio were taken to be the area of the 10Å peak (height x ½ peak width at ½ height). The intensities for the chlorite ratio were taken to be the peak heights of the 4.75Å and the 5Å d-spacings respectively.

The occurrence and abundance of specific minerals were studied by thin-section petrography and SEM methods. Oriented petrographic thin sections about 20-25 μm thick were prepared for each sample selected for study from the cores. The samples studied by SEM-EDS were selected from different cores to represent the four lithofacies types recognized in the New Albany Shale Group by Harvey et al. (1978). The samples were cemented on aluminum stubs for this study. Some were untreated surfaces broken during core drilling or sample handling. Others were polished, then etched with 48-percent hydrofluoric acid for 30 seconds and rinsed free of acid with water. All were oven dried for about 15 hours at 50°C prior to vacuum coating with nickel or chromium. A Cambridge Mark IIA SEM equipped with an EDAX energy dispersive spectrometer was used for these studies.

TABLE VII-1. Calculations used for clay mineral analyses*

Clay Mineral (i)			Ratio
Illite (I):	$\frac{I_{10,g}}{I_{10,g}}$	=	1
Expandables (Ex):	$\frac{I_{10,h} - I_{10,g}}{I_{10,g}}$	=	___________
Chlorite (C):	$\frac{C_{4.73,h}}{I_{5,g}}$	=	___________
Kaolinite (K):	$\frac{K_{3.58,g}}{2\ C_{3.55,g}} \times \frac{C_{4.73,h}}{I_{5,h}}$	=	___________ Σ

- -

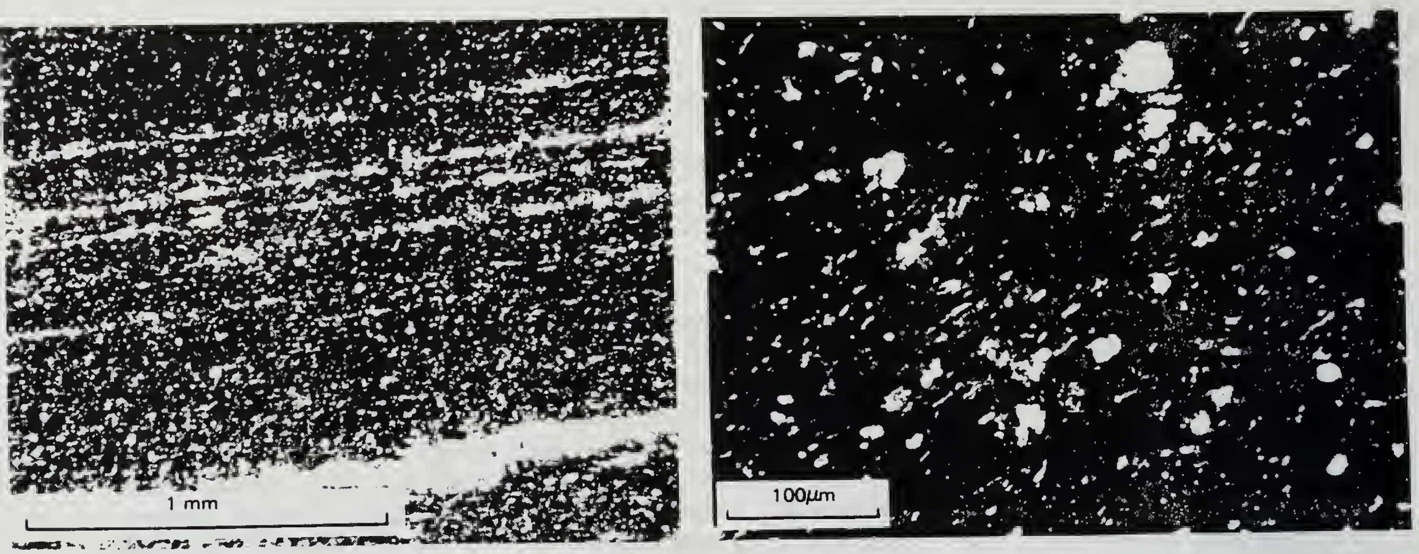
$$\text{Amount of clay mineral (i)} = \text{Ratio of (i)} \times \frac{100}{\Sigma \text{ of all ratios}}$$

*The x-ray intensity of the peak is indicated by I, Ex, C, or K. The first subscript to the intensity is the d-spacing (Å) of the peak and the second subscript refers to glycol (g) or heat (h) treated sample.

RESULTS

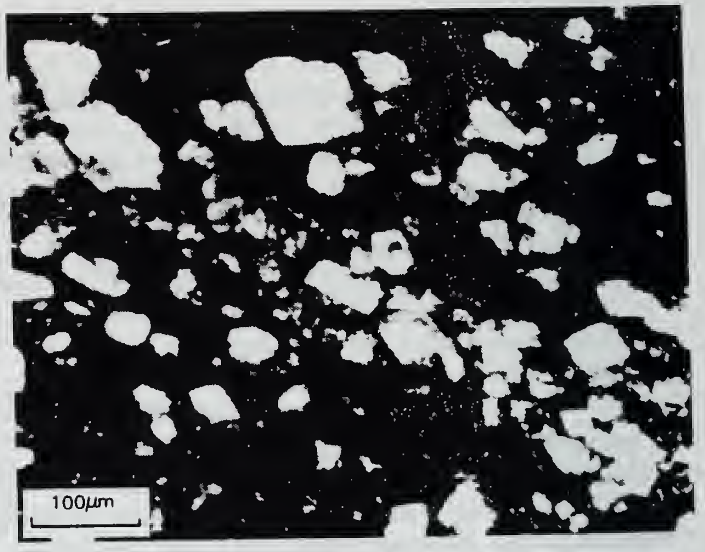
XRD mineralogic analyses of the New Albany were made of 430 samples; 190 of these were selected from approximately every 10-foot (3 m) interval through 14 different DOE and ISGS cores (identified as 10IL, 02IL, 01KY, etc.). The remaining 240 samples were selected from oil well drill cuttings that were available in the ISGS sample library. These samples are identified here by a sequential number prefixed by NAS, referring to the New Albany Shale.

The high degree of lithification of the shales prohibits the use of mechanical methods of grain-size characterization, an important mineralogical property. Thus, thin-section microscopy was employed for this purpose. The results of examination of nearly 200 samples of shales show a rather small range of grain-size distribution (fig. VII-1). To summarize, these results indicate that the shales are composed of about 80 to 90 volume percent of grains and flakes < 2 µm in size. The remaining fraction is composed almost entirely of silt-sized grains (2 to 62 µm). Only trace numbers of larger grains were observed, mainly pyrite nodules.



(a) Quartz silt lamina (bright irregular band) overlain by silty shale and underlain by organic rich shale (dark irregular band). (Sample 01KY07L1)

(b) Mica Flakes (white streaks) aligned parallel to bedding and scattered irregular patches of sparry calcite (large white areas). (Sample 01KY12C1)



(c) Dolomite rhombs in an illitic clay matrix of a finely laminated black shale from the Blocher. (Sample 01KY12C1)

Figure VII-1. Thin section photomicrographs of New Albany Shale.

Clay mineralogy

The results of the clay mineral analyses of the samples from all the DOE cores drilled in Illinois and from the ISGS cores analyzed are shown in figure VII-2. Because only a few types of clay minerals were found to occur in the New Albany shales, the results are expressed in terms of the three important clay mineral types: illite, chlorite, and expandables (mixed-layer clay minerals).

Illite, considered here to be clay particles that have a 10Å basal spacing which neither expands upon exposure to ethylene glycol vapors nor collapses under 375°C temperature, is the most abundant type of clay in all samples studied. The 2M polymorph was the only variety of illite found in the samples. The core studies revealed that there was generally more illite in the southern area of the state than in the northern area (fig. VII-2). Additional data from the NAS samples confirm this trend. The amount of illite in all samples of shales from the Grassy Creek and the Sweetland Creek-Selmier increased from the northern part of the study area to the southeastern part (fig. VII-3).

The crystallinity of the illite occurring in the samples was determined by measurements of the sharpness of the 10Å peak. Although considerable variation of the crystallinity was observed, no correlation was found between these results and the depth of the samples, or with the reflectance of the vitrinite associated with the mineral. The highest degree of crystallinity was observed in samples from the Fluorspar District and neighboring Hicks

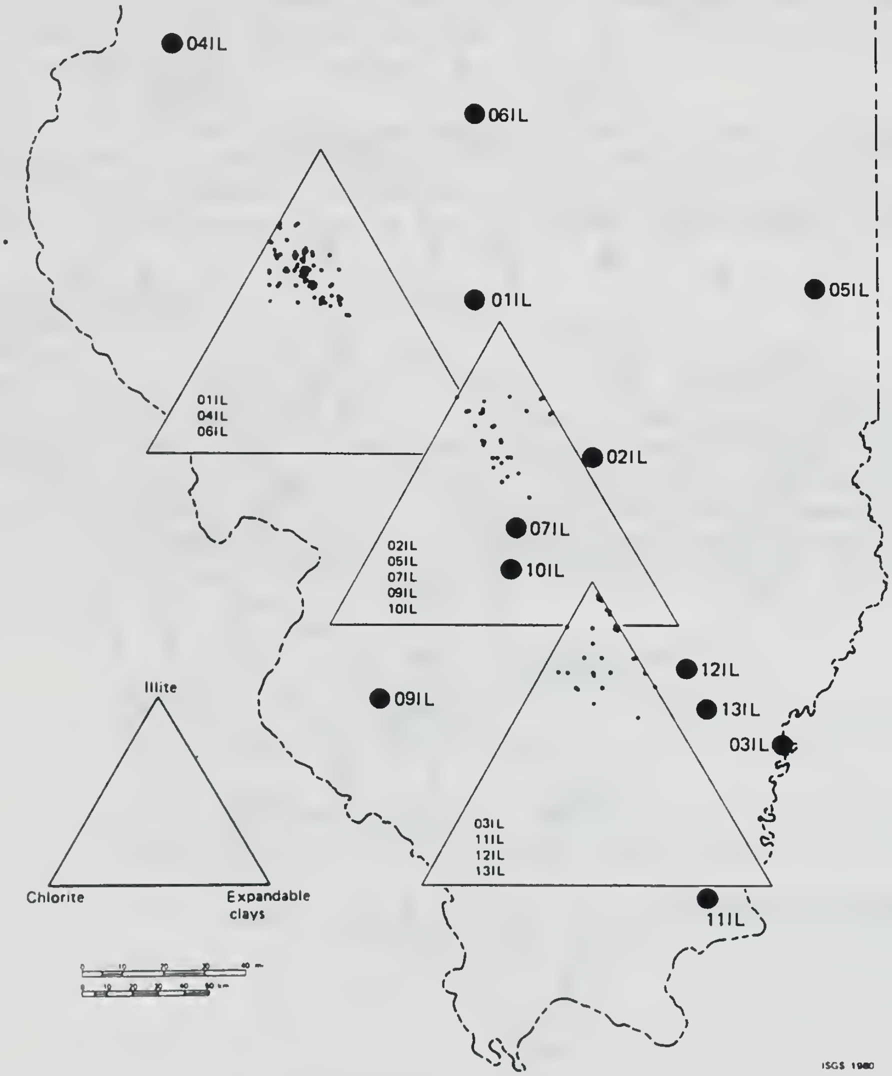


Figure VII-2. Clay mineral distribution in Illinois and ISGS cores.

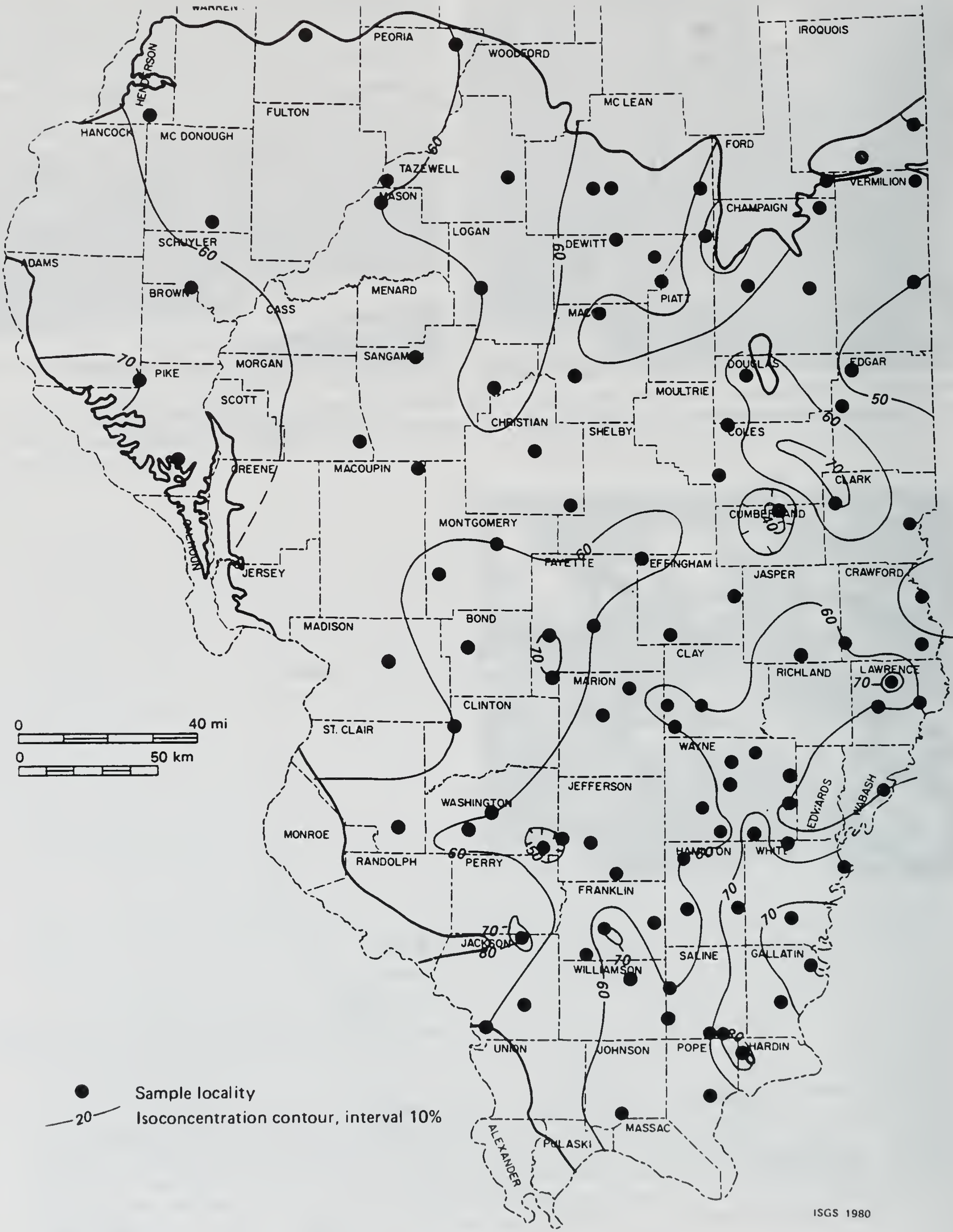


Figure VII-3. Illite distribution in Grassy Creek-Sweetland Creek Shales shown in percentage of the clay fraction.

Dome area (Hardin County, IL) in extreme southern Illinois. The high crystallinity here is thought to result from local mineralization restricted to this district rather than to a regional process. However, the microscopic data show that virtually all the shales contain a minor percentage of mica occurring as flakes mostly 4 to 8 μm long (a type of mica similar in chemical composition and structure to that of illite).

Expandable clay minerals are considered to be mixed-layered minerals that undergo some expansion with ethylene glycol vapors and collapse to 10Å upon heating to 375°C. No 17Å smectite reflections were observed. The expandable material in the samples studied is an illite-smectite type of mixed-layer clay mineral. It is rare for the shales to contain more than 3 parts expandable clay per 10 parts; most shales contain 1 to 2 parts.

Chlorite, a 14Å nonexpanding, noncollapsing clay mineral, occurs widely in the New Albany (fig. VII-4). Chlorite is generally not present in the Blocher and not in the shales within the Fluorspar District. The shales overlying the Blocher generally contain 20 to 30 percent chlorite in the clay fraction from all areas except the southeastern, where it is commonly 10 to 20 percent. No distinction was made in this study between common Mg-chlorite and Fe-bearing chlorite.

Kaolinite is absent in the core and NAS samples, except for a few scattered instances in which trace amounts were detected (these, listed in the computer file for the NAS samples, are interpreted as cavings derived from strata overlying the New Albany during drilling operations).

Silt mineralogy

A summary of the results of the silt mineralogy reported in XRD counts per second are listed in table VII-2. Average values are given for the samples analyzed from the Grassy Creek, the Sweetland Creek-Selmier, and the Blocher Shales. The XRD peak used to indicate the relative abundance of the various minerals is shown in the table. The format of data in table VII-2 shows the nature of the data we obtained on the individual samples during this study. The Survey's computer disk file on this project contains the results of all the samples in this format.

TABLE VII-2. Average observed peak maxima (counts/sec) from x-ray powder diffraction analysis for the New Albany Shale in the southern part of Illinois.

Mineral	MICA	QUARTZ	FELDSPARS	K-SPAR	PLAGIOCLASE	CALCITE	DOLOMITE	APATITE	PYRITE	MARCASITE
deg. 2θ / Fm.	19.8	20.8	~ 23.5	~ 27.5	~ 27.9	29.4	30.8	32.1	33.1	51.9
Grassy Creek Sh	56.4	142.4	30.6	36.7	53.4	29.1	42.5	19.0	28.9	5.2
Sweetland Creek Selmier Shale (Undiff.)	52.1	125.0	24.6	32.5	50.2	23.7	70.4	21.2	23.8	3.1
Blocher Shale	39.9	98.7	24.5	36.6	40.6	98.6	104.5	14.3	23.3	3.2

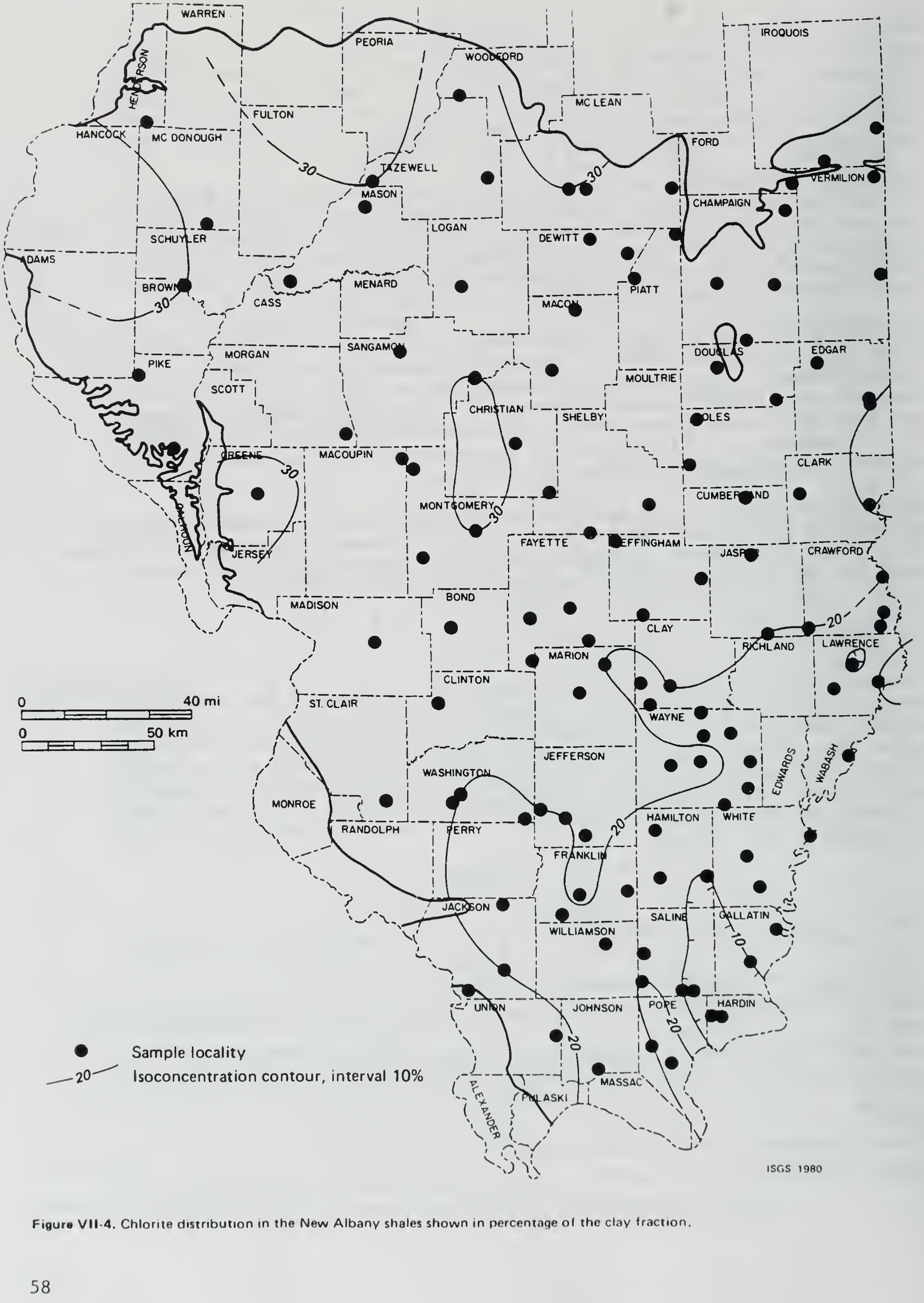


Figure VII-4. Chlorite distribution in the New Albany shales shown in percentage of the clay fraction.

Quartz occurs as detrital grains less than 2 μm in size and in grains up to about 90 μm in diameter (commonly 10 to 50 μm). Quartz was always detected in the <2 μm clay samples; many such samples probably consist of as much as 25 percent quartz. The silt grains occur randomly scattered, or grouped together in distinct laminae (fig. VII-1b) and in cross-bedded siltstones. The average amount of quartz generally decreases in progressively older and deeper shale formations (table VII-2).

Mica occurs as microscopic flakes, usually about 4 to 8 μm long, scattered widely as a minor, but variable, component within the clay matrix. Variations in its abundance are not related to areal distribution or to depth in the shale formations (table VII-2). SEM-EDS analyses of many of these flakes indicate that they are muscovite in composition but with a trace of iron present (fig. VII-5A). Thin-section petrography shows preferred orientation of the flakes parallel to bedding in all but the bioturbated mudstones. These flakes may be clusters of many well-oriented and intergrown illite crystallites (possibly diagenetically altered) or they may be entirely detrital in origin; however, the 2M variety of the associated illite suggests that some diagenetic crystal growth took place on one or both of these mineral types.

Feldspar. Potassium feldspar (K-spar in table VII-2) and plagioclase were detected and distinguished by XRD. The grain size was generally too small to be distinguished from quartz in thin section, although some plagioclase was identified in silt laminae. Plagioclase usually becomes increasingly more abundant than potassium feldspar toward the southern part of the state. Samples from the area around the Hardin County core (11IL) have greatly enhanced plagioclase and dolomite and reduced potassium feldspar, quartz, and mica. SEM analyses of a plagioclase-bearing shale (fig. VII-5B) shows some well formed euhedral crystals of plagioclase, indicating an authigenic origin for this mineral (Barrows, 1980).

Calcite occurs primiarily in the limestones interbedded with shales in the upper part of the New Albany in western Illinois and in thin calcareous siltstones in western Kentucky. In the Blocher Shale, calcite occurs as abundant, scattered silt-size grains and in laminar silt bands. The abundance of calcite in the Grassy Creek, Sweetland Creek, and Selmier Shales is quite variable over the study area.

Dolomite occurs throughout the New Albany Shale as thin laminae of small crystals, as a cement in some quartz silt laminae, and as groupings of single rhombs (fig. VII-1c). Its origin is probably related to bacterial precipitation. The major peak of dolomite was observed shifted somewhat to a larger d-spacing than normal, indicating a rather consistent iron substitution for some of the magnesium in the structure of the dolomite. On the average, dolomite increases in abundance with depth in the New Albany (table VII-2).

Apatite and siderite occur in phosphatic fossil debris, mainly fragments of conodonts, brachiopods, fish scales, bones, and shark teeth, and in sedimentary nodules. It occurs widely but is of minor abundance in the New Albany Group (table VII-2). In such minor amounts, apatite cannot be distinguished from siderite by XRD; however, Mössbauer studies (Shiley et al., in preparation) confirm that no iron occurs as siderite in the few samples they studied.

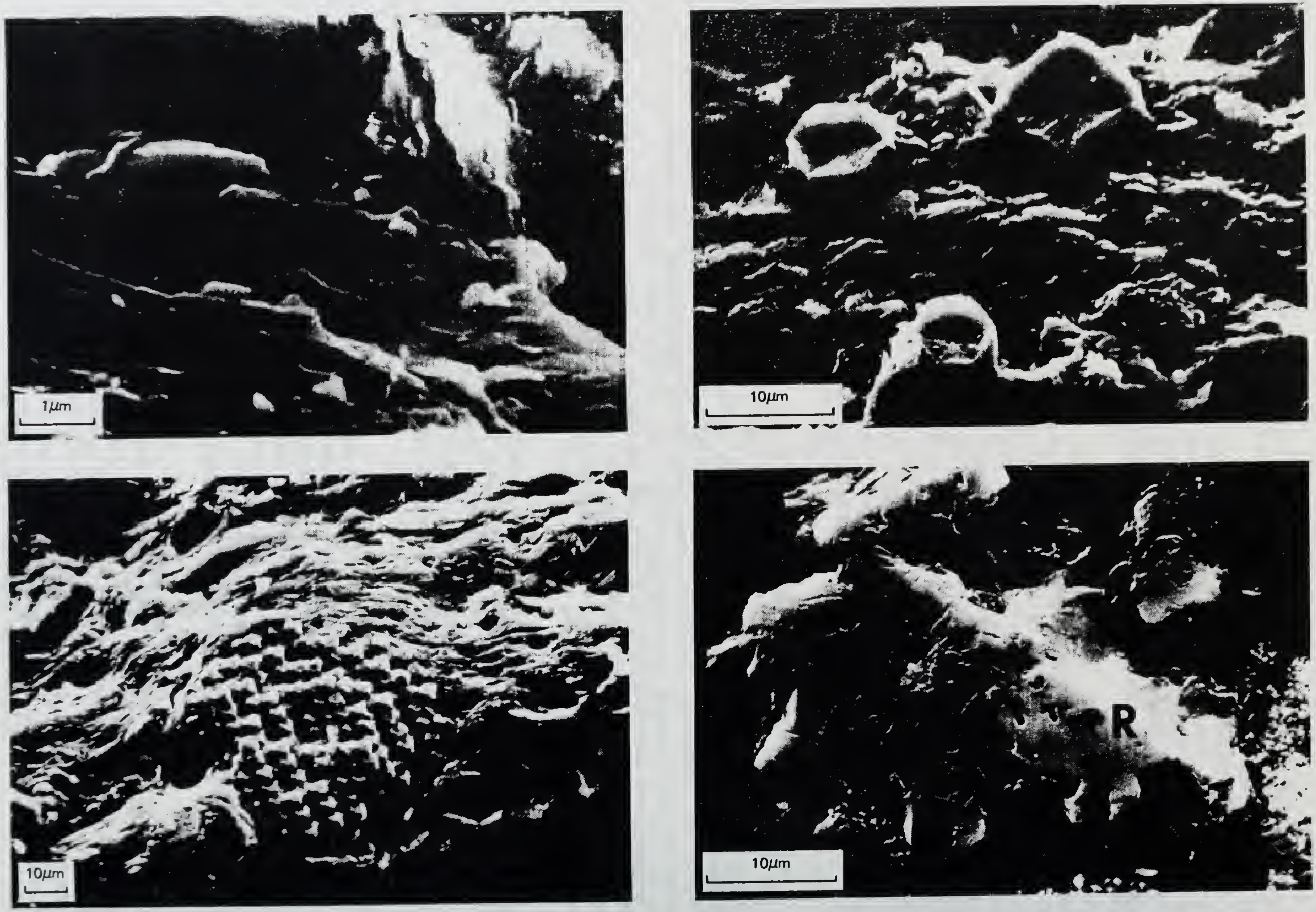


Figure VII-5. Scanning electron micrographs of distinctive mineral grains: (a) Cleaved muscovite on broken surface, normal to bedding, of a greenish-gray mudstone (04IL27L1) in the Sweetland Creek (bar=1μm); (b) Na-rich plagioclase crystals on etched bedding surface of a finely laminated black shale (02IL6C1) in the Grassy Creek; authigenetic in origin (bar=10 μm). (c) very fine crystals in a mciroporous framboid of pyrite surrounded by illitic clay. Same samples as in B (bar=10 μm); (d) rutile grain 10μm across (R), intergrown with an adjacent silt grain of quartz shown ⊥ to bedding surface (polished and etched); same sample as in B (bar=10 μm).

However, siderite occurs within the upper 80 feet of the Hardin County core (11IL), in the lowest sample taken from the Grassy Creek (11IL04C1) and in those from the upper 50 feet of the underlying Sweetland Creek. These samples are from dark gray or olive gray shales, not otherwise different from other samples that are free of siderite.

Pyrite and marcasite occur together in many samples. Pyrite is much more abundant than marcasite: it occurs in widely variable forms throughout the New Albany, as silt-sized framboids (fig. VII-5C); as nodules of varying size; as lenticular forms along bedding planes and burrow fillings; and as isolated euhedral crystals. All these forms probably grew in place near the sediment-water interface in response to bacterial activity. Distinction between pyrite and marcasite, two dimorphous forms of FeS_2, was recognized by the presence of the XRD peak of marcasite at 51.9° 2θ. Marcasite is present in many samples, but only as a trace constituent (table VII-2). Its petrographic association was not determined, as the mineral was not recognizable in thin section and SEM microscopy. Pyrite tends to occur more abundantly in the more organic-rich and less bioturbated shales in the deeper, basinward portions of the New Albany.

Heavy minerals. Traces of rutile (fig. VII-5D), zircon, amphibole, pyroxene, and glauconite grains were identified by thin section microscopy and SEM analysis but were not detected by XRD methods. Rutile is often found associated with organic matter concentrates.

It is worth noting that a trace amount of basaluminite ($Al_4SO_2(OH)_{10}\cdot(5H_2O)$) was found by XRD to occur in the lowermost 5 to 7 feet of the Blocher Shale, in the 01KY core, Christian County, Kentucky. The significance of this one occurrence of basaluminite from all the samples studied is not known. No indications of paleoweathering were noted within this interval of the core, as was found in basaluminite bearing shales of equivalent strata some 100 miles to the south and southeast of the core (Milton et al., 1955).

Mary Barrows collects vitrinite reflectance data on the Lietz MPV-II microscope-photometer.

VIII. ORGANIC PETROGRAPHY

M. H. Barrows, R. M. Cluff, and R. D. Harvey

ABSTRACT

As part of the study to evaluate the potential of the New Albany Shale Group of the Illinois Basin to yield hydrocarbons, coal petrographic techniques were employed to evaluate the composition and thermal maturity of dispersed organic matter in the shales.

Vitrinite reflectance was measured on acid-macerated kerogen concentrates from 16 cores and 132 other drill holes through the New Albany Shale in Illinois, Indiana, and western Kentucky. No significant variations in reflectance values were observed within the New Albany at any single location with respect to either depositional facies or depth. An isoreflectance map prepared from the data shows large areas in the Illinois Basin where reflectance is uniformly low (<0.5% $\bar{R}_o$) and the organic matter has not yet reached the stage of petroleum generation. Several areas of higher reflectance are also present: (1) near the northern erosional truncation of the New Albany in central Illinois; (2) in east-central Illinois, within a broad southward-plunging syncline immediately west of the Clay City Anticlinal Belt; (3) in Wayne and Hamilton Counties, Illinois, the present-day area of maximum burial depth; and (4) in extreme southeastern Illinois, where the highest reflectances yet observed (>1.0% $\bar{R}_o$) correspond to a complexly-faulted and mineralized area with nearby igneous intrusions. Changes in color and intensity of UV fluorescence of liptinites generally agree well with reflectance data.

The occurrence and abundance of amorphous organic matter, liptinites (mainly *Tasmanites)*, vitrinites, and exinites are facies dependent. Solid hydrocarbons that occur as pore fillings in fusinite are found mainly in samples from southeastern Illinois. Their presence suggests that hydrocarbon generation and expulsion have occurred in the New Albany in southeastern Illinois.

INTRODUCTION

Geologists have long regarded most dark-colored, fine-grained, sedimentary rocks in which abundant organic matter has been preserved as probable petroleum source rocks. It has been suspected that, as the thickest and most continuous black shale in the Illinois Basin, the New Albany Shale Group has played a major role in petroleum generation throughout the basin. However, few data have been collected and published to evaluate the quality of the source beds in the New Albany and identify regions where petroleum generation is likely to have occurred.

In assessing a potential petroleum source rock, geologists use various petrographic and geochemical techniques to determine if the criteria necessary for the generation of hydrocarbons have been met within the unit. Oil source capacity depends on at least four factors: the quantity, the quality, and the thermal maturity of organic matter in the source beds, and the expulsion efficiency of the source sequence (Waples, 1979). Previous studies by Stevenson and Dickerson (1969) and geochemical studies done in connection with this project suggest that sufficient organic matter has been preserved within at least some beds of the New Albany Shale Group to produce hydrocarbons (quantity). The critical lower limit of organic carbon required for significant quantities of petroleum generation in detrital rocks is widely accepted by researchers to be between 0.50 and 1.0 weight percent (Tissot and Welte, 1978). Studies by Stevenson and Dickerson (1969) indicate that organic carbon values range from slightly less than 1.0 to more than 9 weight percent for core and drill cutting samples selected from the lower 50 feet of the New Albany Shale in 350 drill holes throughout Illinois. Most of the organic carbon data collected for the present study show organic carbon values greater than the critical lower limit range cited by Tissot and Welte: of 371 core and well cutting samples analyzed, 319 samples had organic carbon contents greater than 1.0 percent (up to 15.6 percent); 40 samples had values of between 0.50 and 1.0 percent; and only 12 samples had less than 0.50 percent organic carbon. The organic carbon data from Stevenson and Dickerson and from the present study suggest that significant portions of the New Albany Shale contain enough organic carbon to produce significant quantities of hydrocarbons.

This portion of the present study of the New Albany Shale had two major goals: to characterize the type of organic matter in the shales and their stratigraphic and areal distribution (quality); and to characterize the degree of organic metamorphism (maturation) of the organic matter. Primary pathways necessary for migration of the generated hydrocarbons out of the shales are assumed to have existed and were not an object of this study.

METHODS

More than 350 samples of shale and associated sediments were selected for organic petrographic analyses from 148 drill holes penetrating the New Albany Shale Group in Illinois, Indiana, and western Kentucky. Samples from cores and washed drill cuttings were examined. Because the organic matter is widely dispersed in the shales, all organic petrographic analyses were done using pellets of acid-concentrated organic matter (HCl, HF). Some polished blocks of shale cores and thin sections were also examined to observe the distribution of organic matter within the shale. Physically-separated vitrain bands were mounted in epoxy, polished, and examined to evaluate the effect, if any, of acid maceration on the results of petrographic analyses. Modified coal petrographic techniques were used to evaluate the hydrocarbon potential of the New Albany Shale. Visual identification of occurrences and estimates of the abundance of amorphous organic matter, liptinites, vitrinites, and inertinites were made in reflected light to determine if the organic matter in the shales is the appropriate type (quality) for hydrocarbons to have been generated. The well-established tool of vitrinite reflectance and the more recently-employed technique of blue light fluorescence were used to determine the degree of thermal maturation. Details of sample selection, sample preparation, and petrographic techniques used in this study are discussed more fully in Barrows, Cluff, and Harvey (1979).

RESULTS AND DISCUSSION

Types of organic matter

Reflected light studies of concentrated organic matter samples from the shales indicate that the occurrence and abundance of the types of organic matter (amorphous organic matter, liptinite, vitrinite, inertinite) are facies dependent. The greenish-gray shale facies contain little organic matter (fig. VIII-1a) and often the acid-maceration treatment of the shales does not yield sufficient material to permit characterization of the types of organic matter present. Only vitrinite (fig. VIII-1b) and inertinite are commonly observed in the concentrated organic-matter pellets of these shales, although some isolated patches of undissolved mineral matter with small, unconnected stringers of amorphous organic matter can be observed within the pellets of the greenish-gray shales. This predominance of humic material corresponds to the Type III kerogen of Tissot and Welte (1978). The brownish-black and black shale facies are, in comparison, rich in organic matter (fig. VIII-1a). Amorphous organic matter usually accounts for 90 to 95 percent of the sample, whereas macerals (liptinite, vitrinite, inertinite) generally makeup only 5 to 10 percent of the organic matter concentrate (fig. VIII-1c). This amorphous matter is believed to be derived primarily from marine algae, although very small, unrecognizable fragments of humic material may also be included in our estimates of the amounts of amorphous organic matter. The alginite *Tasmanites* is the most commonly recognized liptinite maceral; its abundance appears to vary randomly. Vitrinite is generally more common than inertinite except in southeastern Illinois, where the inertinite maceral semifusinite is commonly observed.

This mixed assemblage of predominately marine (with some nonmarine) organic matter constituents is typical of Type II kerogen as defined by Tissot and Welte (1978). Although in the polished blocks of shale the amorphous organic matter surrounds and is not clearly distinguishable from the inorganic constituents, the network-like nature of this material is clearly apparent in the acid-concentrated organic residues of shale samples from most of the state. In the southeastern portion of Illinois, however, the network-like amorphous material is rare, and a lighter-gray hash of unidentifiable fragments is more commonly observed (fig. VIII-1d). Surrounding this region is an area in which a mixture of both the network and the hash of unidentifiable fragments are observed within the same sample. The distribution of these regions is illustrated in figure VIII-2.

Numerous studies on the chemical composition of kerogens and their pyrolosis products have shown that Type II kerogen is capable of generating large quantities of oil and gas and is a favorable source-rock material. Because of its chemical composition and structure, Type III kerogen is much less likely to generate oil, but may generate gas. Type II kerogens are therefore said to be "oil prone," while Type III kerogens are "gas prone."

The high organic-carbon content in the New Albany black shales documented by Stevenson and Dickerson (1969) and this report, and the predominance of Type II kerogen in the black shales, indicate that the New Albany contains both

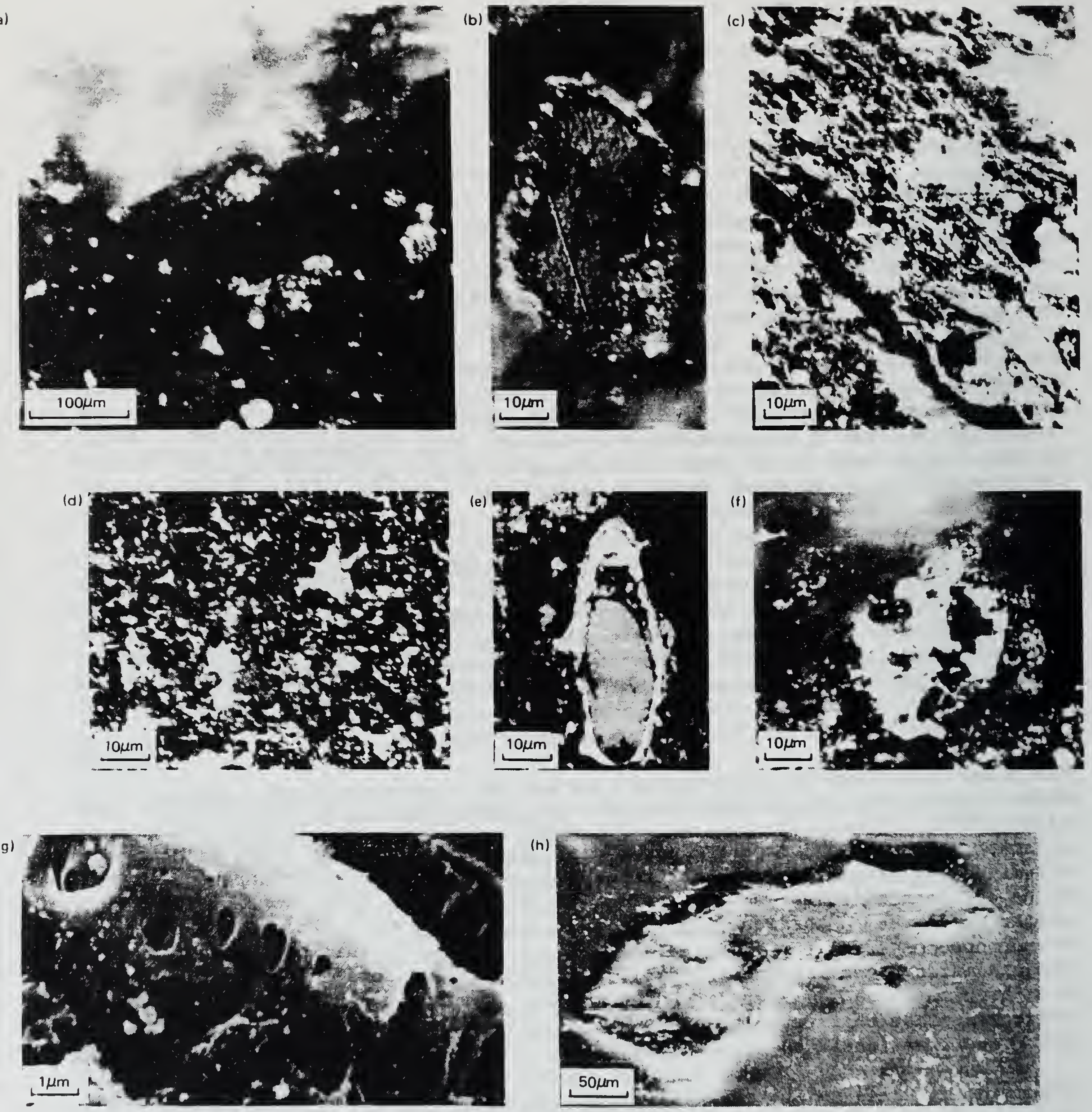


Figure VIII-1: Photomicrographs of organic matter from the New Albany Shale:
(a) Polished block in reflected light (10IL01L2) of the contact between greenish-gray shale with little organic matter (top) and brownish-black shale with abundant organic matter (bottom); (b) Poorly preserved vitrinite in kerogen concentrate from greenish-gray shale (11L01L2); (c) Network of organic matter in kerogen concentrate of brownish-black shale (NAS-045); (d) Hash of unidentifiable fragments in kerogen concentrate (11IL12C1); (e) Filling in fusinite pore (NAS-114); (f) Angular solid hydrocarbon (NAS-360); (g) SEM photomicrograph of maceral with a morphology reminiscent of humic matter (NAS-173); (h) SEM photomicrograph of fragment of vitrinite (NAS-061).

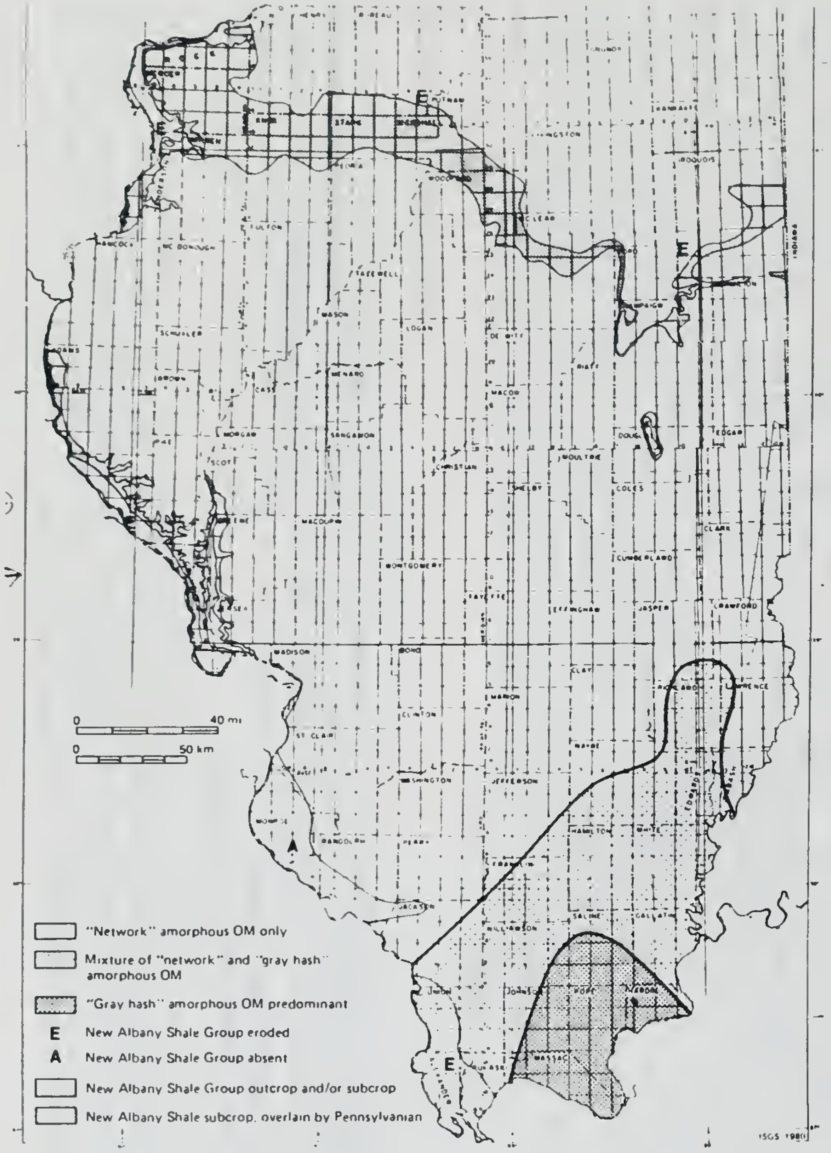


Figure VIII-2. Areas in which kerogen contains distinct network or gray hash of amorphous organic matter.

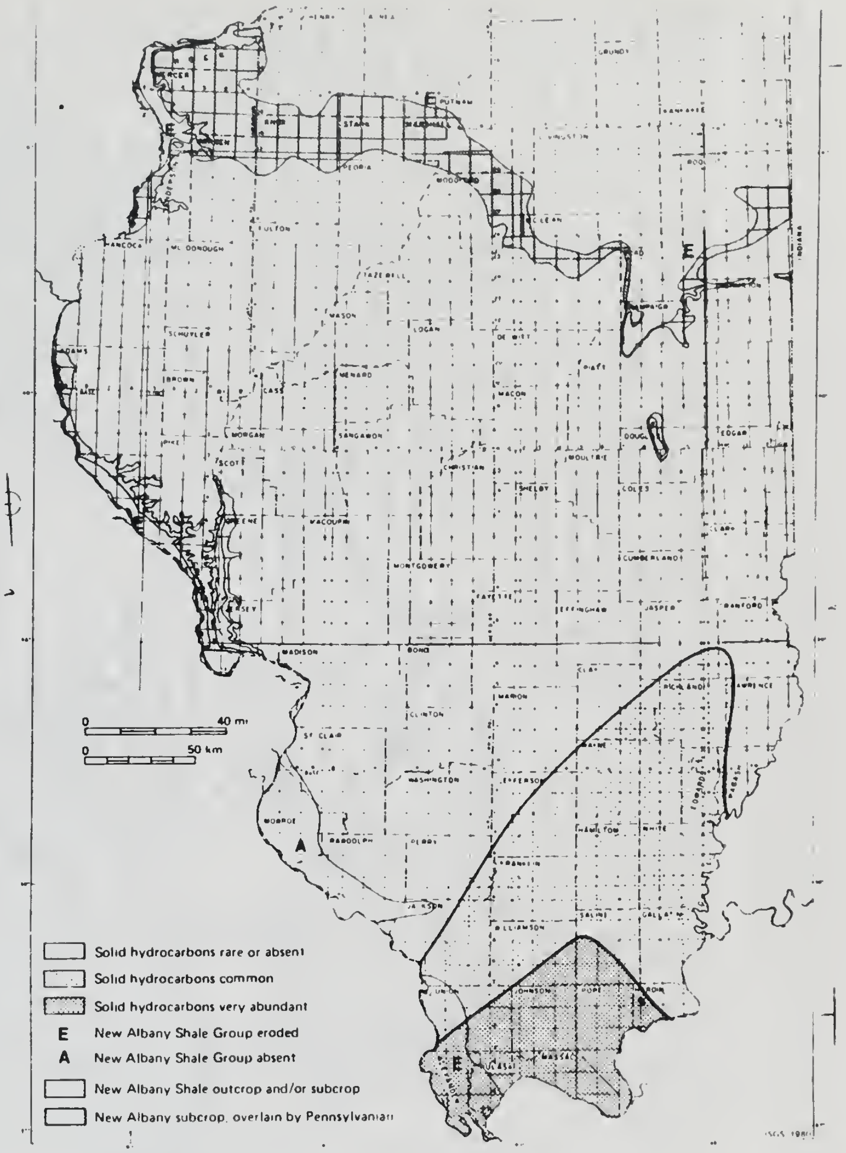


Figure VIII-3. Areas in which kerogen contains solid hydrocarbon occurring as fillings or angular particles.

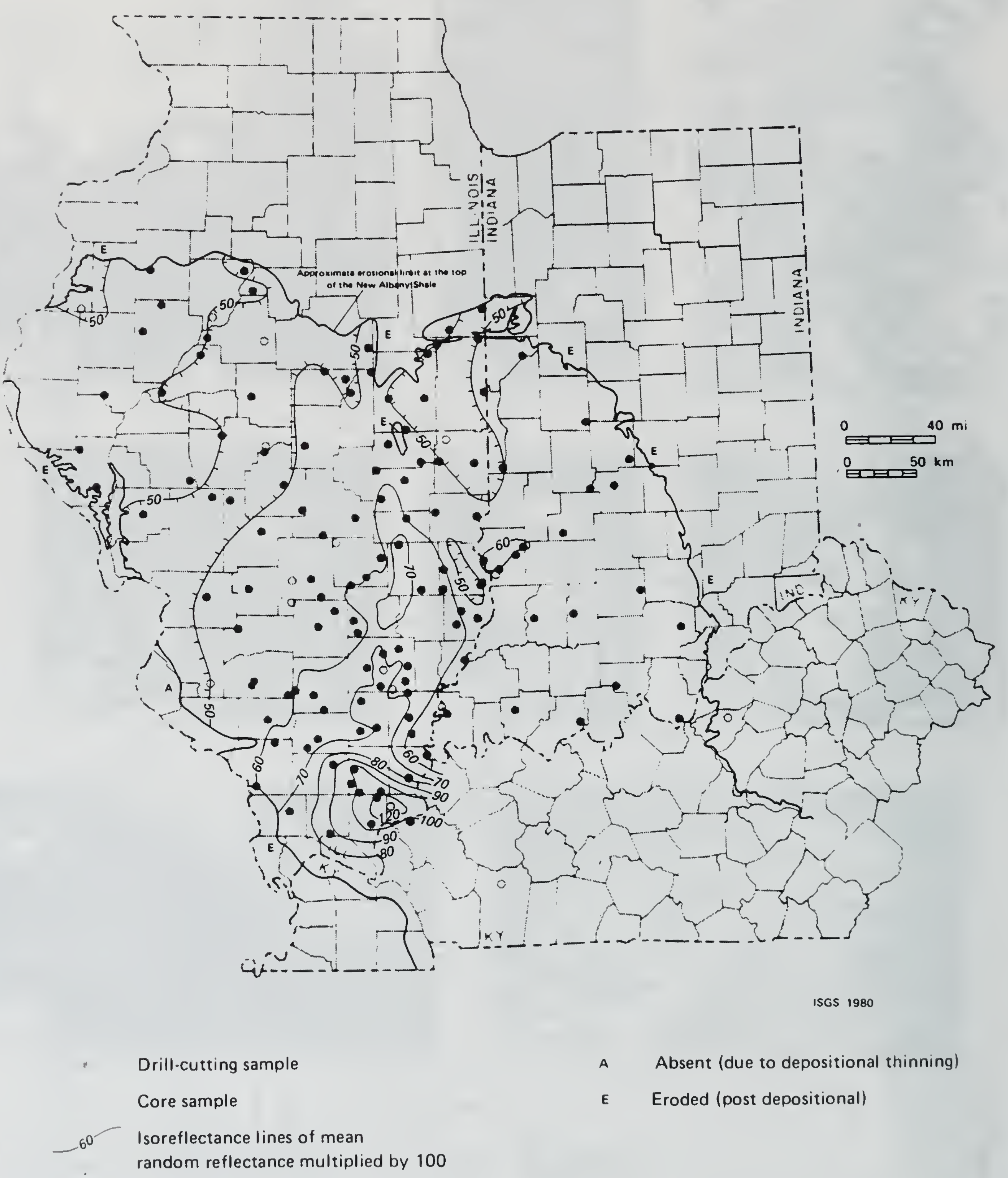


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Figure VIII-4. Mean random relectance of vitrinite in the New Albany Shale (R_o % x 100).

sufficient quantity and quality of organic matter to be a source of considerable petroleum.

During the examination of the occurrence and abundance of the organic constituents, dark- to medium-gray materials, generally of lower reflectance than vitrinite within the same sample, were observed as fillings in fusinite pores (fig. VIII-1e). No fluorescence of the filling materials was observed. Angular particles, also dark- to medium-gray and of lower reflectance than vitrinite within the same sample, that appear to have been fillings of inorganic material dissolved by the acid maceration process, were also observed (fig. VIII-1f). No fluorescence of these angular particles was observed. Both the fillings and the angular particles may be solid hydrocarbons (Castaño, personal communication). Other researchers have referred to similar particles as metabituminite (Teichmuller, in Stach et al., 1975), pyrobitumen (Alpern, 1970), or bitumen (Robert, 1973). Such particles are thought to be one of the residues produced during the maturation process (Stach et al., 1975), and their presence is strong evidence of liquid hydrocarbon generation. The occurrence of these two types of particles is shown in figure VIII-3.

Scanning electron microscope studies of organic matter within the shale matrix and of concentrated organic matter were also conducted. Details of most of this work are presented in a paper to be published in Scanning Electron Microscopy/1980 (Barrows, 1980), and in the March 1980 quarterly report to DOE. The studies indicate that the relatively flat surfaces of amorphous organic matter are aligned parallel or nearly parallel to bedding. Some of the macerals within the shale matrix are difficult to identify under the Scanning Electron Microscope (SEM) because they are widely dispersed in the shale, and do not have unique shapes or responses to energy dispersive analysis. Preliminary results of SEM analyses of four organic matter concentrates of various levels of maturity indicate that there are some observable differences in the forms of organic matter that may be related to changes imposed during maturation. In the immature sample ($R_o = 0.49\%$), macerals with a morphology reminiscent of humic matter were observed (fig. VIII-1g). In the samples selected from the shales in which the organic matter has reached the stage of initial maturity, only angular fragments of macerals were observed (fig. VIII-1h). However, it is difficult to determine how much (if at all) sample preparation affected the observed differences in the forms of organic matter; further work is warranted to better define these differences.

Vitrinite reflectance

An updated map of average vitrinite reflectance, by location, for the New Albany Shale (fig. VIII-4) shows distinct patterns of increasing reflectance indicating trends of maturation of the organic matter with the shales. These maturation trends can be related to structural controls as discussed by Barrows, Cluff, and Harvey (1979).

The map is based on data collected from 278 samples representing 142 wells. The reflectance data for all shale samples collected in this study is provided on the computer tape accompanying this report, but samples having fewer than 20 readings or having high standard deviations (generally <0.15) were excluded from the final compilation of the data. If more than one sample was examined per well, the mean random vitrinite reflectance values ($\bar{R}_o$) were averaged. Samples within a well which appeared to be anomalous were also excluded.

A comparison of reflectance values of untreated vitrain bands (large compressed pieces of coalified wood—principally *Callixylon* in the New Albany Shale) and values of closely-associated acid-concentrated samples indicates that the acid-maceration treatment used in preparation of samples did not significantly alter the reflectance results. However, for some samples, unusually high or low values may have been reported because of the difficulty in distinguishing between vitrinite and other macerals in the organic matter concentrates. The difficulty arises because the particles are generally the size of fine silt or smaller and are widely dispersed even in the concentrates. In such cases the distinguishing characteristics of reflectance and morphology may not be clearly visible and comparisons between two or more macerals in the same field of view (which would aid in particle identification) is often impossible. In samples having relatively large amounts of liptinite, the reported mean random vitrinite reflectance value may be low if the small liptinite fragments are similar to vitrinite fragments. Likewise, in samples having relatively high amounts of inertinite, the reported mean random vitrinite value may be high if there is an overlap in the optical properties of the vitrinite and semifusinite. By carefully evaluating the reflectance histograms of each sample (fig. VIII-5), most, but not all, of this type of error can be eliminated.

In recent years it has been recognized that oil is generated within a relatively narrow maturation range (the "oil window"), and natural gas is formed over a much broader range. The range of vitrinite reflectances corresponding to the oil generation window is between 0.5 and 1.3 percent $\bar{R}_o$ (fig. VIII-6); peak oil generation and expulsion occur at maturation levels corresponding to reflectances greater than 0.6 to 0.7 percent $\bar{R}_o$ (Hood, Gutjahr, and Heacock, 1975; Dow, 1977). The maturation level described as the immature stage corresponds to vitrinite reflectance values less than 0.50 percent.

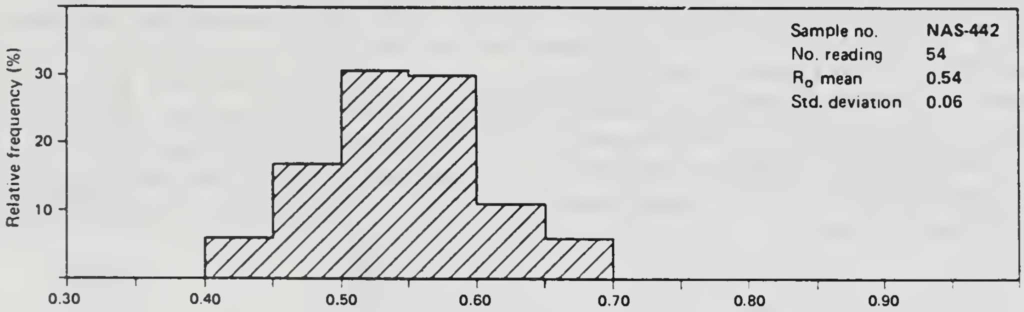
Much of the New Albany Shale in the Illinois Basin is within the immature stage. Those areas on figure VIII-4 in which the reflectance is less than 0.5 percent $\bar{R}_o$ are unlikely to have generated petroleum, although small amounts of gas may be present within the shale. Isotopic analysis of released gases from several core samples in one of these low-maturity areas (Christian County, Kentucky) indicates a low-maturity thermogenic origin for the gas (Dickerson and Coleman, 1977).

Those areas (fig. VIII-4) where the reflectance lies between 0.5 and 0.7 percent $\bar{R}_o$ are within the earliest stage of oil generation for Type II kerogen (Tissot and Welte, 1978). Oil and gas generation may have occurred, but there is some question as to whether sufficient amounts have been generated for expulsion of the hydrocarbons to begin (Hood, Gutjahr, and Heacock, 1975).

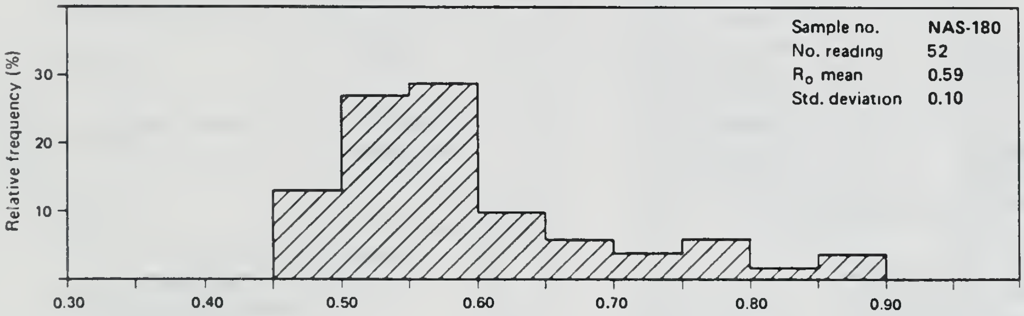
Oil generation and expulsion are most likely to have occurred in areas where vitrinite reflectance exceeds 0.7 percent $\bar{R}_o$ (fig. VIII-4).

Nowhere within the Illinois Basin have levels of maturation corresponding to the main zone of gas generation been observed. Although the reflectance map (fig. VIII-4) indicates large areas where petroleum generation has probably occurred, the only gas likely to have been formed is biogenic gas in relatively small amounts, and the considerable amount of gas associated with oil generation (Harwood, 1977). Indeed, most of the oil fields in Illinois have relatively small amounts of associated gas production, and no major gas fields are present in the Illinois Basin portions of Illinois or Indiana. There are several large gas fields in western Kentucky, which suggests that high maturation levels may be found there, possibly within the Moorman Syncline.

Normal distribution, only vitrinites measured.



Skewed to the right, confusion between vitrinites and inertinites.



Skewed to the left, confusion between vitrinites and liptinites.

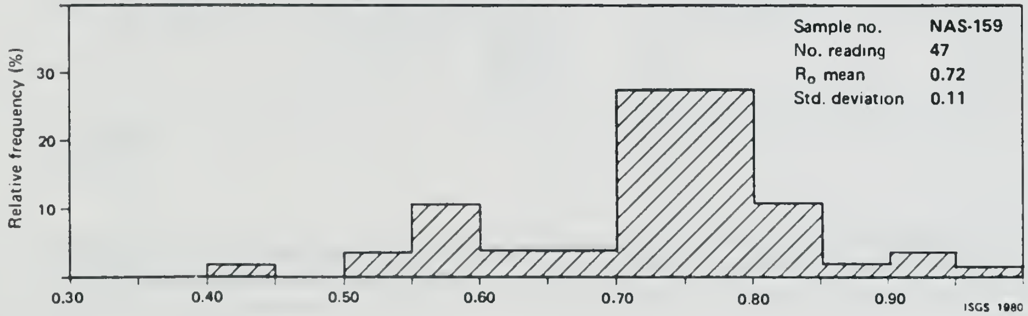


Figure VIII-5. Typical relectance histograms.

Plots of mean random reflectance values of vitrinite and vitrinite-like substances taken from two deep wells in the basin show that through depths of several thousand feet of strata, reflectance values generally increase (fig. VIII-7). Mean random reflectance values were plotted against depth on a log scale because on such a scale the increase in reflectance with depth becomes linear (Dow, 1977). A line fit by the least squares method through the $\bar{R}_o$ values gives the reflectance gradient for the well. A reflectance gradient of 0.003% $\bar{R}_o$/100 feet (30 m) was determined for the Effingham County well and gradients of 0.002% $\bar{R}_o$/100 feet and 0.009% $\bar{R}_o$/100 feet (30 m) were determined for the Hamilton County deep well. Both gradients are shown for the Hamilton County well because previous work has indicated that the reflectance of vitrinite in the New Albany is anomalously low in comparison with the overlying Pennsylvanian age coals (Barrows, Cluff, and Harvey, 1979). Although for both wells reflectance data was collected from vitrinite-like substances found in Silurian and older rocks, these reflectance values were not used in calculating the reflectance gradients for the deep wells because the relationships between the maturation of these vitrinite-like substances and vitrinite are not fully understood. The samples for the deep-well studies were collected from drill cuttings at regular intervals. Because of the limited material available, samples were sometimes selected from 60-foot intervals and included a mixture of rock types.

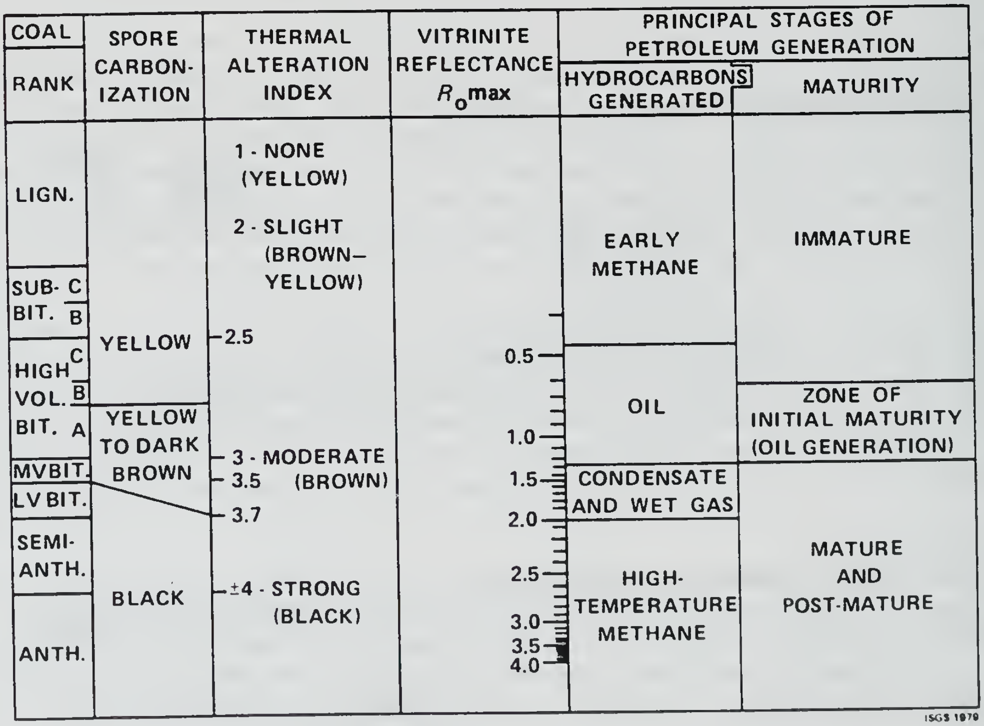


Figure VIII-6. Relation of coal rank, vitrinite reflectance, and other measures of rank in sediments to the principal stages of oil and gas generation (after Hood, Gutjahr, and Heacock, 1975). Note that the reflectance scale is for maximum reflectance readings, not mean random reflectances as used in this study. At low maturity levels (<1.0% R_o), the difference between the two methods is negligible (Dow, 1977).

A number of other reflectance gradients have been determined for other parts of the state in previous studies. In northern Illinois, reflectance gradients ranging from .007% $\bar{R}_o$/100 feet (30 m) to .022% $\bar{R}_o$/100 feet (30 m) were determined in mixed rock sequences (unpublished data from Survey files); in eastern Illinois reflectance gradients ranging from .007% $\bar{R}_o$/100 feet (30 m) + 0.032% $\bar{R}_o$/100 feet (30 m) were determined in coal-bearing strata (Kaegi, 1971); in southeastern Illinois a reflectance gradient of .005% $\bar{R}_o$/100 feet (30 m) was determined for coal-bearing strata (unpublished data from Survey files).

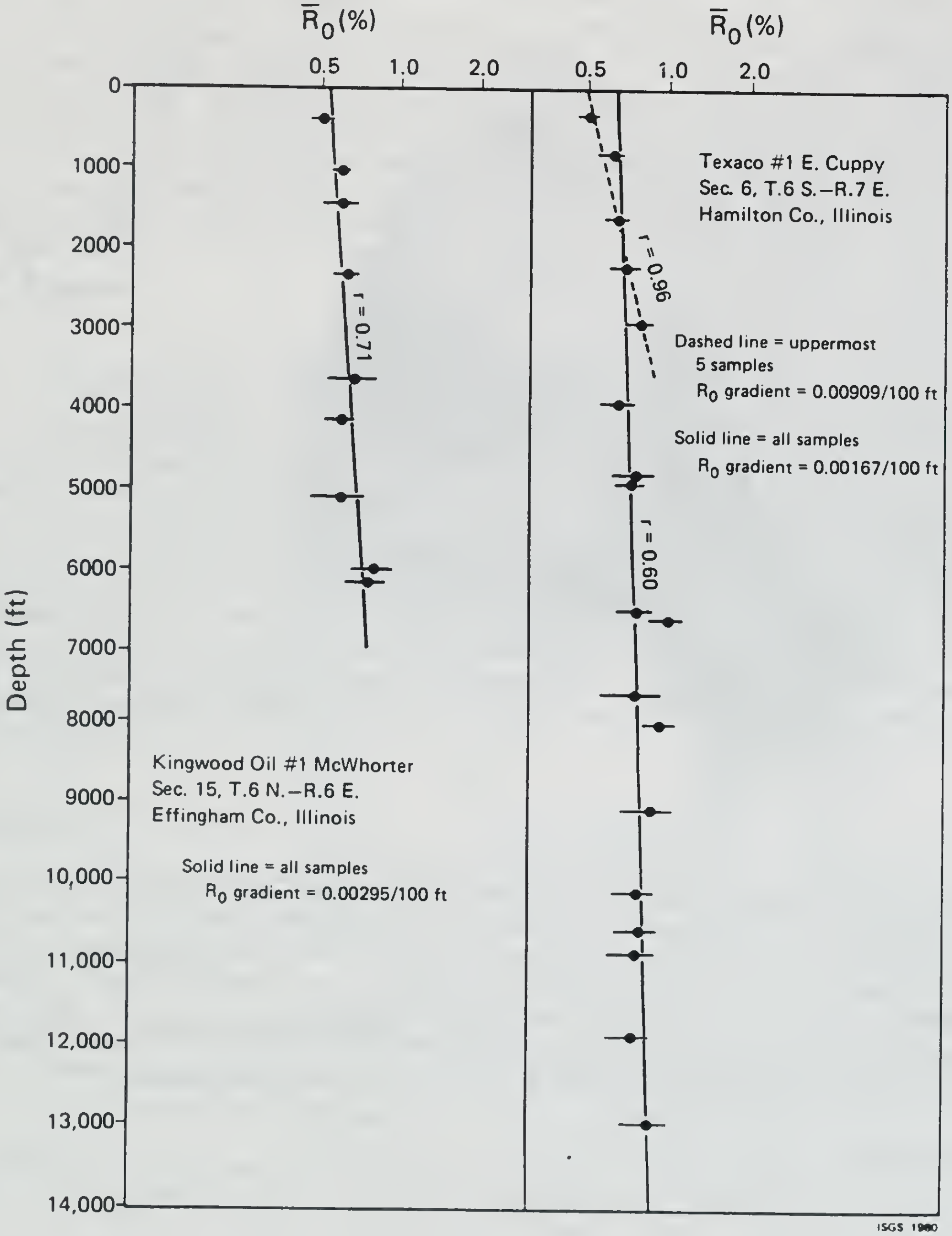


Figure VIII-7. Plots of mean random reflectance values of vitrinite and vitrinite-like substances taken from two deep wells in the Illinois Basin.

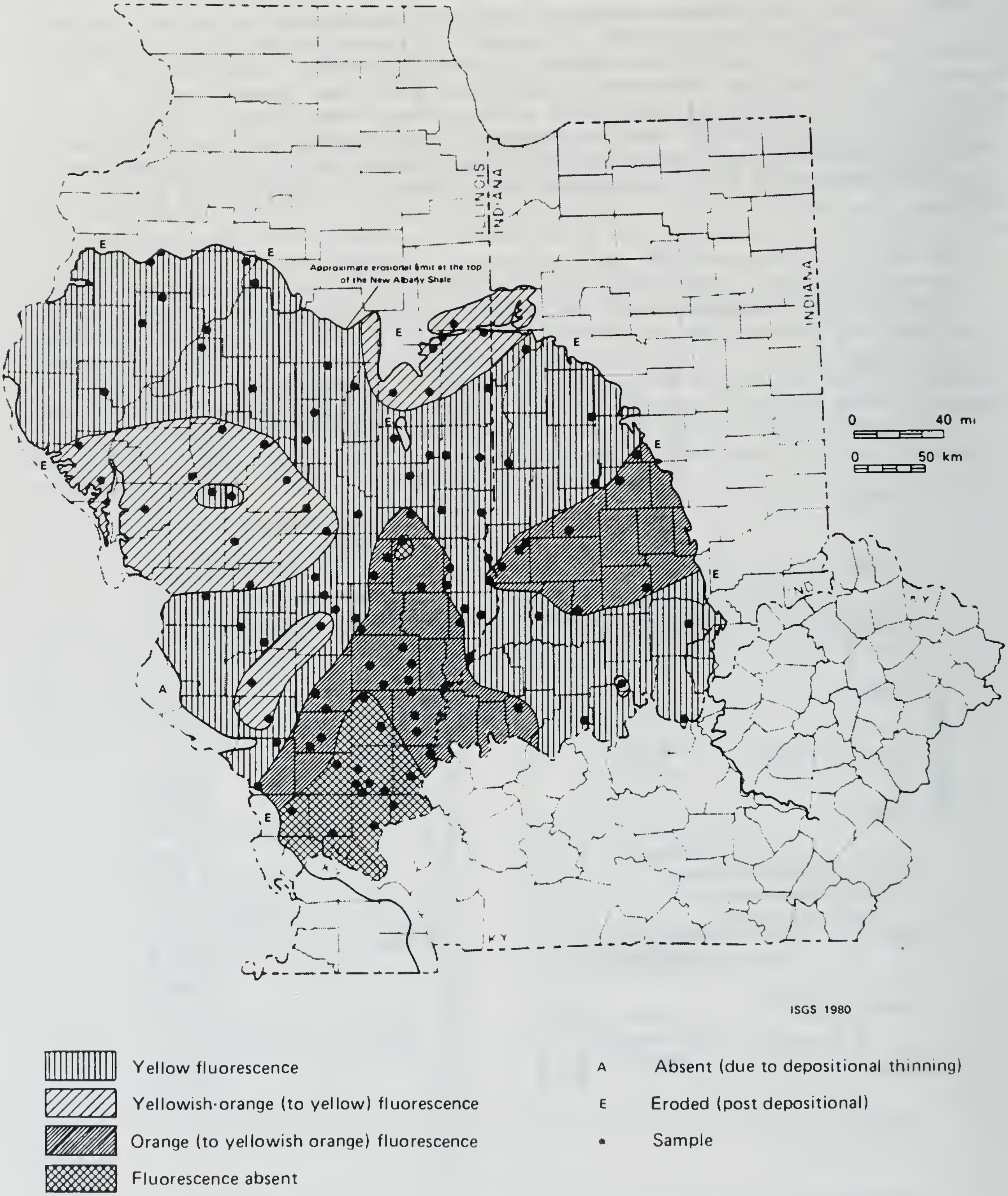


Figure VIII-8. Color of liptinite fluorescence in the New Albany Shale.

The accuracy of the reflectance gradients determined in this study and in previous studies is not known for a number of reasons. First of all, at low ranks (R_0 values of less than about 0.80 percent), vitrinite reflectance is less reliable (Dow, 1977). Furthermore, studies have shown that there is some difficulty in comparing reflectance values of vitrinites from different rock types. For example, Bostick and Foster (1971) demonstrated that the reflectance of vitrinite dispersed in sedimentary rocks often differs from the reflectance of vitrinite in closely-associated coals. Even within closely-associated samples from the same rock types there are variations in reflectance that may be due to differences in vitrinite types and organic matter preservation (Tissot and Welte, 1978).
It is clear from these studies that more work on reflectance gradients from various parts of the state is necessary before the geothermal history of the Illinois Basin can be fully evaluated. Despite the difficulties in assessing the accuracy of the reflectance gradients, this study and others suggest that except in the area near Hicks Dome and the fluorspar district of extreme southern Illinois and adjacent Kentucky, the Illinois Basin was not subjected to unusually high geothermal gradients during past geologic periods.

Fluorescence

Recent work (van Gijzel, 1967; Ottenjahn, Teichmuller, and Wolf, 1975; Robert, 1979) indicates that the fluorescence of liptinites may also be used as a guide to the rank of coals and/or the maturity of organic matter dispersed in sedimentary rocks. Although visual fluorescence studies are not as precise as vitrinite reflectance studies, the patterns observed (fig. VIII-8) tend to support patterns of increasing reflectance and maturity illustrated in figure VIII-4. The fluorescence color generally grades from yellow-orange and finally to orange toward the southeast in Illinois. In extreme southern Illinois no liptinite fluorescence was observed. In the east-central portion of the state the fluorescence ranges from yellow-orange to orange to absent. Here, the area where no liptinite fluorescence was observed corresponds closely to the area of 0.70 percent reflectance illustrated in figure VIII-4.

CONCLUSIONS

Considerations of (1) the occurrence and abundance of amorphous-sapropelic organic matter, (2) the thermal maturation as determined by vitrinite reflectance and the character of fluorescence, and (3) the occurrence of solid hydrocarbon pore fillings and isolated angular solid hydrocarbons, strongly suggest that active petroleum generation and expulsion occurred within the New Albany Shale in southern and southeastern Illinois. Nowhere within the Illinois Basin is the thermal maturation known to reach the mature and post-mature zone of gas generation.

Gas within the New Albany is thought to be gas produced during oil generation, possibly diluted by small amounts of biogenic gas. Studies of reflectance gradients in various parts of the state suggest that, with the exception of Hicks Dome and the fluorspar district, the Illinois Basin was not subjected to unusually high temperature gradients during past geologic periods.

Bob Bauer sets up a core sample on the Tinius-Olsen Model 3000T-1 300,000-lb compression testing machine.

IX. PHYSICAL PROPERTIES

Donald Miller, Robert A. Bauer, and Rex Johnson

ABSTRACT

More than 11,000 tests were performed to characterize the physical properties of four oriented cores of the New Albany Shale from the Illinois Basin. A computer filing system was devised and implemented for all test results. Shore hardness, moisture content, and specific gravity were compared with fracture frequency and drilling rate. Physical tests of selected cores characterized orientation of point-load induced fractures, "Brazilian" indirect tensile strengths, acoustical velocity values, triaxial and unconfined compressive strengths, and clay particle orientation. Point load and "Brazilian" tests correlated well with expected regional structure patterns, lithologic differences, and observed natural fractures and anomolies in the core. Triaxial compression tests supported the strength test results. Acoustic velocity tests correlated with lithologic differences, but no significant pattern was correlated with the weakness planes defined by technical testing. Clay mineral orientation studies were inconclusive and may warrant additional work.

INTRODUCTION

This project is a study of the index properties, directional properties, and strength of oriented cores of Devonian shale from the Illinois Basin. Index properties tested were: Shore hardness, moisture content, specific gravity, bulk density, and porosity, directional seismic velocities, point-load fracture strength, and indirect tensile strength (Brazilian split). Not all these tests were performed on all cores. Logs of fractures, triaxial and unconfined tests, and clay particle orientation (x-ray diffraction) were also determined for selected samples.

METHOD OF INVESTIGATION

The group studying physical properties handled orientation and sampling of core, and distributed samples to other study groups (fig. IX-1). A standardized system was set up to handle core, to identify samples and to interface laboratory data with the computer system.

Data compiled in this study resulted from laboratory tests of oriented core samples recovered from four boreholes located in the Illinois Basin. The rock core was first examined with respect to natural fractures.

Groups of specimens were selected from each 10-foot interval of core and designated as a data set to maintain an accurate, representative record of test results. Selected samples of core were characterized by: (1) logging of fractures; (2) orientation of point-load induced fractures; (3) "Brazilian" indirect tensile tests; (4) directional acoustic velocity measurements; (5) triaxial and unconfined compression tests; (6) petrographic examination of thin sections; and (7) clay particle orientation (x-ray diffraction).

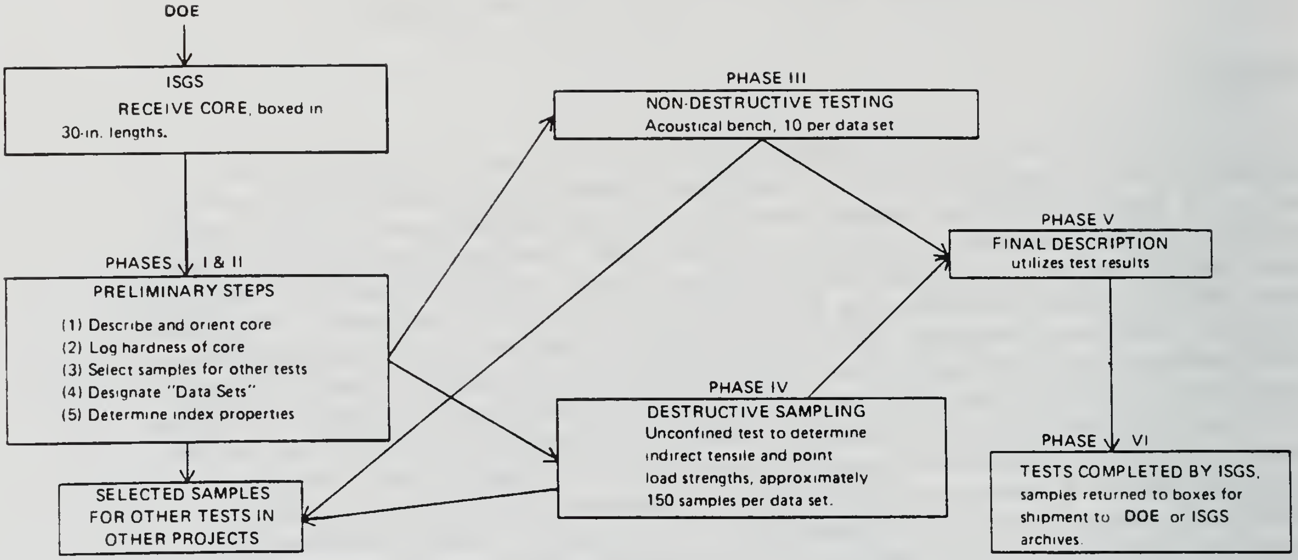


Figure IX-1. Work plan for core routing and analysis of directional properties.

Additional rock index values of Shore hardness, moisture content, specific gravity, drilling rate, and fracture frequency were also determined for each core.

Logging of Fractures

The oriented rock cores studied were about 4 inches (10 cm) in diameter. A device designed by Christensen Diamond Products (Salt Lake City, Utah) was used to scribe the sides of core during drilling. Scribe marks aligned with a compass-inclinometer system photographed at two-foot (.6 m) intervals provided a nearly continuous record of core orientation. The north direction of each piece of core was marked before examination and testing. All fractures were classified and logged as either natural fractures or fractures induced by coring or handling operations (Kulander et al., 1977). Factors suggesting natural fractures include: (1) smooth surface and continuity; (2) mineralization; and (3) slickensides. Coring-induced fractures, handling fractures, and separation parallel to bedding were identified by typical features such as: (1) rough surface; (2) curve to a free face (hook or petal); (3) characteristic propagation flaw features; and (4) fresh surface.

Point-load Test

The point-load test was used to determine the preferred weakness-orientations in the direction normal to bedding. The test is also an index of rock strength. In this test, the load is applied normal to bedding through the central axis of an unconfined disk-shaped specimen by means of opposing, coaxial steel points (fig. IX-2). Specimens were loaded to failure and the orientations of the induced fractures were plotted with respect to magnetic north.

Standard point-load testing procedures were used in accordance with USBM (D'Andrea et al., 1965) and ISRM (1973) standards. Steel indentors with 60 degree cones and spherical points with 2-inch (5 mm) radius were coaxially aligned with each other in an especially-designed subpress. The tests were all performed on a Tinius-Olsen Model 3000T-1 300,000 lb compression testing machine. The machine uses an electronic load indicator, digital load readout, electronic strain deflectometer, and servo-controlled loading. The measured load accuracy is better than 0.3 percent at all load levels. Disk-shaped samples of core with a length/diameter ratio of approximately 1:2 were tested. The diameter of most samples was approximately 4 inches (10 cm). End surfaces of the disks were machined to less than 0.02 inches (0.05 cm) of parallel on a dry grinding wheel. The dimensions of the sample were recorded and the specimen was inserted in the test machine between the

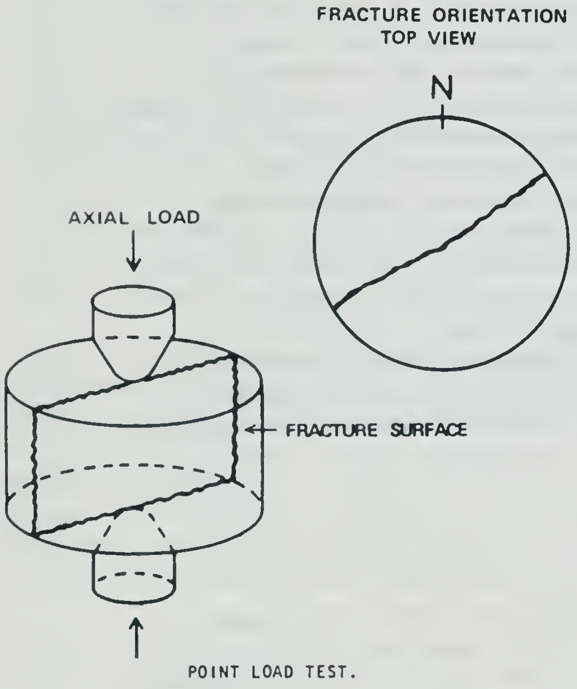


Figure IX-2. Point load test. Bedding is normal to the applied load direction. Fracture orientation is random unless a "preferred direction" of failure exists in the test specimen (as shown by multiple samples).

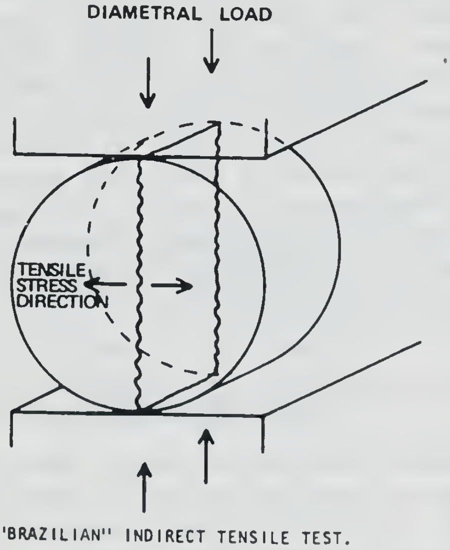


Figure IX-3. "Brazilian" indirect tensile test. Bedding of the sample is parallel to the plane of the paper.

loading points. The sample was loaded to failure, and the mode and orientation of failure noted and recorded. The applied load and point deflections were recorded on a chart recorder during testing. A "reliability factor" was used to assign a value to the degree of influence caused by flaws and irregularities in the sample so that a better comparison of test results for different samples could be statistically made in determining representative mechanical characteristics of the rock unit. Preferred azimuth orientation ($\bar{\Theta}$) of point-load fractures was statistically determined using a resultant vector technique (Curray, 1956). The scatter in the distribution of fracture orientations is indicated by the standard deviation (σ) which is a "true" standard deviation calculated for a circular distribution.

"Brazilian" indirect tensile test

In this test, a tensile stress field was developed perpendicular to the loading direction when a compressive load was applied to opposing edges of a disk-shaped specimen (fig. IX-3). The stress analysis of a circular element subjected to concentrated loads has been studied in detail by several geologists and engineers. The equation:

$$S_t = \frac{2P}{DT}$$

describes the indirect tensile strength (S_t) of a sample in which P is the maximum load at failure, D is the diameter of the disk loaded, and T is the thickness of the disk (Timoshenko, 1934; Frocht, 1948; Muskhelishvili, 1953; Sokolnikoff, 1956; Hondros, 1959; Fairhurst, 1964). Test specimens were oriented between loading platens with respect to the north direction of the core at 30 degree increments of azimuth direction, and tensile strengths were measured. The indirect tensile tests were performed at a constant strain rate of 0.001 cm (.0004 in)/minute. This rate increased the load on test specimens at less than 0.25 Mega Pascals/minute (36.25 psi/minute) and allowed time for stresses to equilibrate throughout the sample. Because the maximum tensile stress was induced in the center of the sample, technique in sample preparation was not crucial. Good dimension control and an evenly distributed load across the edge of the disk were given careful attention. These disk-shaped test specimens cut from the oriented core were prepared in the same manner as point-load test specimens. Flaws in the samples, such as scribe grooves, fossils, and pyrite nodules were oriented so as to minimize effects that might alter the theoretical stress field and produce non-representative results of the rock tested.

Triaxial compression tests

Triaxial compression tests were performed on selected shale specimens prepared both normal to the bedding and parallel to the bedding of core 01KY. A triaxial load apparatus (Donath, 1966) was used for all triaxial compression tests performed. An auxillary pressure generator and sensitive pressure gauge were added to the confining pressure system in order to accurately maintain the confining pressure during the testing. Confining pressures of 1000 psi, 3000 psi, 5000 psi, and 10,000 psi were used (1000 psi = 70.3 kg/cm^2). Loading strain rate was approximately .001 cm/minute (0.0004 in/min) and each test lasted 5 to 8 minutes. Load and displacement were automatically measured by a load cell and electrical strain transducer and recorded on a chart recorder during testing. Cores were prepared appxoimately three-quarters of an inch (19 mm) in diameter and 38 mm in length. Coring was done with a thin wall diamond rotary bit on a modified machine shop drill press using water as a lubricant. Ends were cut and ground to a consistent length, with a length/diameter ratio slightly greater than two. Specimen ends were ground flat with ends parallel to within 0.0003 inches (.0008 cm). Dimensions and tolerances were checked with a micrometer. Unlubricated contact between the steel platens and the rock specimen provided some radial constraint during testing.

Directional acoustic velocity measurements

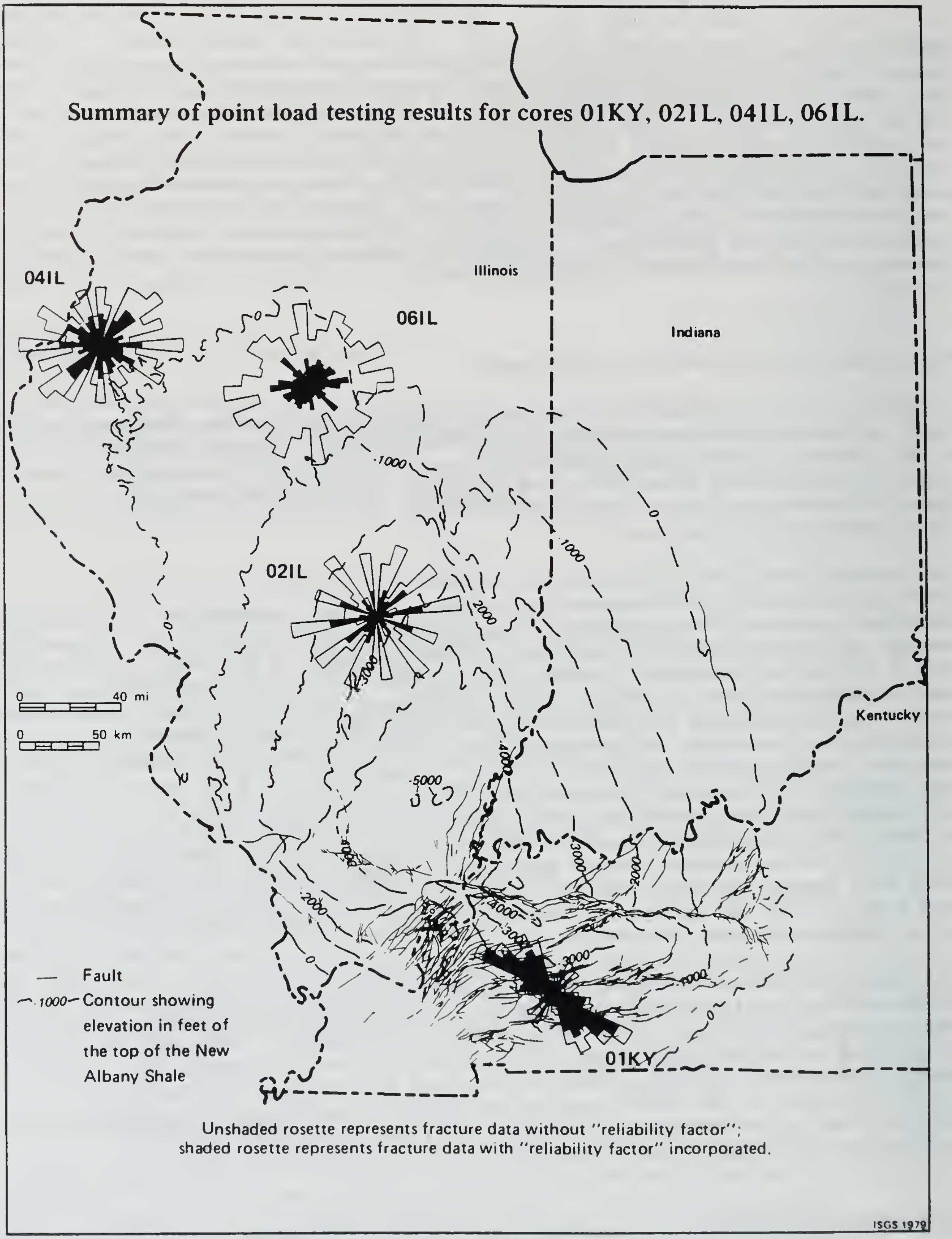
Directional acoustic velocity measurements were performed using an acoustic bench with a direct pulse transmission technique of USBM design (Thill et al., 1968). Compressional wave velocities transmitted through shale samples were measured parallel to the bedding at six orientations in order to investigate the transverse directional nature of the acoustic fabric and elastic properties.

The acoustic bench system measures the travel time required for a disturbance initiated by a transducer at one end of a test specimen to traverse a measured distance through the rock to another transducer located at the opposite end. Accuracy of the equipment is 0.01 km/second (33 feet). However, accuracy due to errors in velocity measurement and repeatability of transit time measurements due to operator error is no better than 0.02 km/second (66 feet) when standard testing procedures are followed. A micrometer was used to measure the distance traveled, with accuracy of better than 10^{-8} kilometers, and the time interval was measured with an accuracy of 10^{-8} seconds by a calibrated dual-channel Tektronix 465 Oscilloscope equipped with a Tektronix DM44 Digital Multimeter which displayed the transit time for an acoustic pulse to pass through the sample. Calibration of the machine delay time was performed by using a linear regression analysis in velocity data from a steel bar cut to 5 different lengths. The calculated correlation coefficient was 0.99998.

Rock fabric is commonly a major factor contributing to rock strength and anisotropic deformational behavior (e.g., Odom, 1967; McWilliams, 1966; Friedman and Logan, 1970). A predictable mechanism of deformation and failure in the shale is necessarily founded on the arrangement of mineral components, including both textures and structures. The investigation of fabric in the shale involved microscopic examination of oriented thin sections and determinations of clay particle orientation by x-ray diffraction techniques (See Section VI).

Shore hardness test

Shore hardness was determined at 1-foot (.3 m) intervals with measurements taken on the side of the core length of the core tested. The Shore hardness test measures the rebound of a diamond-tipped hammer dropped from a predetermined height. A Model



Unshaded rosette represents fracture data without "reliability factor"; shaded rosette represents fracture data with "reliability factor" incorporated.

Figure IX-4. Summary of point-load testing results for cores 01KY, 02IL, 04IL, and 06IL showing locations of test cores relative to regional structure of the New Albany Shale. Polar frequency of fracture occurrence diagrams shows directional trends. (Regional structure map after Stevenson and Whiting, 1967; Basset and Hasenmueller, 1978; and Schwalb and Potter, 1978.)

D Scleroscope, manufactured by Shore Instrument and Manufacturing Company, Jamaica, New York, was used for hardness determinations. Each of the values in the summary tables is an average of 10 of the 12 readings taken over a 1-square-inch area of core, the high and low values being disregarded.

Moisture/specific gravity measurements

Moisture content and specific gravity measurements were collected from fresh core samples at the drilling site. The samples were canned or placed in plastic containers in order to prevent evaporation. Samples were dried in an oven maintained at a temperature of approximately 110°C. Moisture content was calculated as a percentage of the dry weight of the sample. A Mettler Balance P162 was used to weight samples. Specific gravity of samples was determined in accordance with ASTM procedure D-1188-71. Oven-dried samples were placed in a Jolly Balance to obtain the weight in air and the weight submerged in distilled water (approximately 20°C).

Additional rock index values

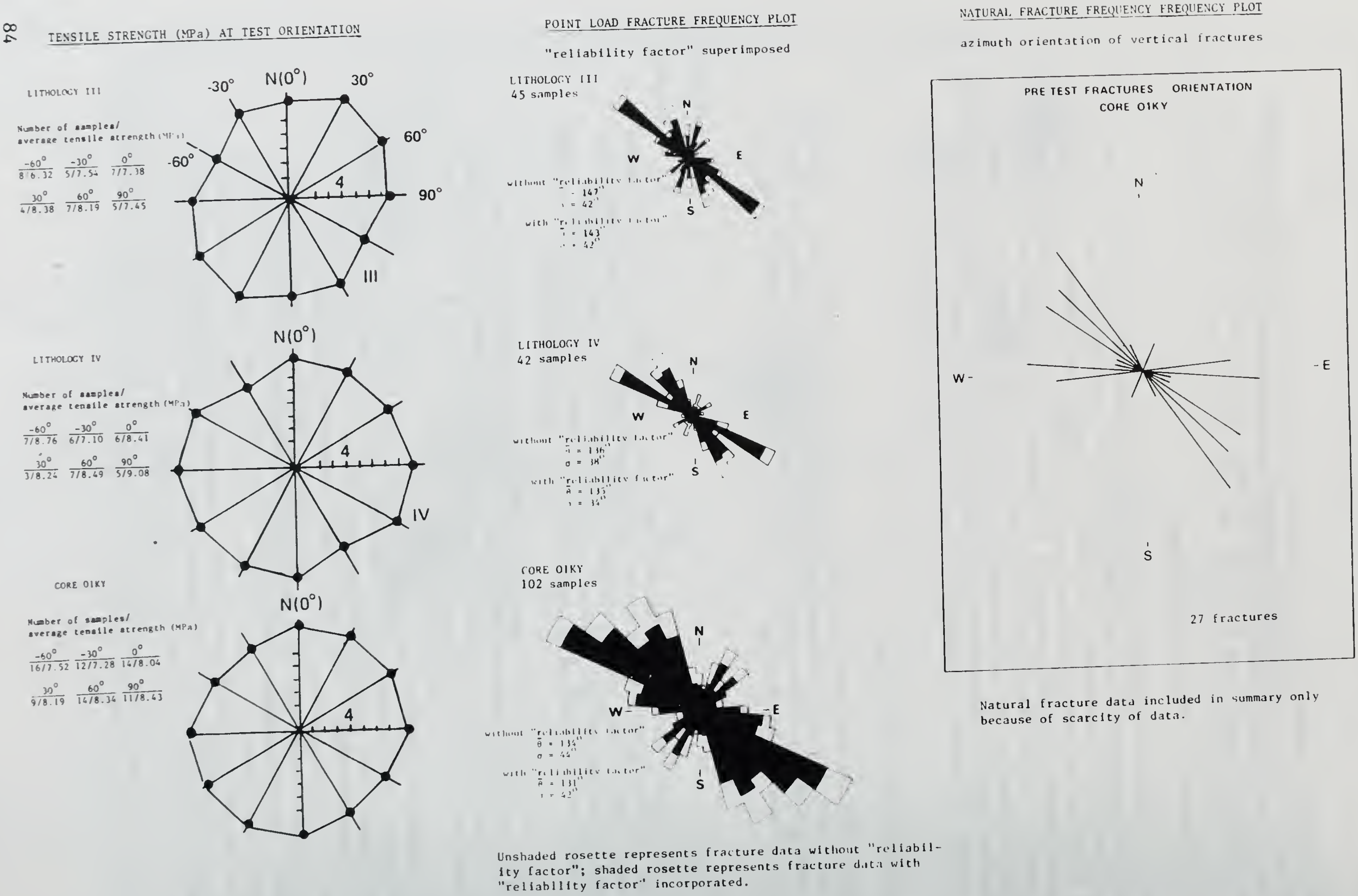
Drilling penetration rates were acquired from the driller's log. Fracture frequency data include both natural fractures and coring-induced fractures, with coring-induced fractures occurring predominantly as stress-relief fractures parallel to bedding.

RESULTS

More than 11,000 test determinations have been performed on four oriented cores of the New Albany Shale from the Illinois Basin. Induced fracture directional properties are summarized in figure IX-4. The preferred orientations of point-load induced fractures normal to bedding in the New Albany Shale are plotted on a regional map of the Illinois Basin.

Mechanical test results and natural fracture data for the cores 01KY, 02IL, 04IL, and 06IL investigated in this study are summarized in figures IX-5,-6,-7, and -8. The comprehensive results of all tests for each of these cores was compiled (Miller, 1979).

Natural fractures observed in core 01KY (fig. IX-5) tend to strike northwest-southeast and dip vertically. Most of the fractures noted were calcite filled. The small fractures were difficult to see and were generally discontinuous. Many very small fractures were only noted when the rock was wetted and partially dried. The orientation of the observed natural fractures in core 01KY corresponded to the orientation of planes of weakness shown by the point-load test. No natural fractures were observed in core 02IL (fig. IX-6). Cores 04IL and 06IL contained several slickensided fracture surfaces. Neither the orientation of fractures nor the direction of slickensides forms a consistent pattern for core 04IL (fig. IX-7) and core 06IL (fig. IX-8).



Unshaded rosette represents fracture data without "reliability factor"; shaded rosette represents fracture data with "reliability factor" incorporated.

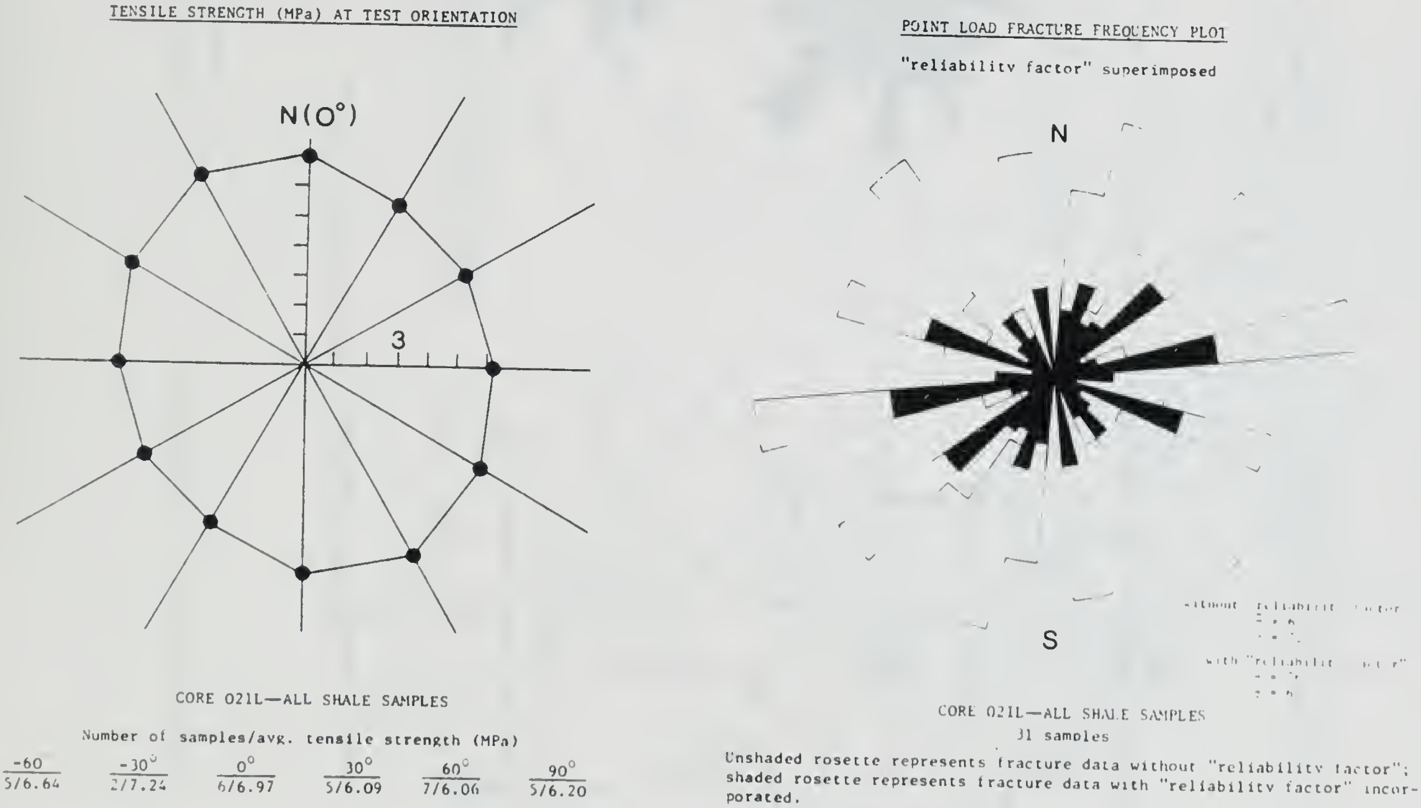
Natural fracture data included in summary only because of scarcity of data.

Figure IX-5. Summary of "Brazilian" tests, point-load tests, and natural fractures for core 01KY.

Point-load test results displayed a tendency for the shales to fracture in a northwest-southeast direction in core 01KY (fig. IX-5). The following central tendencies of fracture orientations ($\bar{\Theta}$) and standard deviations (σ) were determined for each tested lithofacies (See Section VI) from this core:

Samples	Orientation		No. of samples tested
	$\bar{\Theta}$	σ	
Lithofacies II	90°	29°	15
Lithofacies III	143°	42°	45
Lithofacies IV	135°	34°	42
Total	131°	42°	102

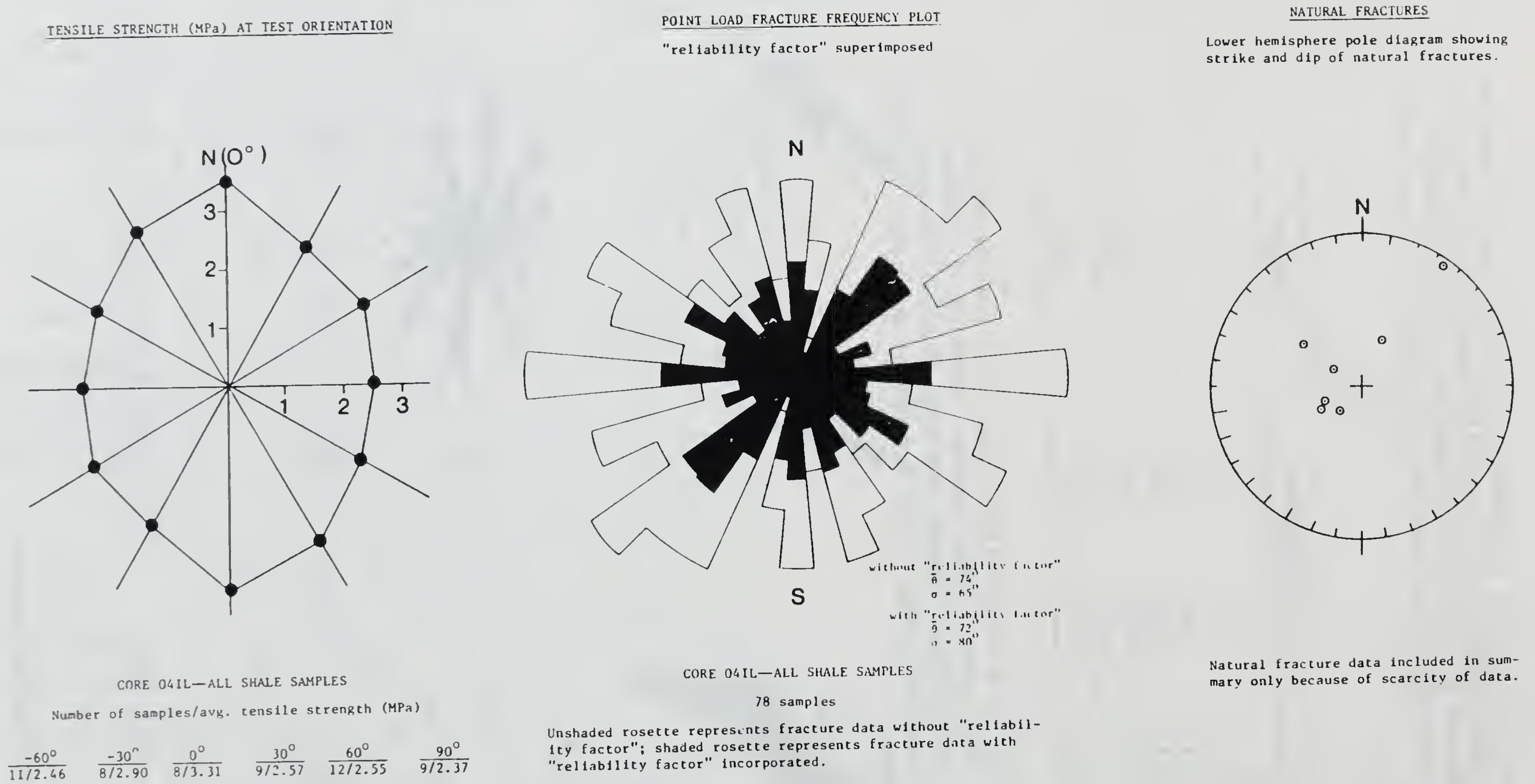
Point-load test data for core 02IL indicate less of a preference for fracture orientation (fig. IX-6). Most samples, however, fractured at an east-northeast orientation. Point-load test results for core 04IL (fig. IX-7) and core 06IL (fig. IX-8) suggest no dominant preferred orientation of fractures.



Unshaded rosette represents fracture data without "reliability factor"; shaded rosette represents fracture data with "reliability factor" incorporated.

Figure IX-6. Summary of "Brazilian" tests and point-load tests for core 02IL.

ISGS 1979



TENSILE STRENGTH (MPa) AT TEST ORIENTATION

CORE 04IL—ALL SHALE SAMPLES

Number of samples/avg. tensile strength (MPa)

-60°	-30°	0°	30°	60°	90°
11/2.46	8/2.90	8/3.31	9/2.57	12/2.55	9/2.37

POINT LOAD FRACTURE FREQUENCY PLOT

"reliability factor" superimposed

without "reliability factor"
$\bar{\theta}$ = 74°
σ = 65°

with "reliability factor"
$\bar{\theta}$ = 72°
σ = 80°

CORE 04IL—ALL SHALE SAMPLES

78 samples

Unshaded rosette represents fracture data without "reliability factor"; shaded rosette represents fracture data with "reliability factor" incorporated.

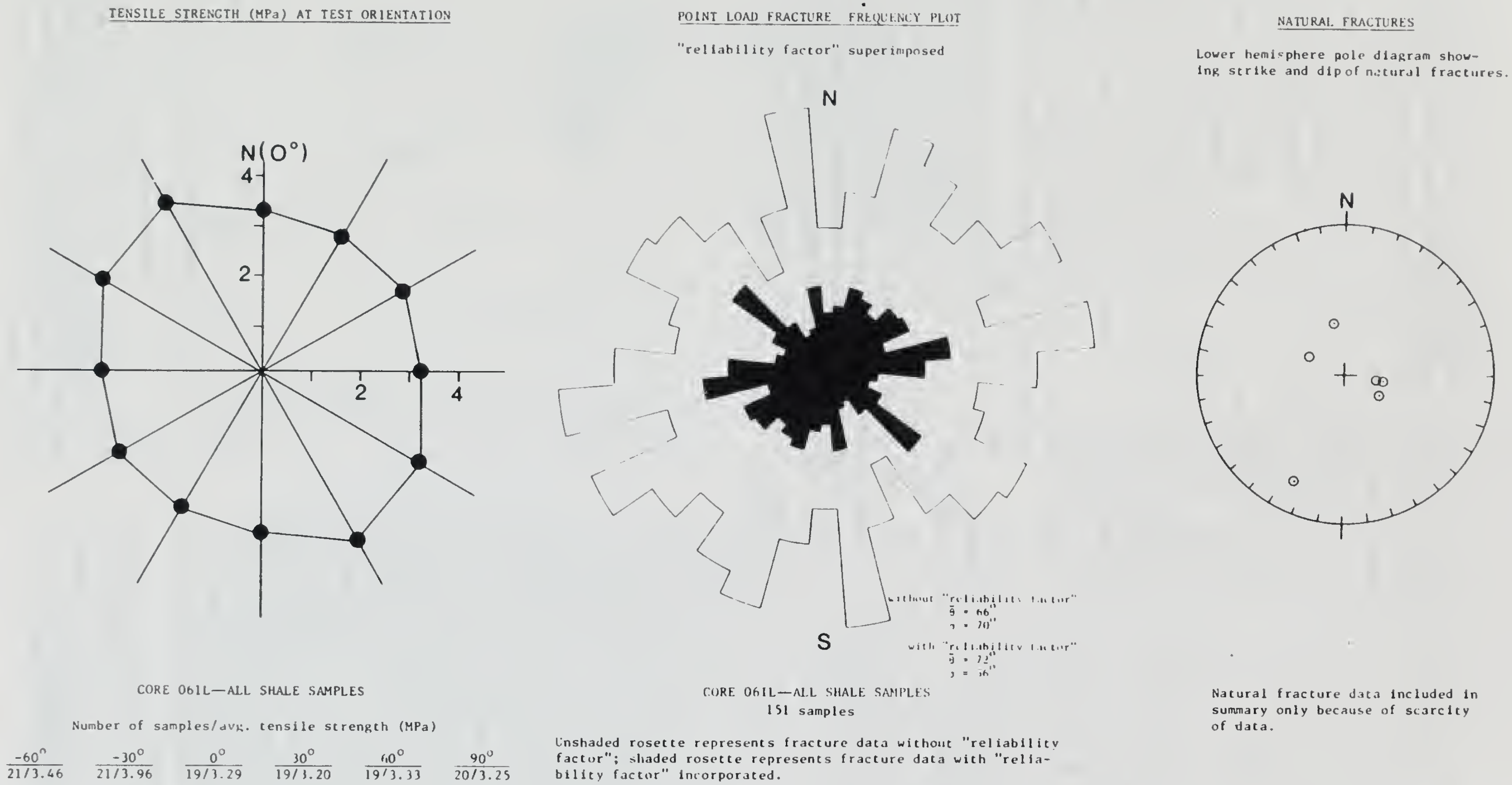
NATURAL FRACTURES

Lower hemisphere pole diagram showing strike and dip of natural fractures.

Natural fracture data included in summary only because of scarcity of data.

ISGS 1979

Figure IX-7. Summary of "Brazilian" tests, point-load tests, and natural fractures for core 04IL.



CORE 061L—ALL SHALE SAMPLES

Number of samples/avg. tensile strength (MPa)

-60°	-30°	0°	30°	60°	90°
21/3.46	21/3.96	19/3.29	19/3.20	19/3.33	20/3.25

CORE 061L—ALL SHALE SAMPLES
151 samples

Unshaded rosette represents fracture data without "reliability factor"; shaded rosette represents fracture data with "reliability factor" incorporated.

Natural fracture data included in summary only because of scarcity of data.

ISGS 1979

Figure IX-8. Summary of "Brazilian" tests, point-load tests, and natural fractures for core 061L.

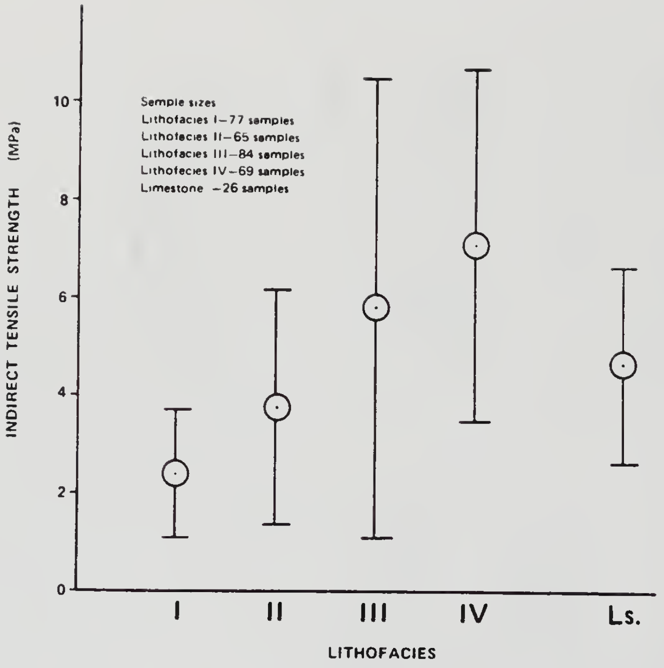


Figure IX-9. Relationship between indirect tensile strength and lithofacies classification of the New Albany Shale and limestone. Results are from cores 01KY, 02IL, 04IL, and 06IL.

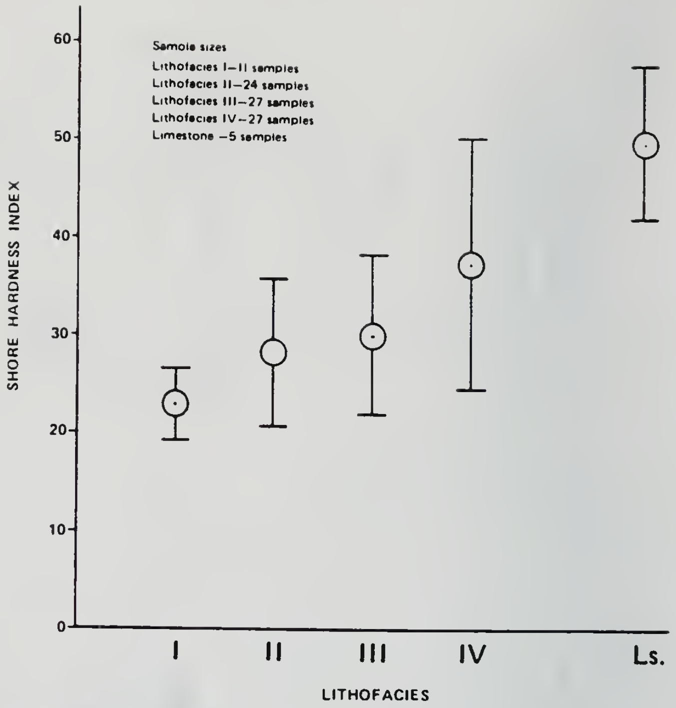


Figure IX-10. Relationship between Shore hardness index and lithofacies classification of the New Albany Shale and limestone. Results are from samples from cores 01KY, 02IL, 04IL, and 06IL (selected at intervals of 10 ft).

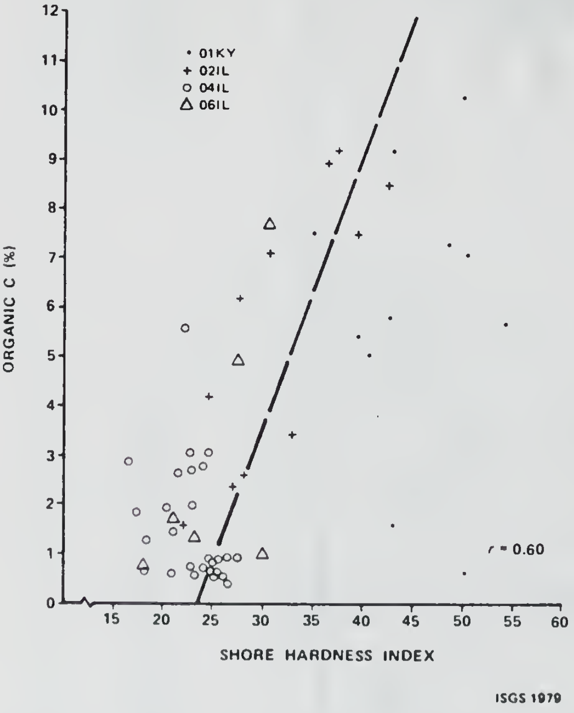


Figure IX-11. Relationship between organic carbon content of shale and Shore hardness index. Results are from cores 01KY, 02IL, 04IL, and 06IL.

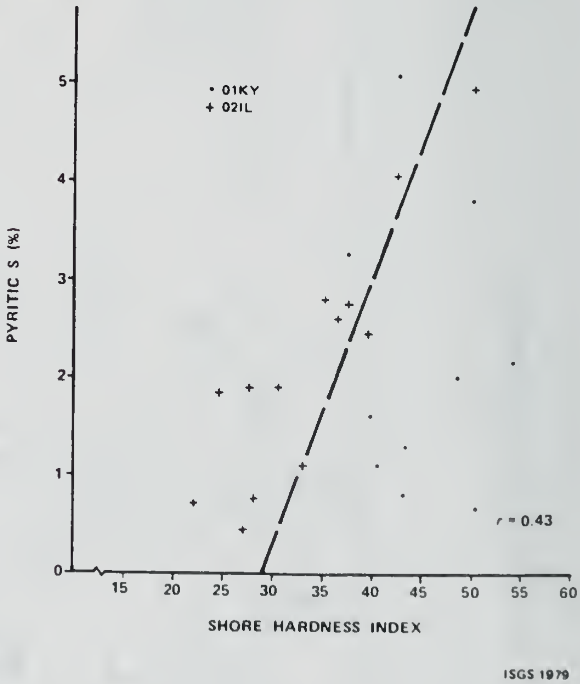


Figure IX-12. Relationship between pyritic sulfur content of shale and Shore hardness index. Results are from cores 01KY and 02IL.

"Brazilian" indirect tensile tests corroborated the orientations of bedding-normal weakness suggested by point-load test results. The cores of shale exhibiting low transverse tensile strength and greatest scatter in the point-load directional data, also showed the most directional strength variations in indirect tensile test results. The average tensile strength for core 04IL (fig. IX-7) is 2.66 MPa and the orientation of greatest average tensile strength is 40 percent stronger than the weakest (N90°E) orientation. Tensile strength for core 06IL (fig. IX-8) averages 3.42 MPa and the strongest orientation is 24 percent greater than the weakest (N30°E) orientation. Core 02IL (fig. IX-6) has an average tensile strength of 6.45 MPa and the strongest tested orientation is 19 percent greater than the weakest (N60°E) orientation tested. Core 01KY (fig. IX-5) has an average tensile strength of 7.94 MPa and an orientation of greatest tensile strength which is 16 percent greater than the weakest orientation. In general, the orientation of highest tensile strength perpendicular to the bedding is orthogonal to the weakest tensile strength orientation.

Several physical characteristics show systematic correlations with the shale lithofacies classification. The dependence of point-load fracture orientation on lithofacies for core 01KY has been previously noted. The tensile strength of the shales also varies significantly with the lithofacies (fig. IX-9); the tensile strengths of the heavily bioturbated shales of low organic content are significantly weaker than unbioturbated, finely-laminated black shales of higher organic content. Data for figure IX-9 include all "Brazilian" indirect tensile test results performed on all cores at all orientations. The relationship of lithofacies classification to Shore hardness is shown in figure IX-10. It is apparent from this graph that the lower the lithofacies class, the softer the shale. Although many samples of lithofacies IV tested as soft as those of lithofacies I, average Shore hardness values show a steady increase with increasing lithofacies number. Figures IX-11 and IX-12 correlate the hardness with chemically-analyzed organic carbon content and pyritic sulphur content in the shale. These results, in conjunction with results summarized in figure IX-4, suggest that shales associated with reducing environments, as indicated by presence of pyrite and organic carbon, are harder and more competent than shales whose sediments were deposited in more oxidizing environments (Section VI).

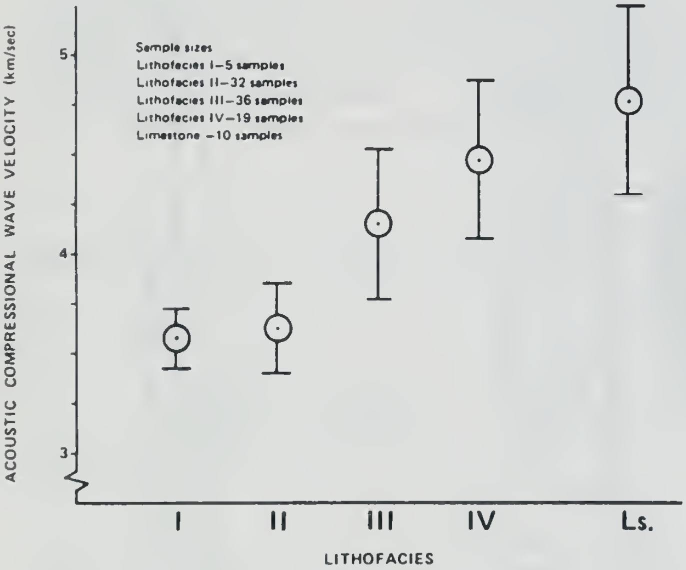
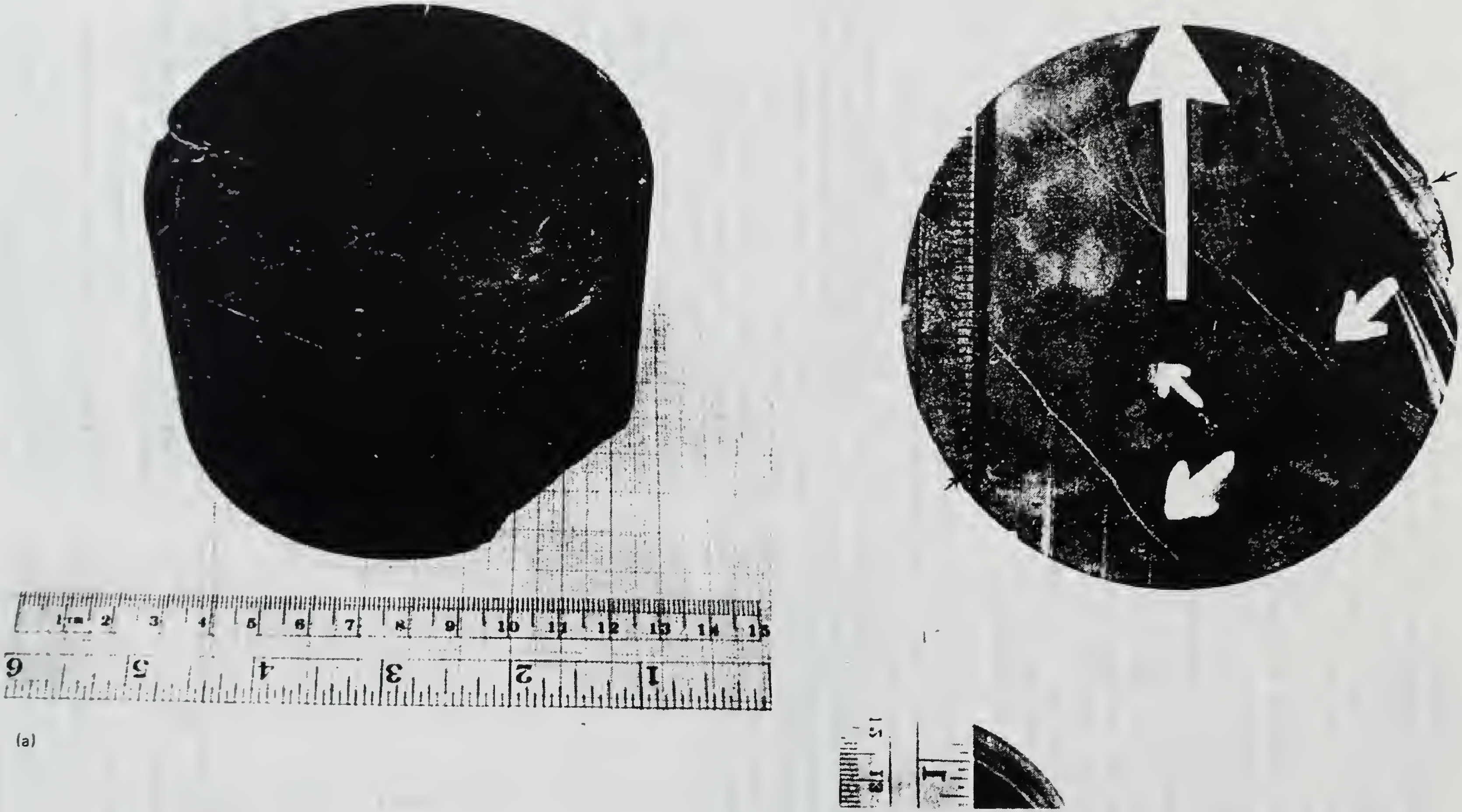


Figure IX-13. Relationship between acoustic compressional wave velocity and New Albany Shale lithofacies classification and limestone. Results are from cores 01KY, 02IL, 04IL, and 06IL.

Acoustic velocity tests also show a correlation with the lithofacies classification (fig. IX-13.) The acoustic compressional wave velocities



(a)

(b)

Figure IX-14. Photographs of calcite-lined natural fractures in core O1KY: (a) discontinuous, sub-vertical natural fractures trending northwest, depth 2,288 feet; (b) set of calcite-lined natural fractures trending northwest (1) which cut an earlier northeast trending fracture (2) which is filled by silty sediment; northeast trending fracture is enhanced to make it visible on the photograph (black arrows at ends of fracture).

show a significant increase with increased lithofacies classification number. A common range of velocities in different directions parallel to bedding is between 3.22 km (2 mi)/sec and 5.37 km (3.3 mi)/sec. Compressional wave velocities measured perpendicular to bedding range between 2.22 km (1.4 mi)/sec and 3.88 km (2.4 mi)/sec. No significant or systematic pattern of fast and slow aximuth velocities measured parallel to bedding was discerned. It was clearly impossible to detect the mineralized fracture system visually apparent in samples from core 01KY on the basis of acoustic velocity measurements.

Core 01KY was studied in detail in order to evaluate the significance of natural fractures which were parallel to the orientation of transverse anisotropy detected by point-load test and "Brazilian" indirect tensile test results (fig. IX-14). A calcite, mineralized natural fracture set normal to bedding is observed in the core (fig. IX-15) and in petrographic thin sections parallel to the bedding (fig. IX-16).

Compression tests were also performed in order to corrobrate the observed mechanical anisotropy normal to bedding in core 01KY. Thirty-seven samples tested parallel to bedding were apparently unaffected by this transverse anisotropy. The orientation of failure was consistently controlled by the bedding rather than by the anisotropy detected normal to bedding by point-load tests and "Brazilian" indirect tensile tests. Strength values and Young's Modulus values were independent of the sample's orientation to the predicted mechanical anisotropy. Tests were performed unconfined and under confining pressures of 1,000, 3,000, 5,000 and 10,000 psi. The results of compression tests performed normal to bedding, however, did show that the fracture anisotropy detected by point-load tests and "Brazilian" indirect tensile tests also exists in compression. The strike of shear fractures on the six samples tested was consistent with the preferred orientation detected by these other two types of tests. The explosive nature of failure for the unconfined tests performed normal to bedding made the exact orientation of failure difficult to determine. In general, the elastic parameters resulting from these compression tests on air-dried samples are as follows:

Unconfined Tests

	E_{50} ($x10^6$psi)	Ultimate Strength ($x10^3$psi)
Bedding normal	2.02-2.08	15-17
Bedding parallel	3.46-4.33	19-20

Confined Tests (triaxial)

	E_{50} ($x10^6$psi)	Ultimate Strength ($x10^3$psi)
Bedding parallel		
($\sigma 3$ = 1000 psi)	1.43	25
($\sigma 3$ = 10,000 psi)	1.52	36

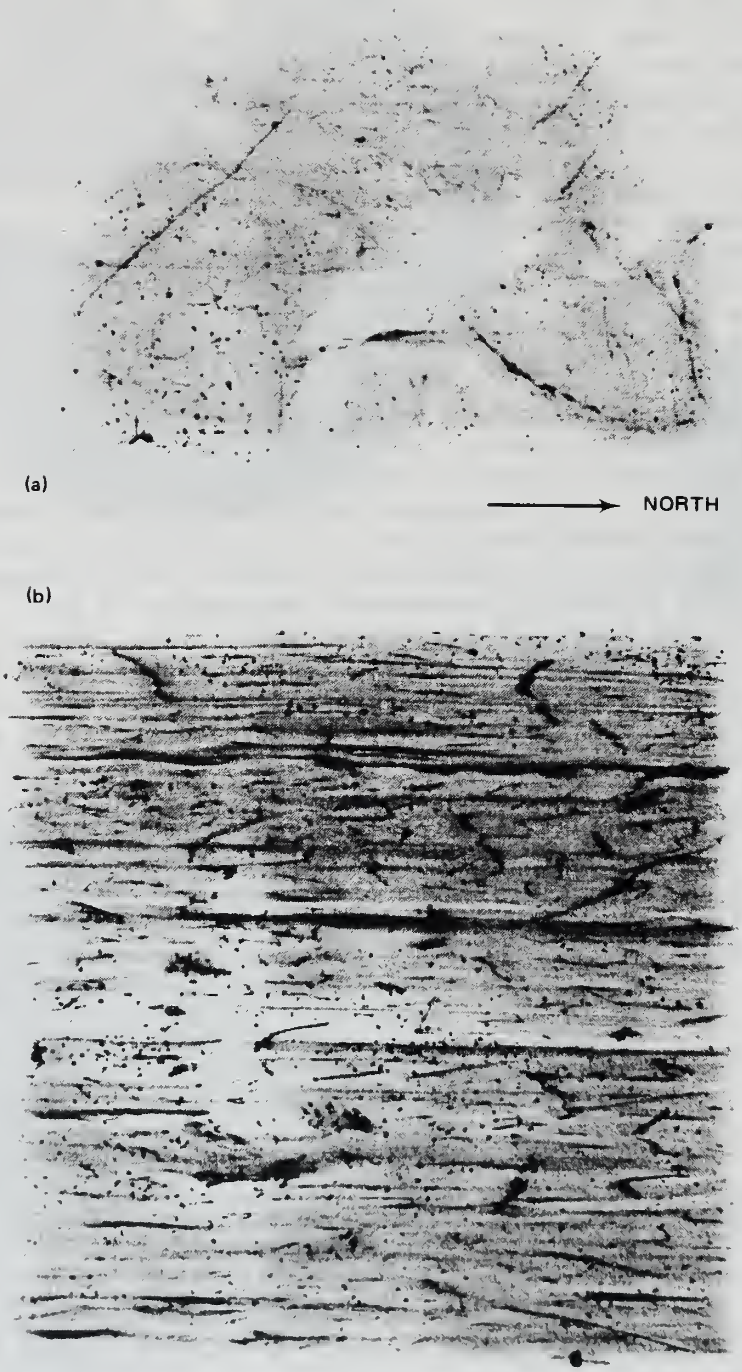
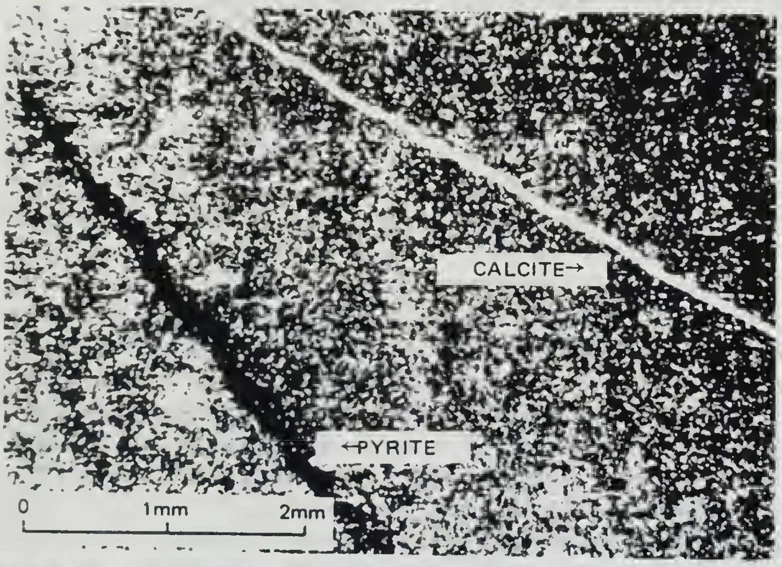
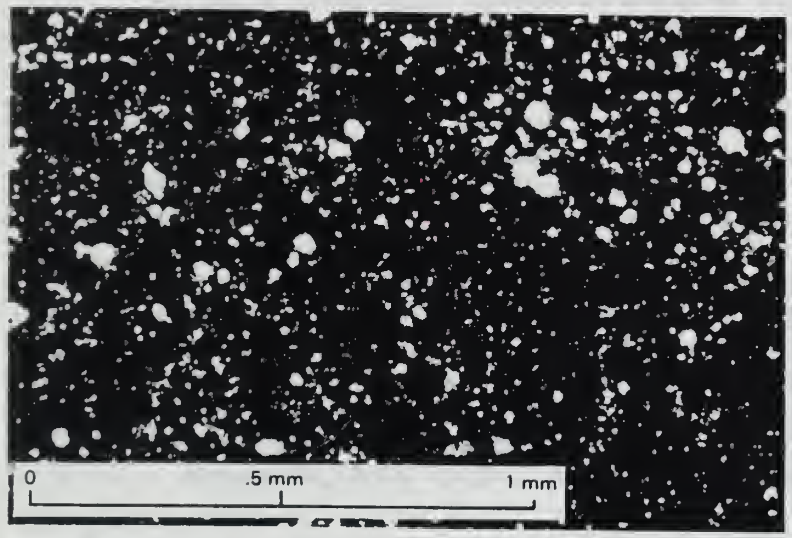


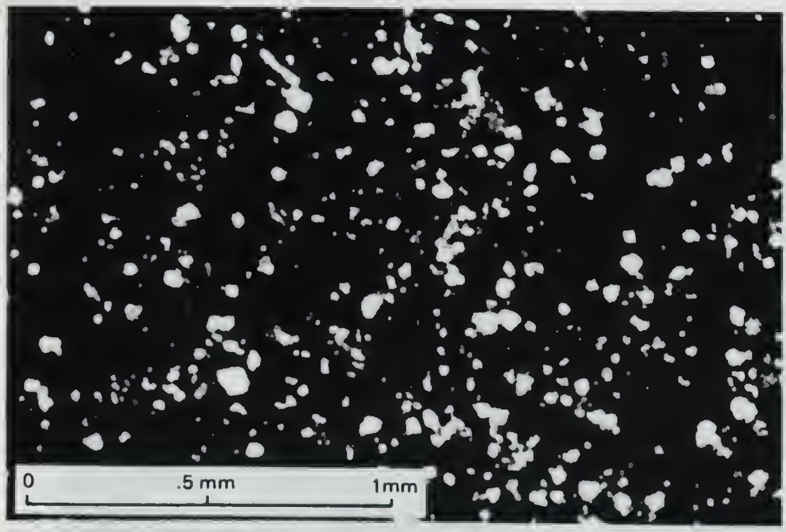
Figure IX-15. X-ray radiograph showing the nature of fractures in core O1KY; horizontal section (a) shows several northwest trending fractures; vertical section (b) shows lack of vertical continuity; black features are probably burrows. Depth is 2,273.5-2,273.9 feet. (Actual size)



(a) Pyrite-filled microfractures trending northwest subparallel to a calcite-lined natural fracture; depth is 2,290 feet.



(b) Microfracture filled with organic material, depth 2, 290.9 feet.

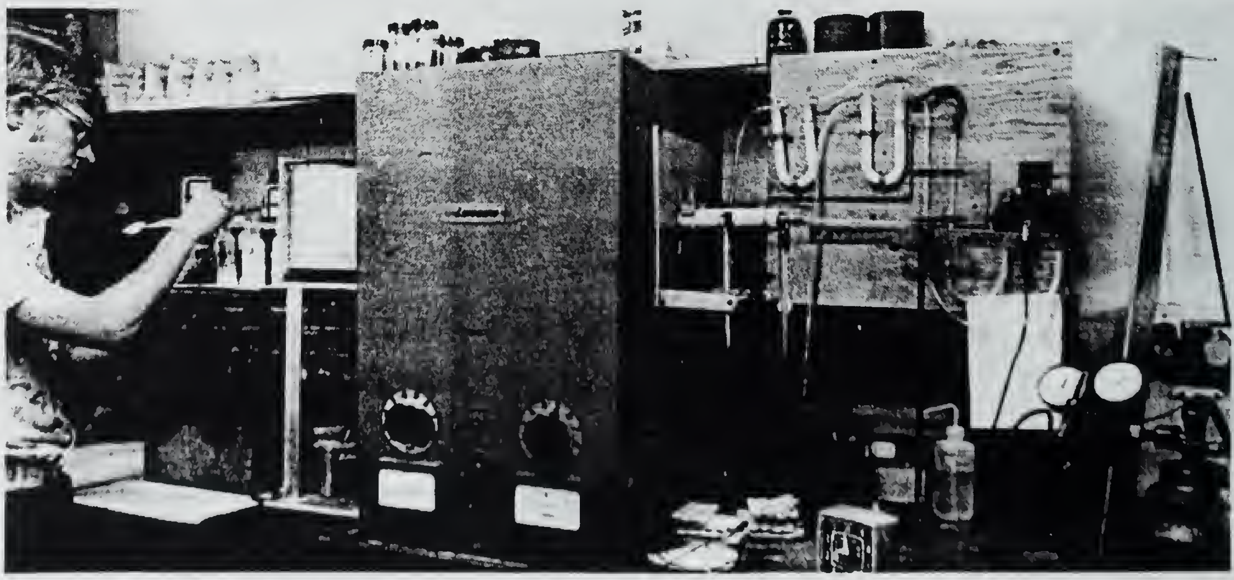


(c) Several microfractures showing the density of occurence; depth 2,318.9 feet.

Figure IX-16. Photomicrographs of oriented microfractures in bedding-parallel thin sections observed in core 01KY:

Thin-section examination showed a random orientation of fossils and other indigenous features in the shale (Cluff, personal communication, 1979). Spores are the only abundant fossils, and two different types, one thick-walled and the other thin-walled, usually occur together. Conodonts, phosphatic fish scales, inarticulate brachiopod fragments, and calcispheres are rare components of the shale but occur in great numbers in a few samples. A variety of macerals, or plant-derived organic fragments other than spores, occur abundantly throughout the brownish-black shales. Short microfractures were observed in thin sections that paralleled the orientation of weakness in core 01KY. These occurrences of orientated microfractures correlate with intervals of core that contain a visible system of fractures in hand specimens.

Results of investigations of clay particle azimuth orientation by x-ray diffraction methods was inconclusive. The ratio of prism diffraction intensity to basal diffraction intensity of illite particles never varied as a function of azimuth orientation by values in excess of machine error. Forty shale samples from core 01KY were x-rayed nearly 200 times. Samples prepared at 30 degree intervals of azimuth orientation displayed consistently random azimuth orientation in three of the four intact core sections studied by this method. One sample displayed a tendency for the basal illite orientation to parallel the north-west-southeast orientation of mechanical weakness in core 01KY. The remaining samples were prepared in sets parallel and perpendicular to fractures induced by mechanical tests. In approximately 70 percent of these tests there was a tendency for the basal diffraction intensity of illite parallel to the fracture orientation to be greater than the basal diffraction intensity of illite perpendicular to the fracture orientation. One interpretation of these results is that illite particles in the shale tend to reorient themselves in an induced stress field with the base of their sheetlike structures parallel to the fracture orientation. These results, however, should be considered tenuous, as interpretation of the diffraction tracks distinguishes intensity variations that are less than the machine error and differences due to sample preparation. The results warrant further work in this area.



Jeff Henricks works at the apparatus used to determine total carbon and total hydrogen.

X. CHEMICAL ANALYSIS OF DEVONIAN SHALES: ORGANIC CARBON CONTENT

J. K. Frost

ABSTRACT

The organic carbon contents of 230 core samples and 160 well- and drill-cutting samples of New Albany Shale from the Illinois Basin are included in this report. The remaining results of the analyses done by the Analytical Chemistry Section, that is, the concentrations of 16 major and minor chemical components and 38 trace elements in these samples, will be described in a separate report. The organic carbon contents of the six cores for which geophysical logs were recorded correlated in general with the gamma-ray intensity recorded on the gamma logs. There was also a significant correlation between organic carbon content and the amount of gas released from canned samples of the Christian County, Kentucky (01KY), Henderson County, Illinois (04IL) and Tazewell County, Illinois (06IL) cores. There was not, however, a good correlation for those cores that did not contain at least moderate quantities of gas or that were extensively fractured.

The Grassy Creek and Sweetland Creek-Selmier Shales are the units of the New Albany Group in Illinois that contain the most organic carbon. Except in the extreme northwestern part of the Illinois Basin, where the organic carbon content is quite low, the Grassy Creek Shale averages 5 to 9 percent in organic carbon content. The Sweetland Creek and Selmier Shales average 2.5 to 6.5 percent organic carbon in the samples studied. The Blocher Shale, which is limited to southeastern Illinois, also averages 4 to 9 percent in organic carbon content. The uppermost shale units in the New Albany Group, the Hannibal and Saverton Shales, are low in organic material, averaging 1 to 2 percent organic carbon in the samples analyzed.

INTRODUCTION

Knowledge of the chemical composition of the New Albany Shale Group (Devonian-Mississippian)in the Illinois Basin is important for evaluating the potential this group has as a source of gas or oil and for evaluating the impact using this resource would have on the environment. The organic carbon content may be expected to be related to the hydrocarbon-bearing potential of the shale. Certain trace elements (e.g., arsenic, molybdenum, and nickel) are enriched in black shales (Mason, 1958) and knowing the levels of concentration of those trace elements that act as indicators of organic enrichment of shales in the Illinois Basin may be useful in exploration. At least one trace element in black shales—uranium—is of potential economic importance. The uranium content of black shales is being studied as part of the National Uranium Resource Evaluation program; for example, a study of uranium in the Ohio Shale in eastern Kentucky and surrounding areas is reported in Fulton (1978). It is also useful to know if the occurrence of any other trace elements is of possible economic importance.

Knowledge of the occurrence of trace metals in Illinois Basin shales is also important for other reasons. Some trace elements may have a catalytic effect on the pyrolysis yield of shale. Analysis of shale also provides information on potential disposal problems from its use. Moreover, a knowledge of the chemical composition of the shales helps the geologist explain the source and deposition of the sediments that constitute the New Albany Shale.

EXPERIMENTAL

The Analytical Chemistry Section characterized the major, minor, and trace element composition of 230 samples from 15 cores, and of 160 well- or drill-cutting samples from various lcoations in the Illinois Basin. Another 28 samples were analyzed for certain elements only (usually organic carbon) and 2 reference shale samples, SDO-1 from the U.S. Geological Survey and SIND-1 from the Indiana Geological Survey, were analyzed in order to illustrate the accuracy of the elemental determinations.

The methods of analysis were outlined in Frost, Dreher, and Kuhn (1977). Table X-1 lists the methods and the elements that were determined by each method. The concentrations of 16 major and minor constituents and 38 trace elements determined on the shale samples are to be reported as outlined in Table X-2.

Since this section deals with the organic carbon concentration of the shales, the method by which organic carbon was obtained is summarized again and the estimated accuracy of the data is given.

TABLE X-1. Methods of analysis of Devonian Shales.

Method	Elements determined
Wavelength-dispersive x-ray fluorescence analysis	Si, Al, Fe, Mg, Ca, K, Ti, P, Cl
Instrumental neutron activation analysis	Fe, Na, K; As, Ba, Br, Ce, Co, Cr, Cs, Dy, Eu, Ga, Hf, La, Lu, Mn, Mo, Nd, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, U, Yb, Zn
Photographic optical emission spectroscopy	Ag, B, Be, Co, Cr, Cu, Ge, Mo, Mn, Ni, Pb, Sn, Sr, V, Zn, Zr
Optical emission spectroscopy—direct-reading instrument	B, Be, Co, Cr, Cu, Ge, Mo, Ni, Sn, Sr, V, Zn, Zr
Energy-dispersive x-ray fluorescence analysis	Ba, Ce, Sr, Zr
Combustion method	Total C and total H
Wet-chemical methods	Inorganic C Total S Pyritic S and sulfate S F

TABLE X-2. Format for report of chemical composition of Devonian Shales.

	Unit of Concentration
Major and Minor Element Composition (16)[a]	
SiO_2, Al_2O_3, FeO, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, S, Cl, CO_2, Org. C, F, H_2O+, H_2O-	%
Trace Element Composition (38)[b]	
As, Ag, B, Ba, Be, (Br), Ce, Cr, Co, Cs, Cu. Dy, Eu, Ga, Ge, Hf, La, Lu, Mn, Mo, (Nd), Ni, Pb, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Th, U, V, Yb, Zn, Zr	ppm
Pyritic S and Sulfate S[c]	%
Surface area -N_2, and -CO_2[d]	m^2/g

---

[a] FeO is total iron, Org. C is by difference, and H_2O+ is a calculated value

[b] Data for Br and Nd are of doubtful accuracy or value.

[c] Data for varieties of sulfur are on 224 core samples.

[d] Surface area data obtained as part of Section XIV are computer-encoded along with the analytical chemistry data.

Procedure for the determination of total carbon (and total hydrogen)

Total carbon and hydrogen contents were determined in the shale samples by burning weighed samples (0.2 to 0.5 g) in a closed-system tube furnace at 1350°C, a variation of method ISO-609 (1975), which is used for coal and coke. A stream of oxygen through the furnace assured complete conversion of all carbon to carbon dioxide and hydrogen to water and carried the combustion products from the furnace through a purification and absorption train. Sulfur dioxide and halogens were removed from the combustion products by reaction with a roll of silver gauze that was sequential to the combustion zone and kept at 700°C. Water was absorbed by anhydrous magnesium perchlorate in an absorption bulb and carbon dioxide in an absorption bulb containing Ascarite. The increase in weight of the two absorption bulbs gave, respectively, the total hydrogen content in the sample, including that contained as moisture and as hydroxyl groups and water of hydration in silicates, and the total carbon content.

Procedure for the determination of inorganic carbon

Inorganic carbon in the shale samples was determined by the common acid evolution—gravimetric method described by Maxwell (1968). Inorganic carbon in a weighed sample (1 to 2 g) was dissolved and the carbon dioxide evolved by treatment with 10 percent HCl by volume in a flask fitted with a condenser, in a closed system. The flask contents were heated to boiling for 15 minutes; the carbon dioxide was purged from the system with CO_2-free air, purified, and absorbed in Ascarite in a tared absorption bulb.

Organic carbon is calculated as the difference between the percentages of total carbon and inorganic carbon.

After the shale project had begun, it was determined that the analyses for total carbon and hydrogen content on the shale samples were subject to variable errors, sometimes quite large. Total carbon and hydrogen concentrations in the reference shale SDO-1 were appreciably higher than the values obtained by other Eastern Gas Shales contractors. The staff of the Minerals Engineering Section determined that the problem lay in the incomplete purification, from sulfur and halogens, of the carbon dioxide and water produced in the combustion procedure. The problem was more acute in the analysis of shales than in the analysis of coal samples because of the much greater ratio of sulfur to carbon in shales. The purification step was perfected and then satisfactory accuracy was obtained, as shown in table X-3, in which current results obtained by the Illinois Geological Survey on the reference standards SDO-1 and SIND-1 are listed. Analyses of samples made early in the project that were suspect were repeated.

It is estimated that the average relative error in the organic carbon concentration of shale samples is 5 to 10 percent.

TABLE X-3. Results for total carbon, total hydrogen, and inorganic carbon in reference shales, air-dried.

	Total C (%)	Total H (%)	Inorg. C (%)
SDO-1			
Ill. Geol. Survey	10.53 ± .01	1.45 ± .01	0.34 ± .02
Reference value*	10.45 ± .2	1.40 ± .04	0.32 ± .04
SIND-1			
Ill. Geol. Survey	9.03 ± .14	1.36 ± .02	0.98 ± .02
Indiana Geol. Survey	9.0 ± .1	1.34 ± .06	1.03 ± .05

* Reference values are an average of results reported by Eastern Gas Shale contractors at a meeting on SDO-1 held at the Morgantown Energy Technology Center, Morgantown, W. Va., April 20, 1978. A moisture content of 0.71% was used to convert the values to an air-dried basis.

RESULTS AND DISCUSSION

Primarily because of problems encountered in the accurate determination of certain elements in the shales and because of a large turnover of analytical chemistry staff during the course of this project, the chemical analyses were not completed in time for inclusion in this report. Tabulation of the final set of concentration values for all the samples is not yet complete. Selection of the most probable concentration for the elements that were determined by more than one method has been done; however, for some of these elements no one method gave consistently more accurate results, and a rigorous evaluation of the selection process must still be made.

Also, the data for the elements are only now being encoded on the computer, and statistical analyses of such a large data base (58 parameters on 390 samples) and geochemical interpretation of the chemical results and the statistical tests will take considerable time. The results of the chemical analyses, therefore, will be submitted as a separate report.

Nevertheless, this report does contain the chemical data most pertinent to the primary purpose of this project, namely, evaluation of the New Albany Shale in the Illinois Basin as a potential source of gas or oil.

Of all the chemical constituents of black shale, the organic carbon content is most indicative of the potential of the shale to produce hydrocarbons. While a high organic carbon content does not necessarily mean that a black shale formation will be a good producer of natural gas, low organic carbon content does indicate that it cannot.

The correlation between organic carbon content and the amount of gas released from canned samples of shale is illustrated in figure X-1 for two of the cores on which released gas measurements were made. The correlation coefficient (r) between the organic carbon content and the amount of released gas is 0.86 for the samples from the 01KY core and 0.89 for the samples from the 04IL core. The values of this correlation coefficient for the other five cores on which released gas measurements were made are:

02IL, 9 samples, r = 0.025
06IL, 22 samples, r = 0.84
11IL, 19 samples, r = -0.10
12IL, 4 samples, r = 0.24
13IL, 21 samples, r = 0.46

The lack of correlation between the organic carbon content and the amount of released gas in samples from the Effingham County (02IL) core was discussed by Dickerson and Coleman (1977). They explained there was no

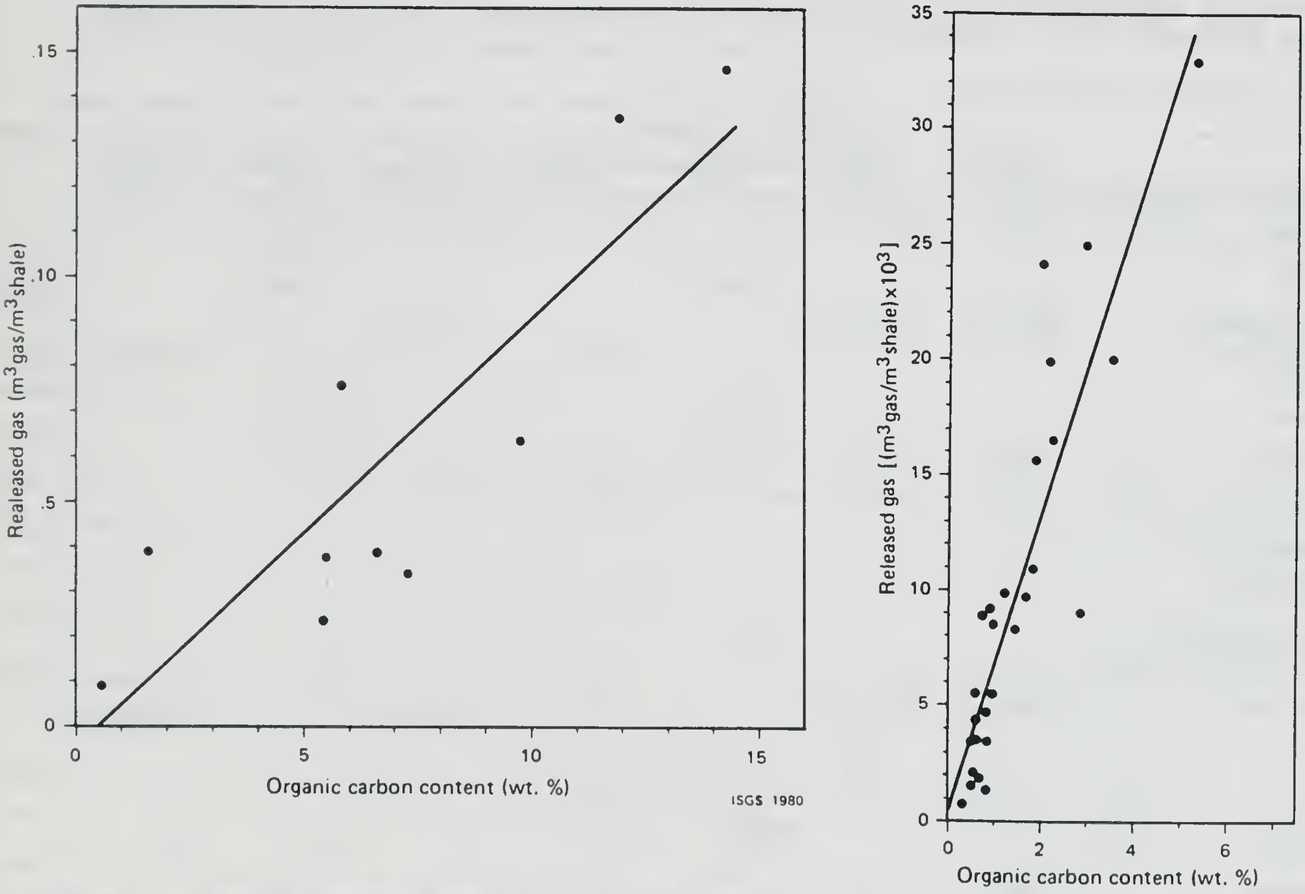


Figure X-1. Relationship between the organic carbon content and the amount of gas released at room temperature from shale samples from (a) the Christian County, Kentucky (01KY core, and (b) the Henderson County, Illinois (04IL) core. The calculated linear regression line is drawn for each core.

correlation because the gas is probably not indigenous to the shale, but rather migrated upward into it from the underlying Devonian oil reservoir.

Just as with the samples from the Henderson County core, only very small amounts of gas were released from the Tazewell County (06IL) core samples; however, the amounts do correlate reasonably well with organic carbon content.

Negligible amounts of gas were released from samples of the Hardin County (11IL) core and the gas that was present was presumably residual from the metamorphic event that occurred in the area during the late Paleozoic or early Mesozoic; therefore, no correlation of released gas and organic carbon content of the samples can be expected. The 12IL core was too short to show a correlation of released gas and organic carbon content. The other Wayne County core, 13IL, exhibited a surprising amount of scatter between organic carbon content and released gas, attributable to the fact that the core was highly fractured, as was core 12IL.

The organic carbon content, the amount of released gas, the hydrocarbon composition, and the core lithology are plotted versus depth in figures 1 through 5 of Section XII for the 01KY, 02IL, 04IL, 06IL, 11IL, and 13IL cores. The organic carbon content of the cores generally correlates satisfactorily with the natural gamma-ray intensity shown by geophysical logs.

Geographical distribution of organic carbon-rich shales

Table X-4 summarizes the organic carbon contents of the 230 core samples that were analyzed. The concentration values for each core are averaged for

TABLE X-4. Organic carbon content, averaged by lithologic unit, of samples from Devonian cores from the Illinois Basin

	County and Core Designation						
	Henderson 04IL	Tazewell 06IL	Sangamon 01IL	Edgar 05IL	Effingham 02IL	Fayette 07IL	Fayette 10IL
Chouteau Ls.					(1) 0.66	(1) 0.14	
Hannibal Sh.			(5) 0.39±0.25			(3) 2.94±2.75	
Hannibal-Saverton Sh. undifferentiated	(14) 1.05±0.68	(19) 1.13±0.90			(2) 1.99±0.38		
Louisiana Ls.						(1) 0.91	
Saverton Sh.			(6) 1.58±1.08			(1) 2.53	
Grassy Creek Sh.	(4) 2.79±0.72	(5) 6.89±2.09	(6) 6.45±1.76		(6) 7.23±2.09	(1) 6.74	
Clegg Creek Sh.*							
Camp Run Sh.*							
Morgan Trail Sh.*							
Grassy Creek-Sweetland Creek Sh. undifferentiated			(1) 3.09				
Sweetland Creek Sh.	(14) 1.66±1.45	(6) 2.56±1.25		(3) 4.71±0.30	(3) 4.33±1.79	(1) 6.94	(2) 6.21±0.46
Selmier Sh.							
Blocher Sh.							
Sylamore Ss.†			(1) 3.79			(1) 0.78	(1) 0.87
Cedar Valley Ls.	(2) 0.57±0.25	(1) 1.52					
Lingle Ls.					(1) 0.34		(4) 1.0±0.72

* Indiana and Kentucky nomenclature.
† Includes small portion of overlying shale and underlying limestone.

each lithologic unit. The number of samples averaged is given; when that number is two, the absolute deviation of the two concentration values is given, and when that number is three or more, the standard deviation (i.e., the deviation that includes the range of concentration of approximately 68 percent of the samples) is given. The cores are listed approximately in order of their location along a north-west to south-east transect of the Illinois Basin (fig. III-1).

Figures X-2 and X-3 show the organic carbon concentrations, averaged by location, of all the Grassy Creek, Sweetland Creek, and Selmier Shales analyzed. Of the 160 drill-cutting samples analyzed, 100 were from the Grassy Creek Shale, 26 were from the Sweetland Creek-Selmier Shale, and 6 were undifferentiated Grassy Creek-Sweetland Creek Shale.

As shown in table X-4, limestone and sandstone layers above and below the New Albany Shale Group have, as expected, low organic carbon contents, generally less than 1 percent. The top shale units, the Hannibal and Saverton shales, also have relatively low organic carbon contents, averaging generally from 1 to 2 percent in the core samples and the 8 drill-cutting samples studied. There evidently are locations in the Hannibal and Saverton shales, however, that have moderate amounts of organic carbon because one drill-cutting sample in Coles County (NAS-0153) had an organic carbon content of 6.14 percent and one sample in Iroquois County (NAS-0195) contained 3.65 percent organic carbon. These higher organic contents, however, could be due to contamination by cavings from overlying Chesterian or Pennsylvanian shales, although every precaution was taken to pick as clean a sample as possible.

TABLE X-4. *Continued*

	County and Core Designation							
	St. Clair 09IL	Wayne 12IL	Wayne 13IL	White 03IL	Hardin 11IL	Sullivan 01IN	Christian 01KY	Bullitt 02KY
Chouteau Ls.								
Hannibal Sh.								
Hannibal-Saverton Sh. undifferentiated			(1) 0.96	(1) 0.86				
Louisiana Ls.								
Saverton Sh.								
Grassy Creek Sh.		(4) 6.99±1.98	(14) 6.78±1.43	(2) 8.97±0.45	(4) 5.10±0.82	(17) 7.40±2.98	(5) 7.58±4.63	
Clegg Creek Sh.*								(2) 14.76±0.80
Camp Run Sh.*								(4) 5.54±0.78
Morgan Trail Sh.*								(2) 7.41±1.91
Grassy Creek-Sweetland Creek Sh. undifferentiated	(1) 9.53							
Sweetland Creek Sh.								
Selmier Sh.			(6) 3.48±1.36	(2) 2.72±0.79	(21) 2.21±1.62	(5) 4.88±3.20	(9) 6.41±3.28	
Blocher Sh.			(3) 3.72±0.27	(2) 7.49±0.38		(3) 5.93±0.52	(4) 6.25±0.98	(1) 8.97
Sylamore Ss.†								
Cedar Valley Ls.								
Lingle Ls.								

Figure X-2. Organic carbon content of samples from the Grassy Creek Shale.

The extreme northwest corner of the Illinois Basin, as illustrated by the Henderson County (04IL) core, has low to moderately low organic carbon contents in the Grassy Creek and Sweetland Creek Shales. The cores taken from all other locations in the basin have moderate organic contents in the Grassy Creek Shale, averaging from 5 to 9 percent. The Grassy Creek Shale has a higher organic content than both the Sweetland Creek and Selmier Shales, which contain an average of 2.5 to 6.5 percent organic carbon in the cores studied, except in the Henderson County (04IL) core from the northwest. Organic carbon concentrations in the drill-cutting samples of Grassy Creek and Sweetland Creek Shales are in the same range as those obtained from the core samples (figs. X-2 and X-3). Core samples and 10 drill-cutting samples from the Blocher Shale in the southeast part of the basin are also moderately high in organic carbon content, averaging 4 to 9 percent.

Results for the core samples from the three areas in Indiana and Kentucky that were studied show that the New Albany Shale in those areas has organic carbon contents comparable to or higher than the shales in Illinois.

In a discussion of the organic carbon contents of New Albany Shale in the Illinois Basin with reference to hydrocarbon-producing potential, the difference of the Hardin County (11IL) core from the others studied should be noted. The Hardin County core contains somewhat less organic carbon than other cores in the southern part of the basin contain, and the nature of the organic material is different from that in the other cores (as discussed in Section XII); the organic material in that core and in the immediate area of Hick's Dome is not believed to be a progenitor of gas or oil.

A good geographical distribution in Illinois of samples analyzed for organic carbon content from the Grassy Creek and Sweetland Creek-Selmier Shales is shown in figures X-2 and X-3. No striking trends in the organic carbon contents of these two units with location in the basin are apparent. Other data on the organic carbon content of the New Albany Shale in Illinois are reported by Stevenson and Dickerson (1969), who analyzed samples representing the bottom 50 feet of New Albany Shale at 350 locations in Illinois. They found the average organic carbon content of the shale to be slightly more than 4 percent with a range of values from less than 1 percent to more than 9 percent. The samples that they analyzed from the extreme northwest part and from the southwest corner (St. Clair, Clinton, Washington, Monroe, and Randolph Counties) of the basin had low organic carbon content, but otherwise, shales with moderately low to moderate organic carbon content were interspersed throughout the basin. The average organic content found by Stevenson and Dickerson for the shale samples they analyzed may not provide an apt estimate of the organic carbon content of the bottom portion of the Grassy Creek and Sweetland Creek Shales and the Blocher Shale in southeastern Illinois because the strata of the New Albany Group are discontinuous (especially near the bottom of the formation) and the results obtained reflect strongly the sampling locations.

Selection of drill-cutting samples for analysis in this study was undoubtedly biased toward the selection of dark-colored shales. Analysis of the core samples showed that the organic carbon content varies appreciably with depth

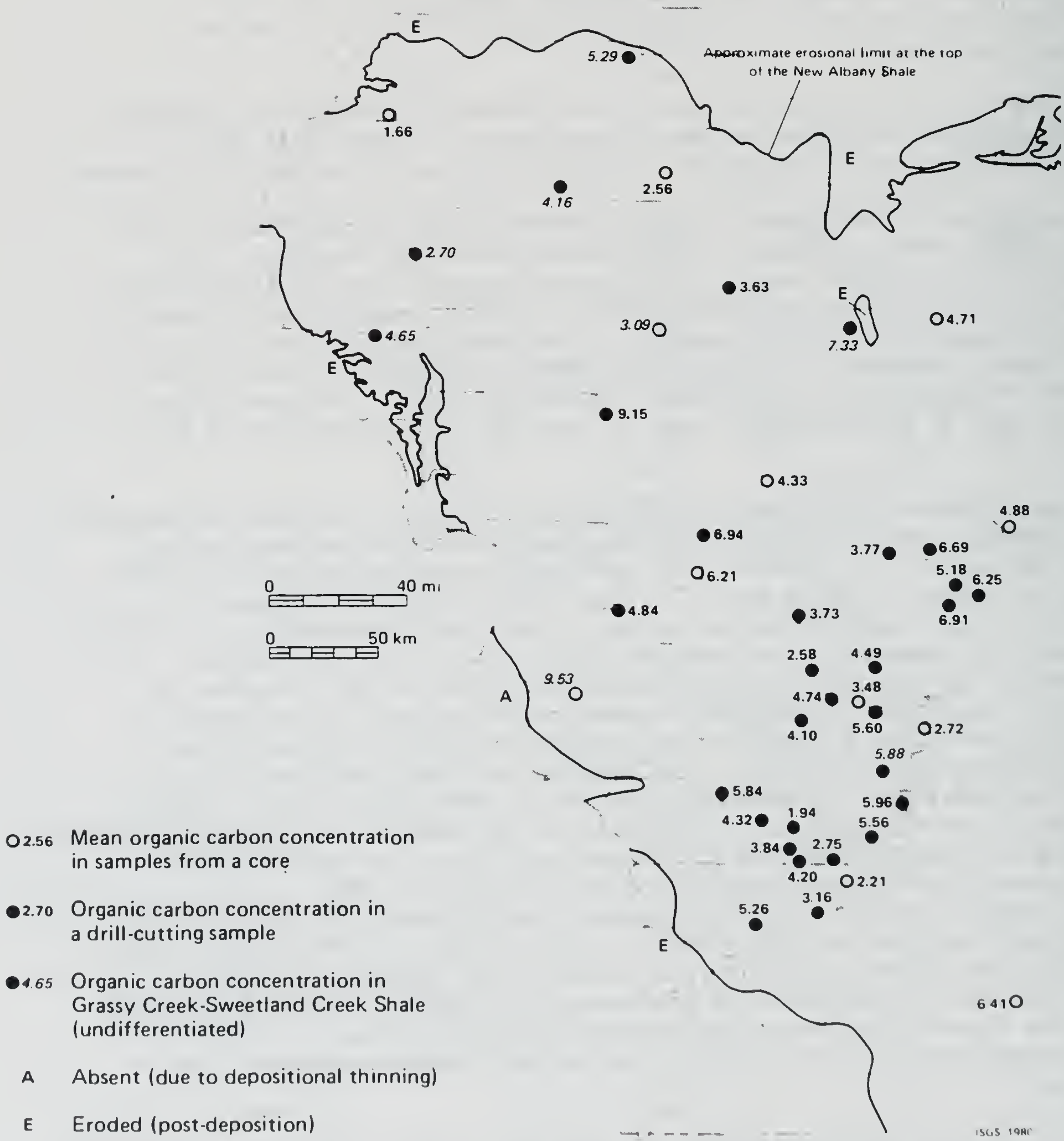
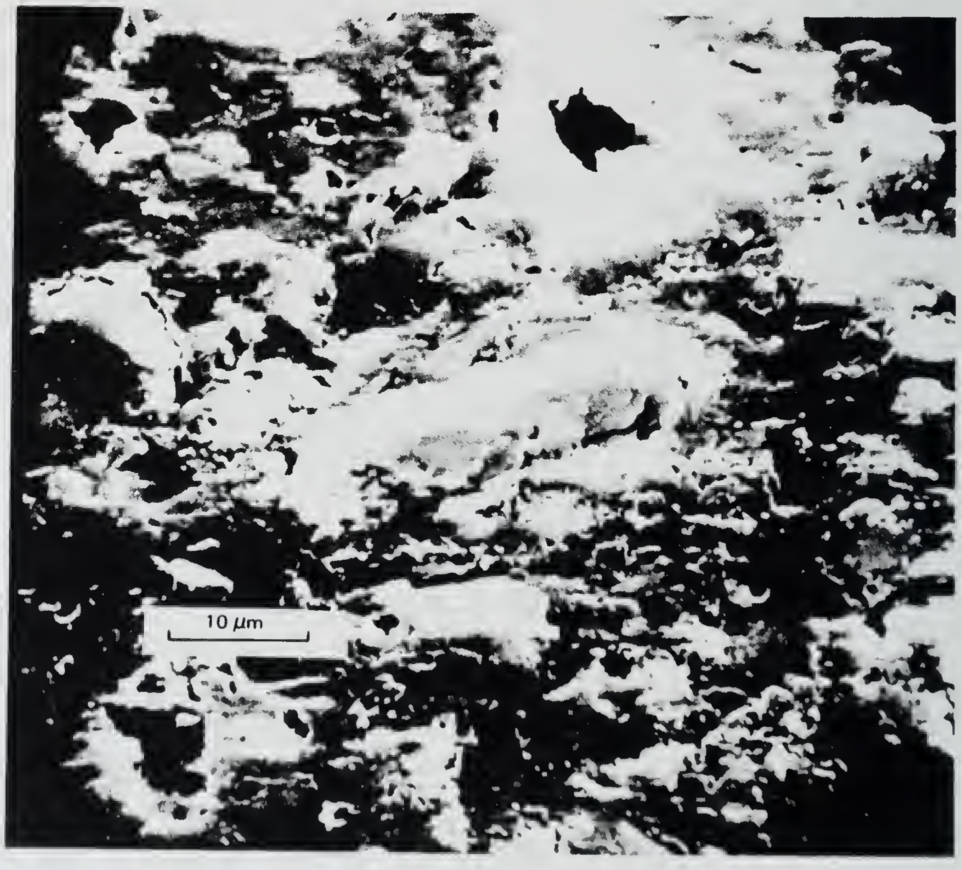


Figure X-3. Organic carbon content of samples from the Sweetland Creek-Selmier Shales.

within each shale unit. Therefore, in figures X-2 and X-3, at any given sample location, there is a layer of Grassy Creek (or Sweetland Creek-Selmier, for fig. X-3) Shale with the organic carbon content shown on the map, but this content is not representative of the whole shale unit; the average for the unit is probably somewhat lower. For this reason, an average organic carbon content of New Albany Group shales is not given. The ranges of organic concentrations in shale units, with sampling as described, can be used together with information on the maturity of the organic material in the shales, as described in other sections of this report, to assess the hydrocarbon-producing potential of these shales in the Illinois Basin.

ACKNOWLEDGMENT

Over this 4-year contract, total carbon and hydrogen determinations were made by 5 staff members of the Minerals Engineering Section. All other analyses were carried out by 21 analysts in the Analytical Chemistry Section.



Scanning Electron Microscope (SEM) photomicrograph of possible plant fragment (center) surrounded by a mixture of clay minerals and amorphous organic matter.

XI. INORGANIC/ORGANIC ASSOCIATIONS OF TRACE ELEMENTS IN BLACK SHALES

Robert A. Keogh

ABSTRACT

Little successful research has been conducted on the direct determination of trace elements in the organic material found in shale. Complete separation of the small amount of organic matter from the available New Albany Shale cores was extremely difficult. Several chemical and physical methods, including zonal centrifugation, were investigated. The most successful method, indicated by the lowest ash content of the resulting organic fraction, was a series of acid extractions (HNO_3, HF, HCl). However, the analysis of the organic fraction prepared by this method indicates that some residual mineral matter remained. The ash content of the isolated organic fractions ranged from .15 to 4.09 percent. The primary contaminants of the organic fraction were Ti, Al, and Fe.

Trace element determinations indicated that many elements were associated with the isolated organic fraction; however, for many elements, differentiating between the organic and inorganic phases was impossible because of the residual mineral matter in the organic phase. Nevertheless, the concentrations of Ni, U, Se, Sb, Mo and V in the isolated organic fraction are thought to be partially due to their association with the organic matter. No relationship was found between these trace elements in the isolated organic fraction and the gas-bearing potential of the whole shale.

INTRODUCTION

The initial goal of the project was to develop, if possible, a method which separated (or nearly separated) the small amount of organic matter from the mineral matrix of black shale. Various chemical and physical methods, including zonal centrifugation, were investigated.

The second goal of the project was to perform a direct determination of trace elements on the extracted organic fraction in order to determine which trace elements are enriched in the organic fraction, and to evaluate how they possibly relate to the gas-bearing potential of the shales.

METHODS

The analytical procedure used to determine the trace elements was predominately instrumental neutron activation (INAA). Details of the procedure used to determine the elements (except vanadium, aluminum, and titanium) can be found in Ruch, et al. (1979).

The procedure for the determination of vanadium, aluminum, and titanium via short-lived ($T_{\frac{1}{2}}$ <10 min) isotopes necessitated different counting techniques.

Samples and standards were irradiated in the TRIGA Mark II reactor for 30 seconds at a flux of 1.6 x 10^{-12} $n \cdot cm^{-2} \cdot sec^{-1}$ and immediately transferred via a rapid sample transfer or Rabbit system to a laboratory in an adjacent building. After a delay time of 120 seconds, the activities were counted for 200 seconds. A Ge(Li) detector, with a resolution (FWHM) of about 2.2 KeV at 1332 KeV, was connected to a 4096 multichannel analyzer with magnetic tape output. The data were reduced using the Cyber computer of the University of Illinois. The isotopes and energies used are summarized as follows:

Element	Isotope produced	Cross section (Barns)	Major Gamma-rays utilized (KeV)	Limit of detection	Mean relative standard deviation (%)
Al	Al-28	.21	1779.0	.01%	20
Ti	Ti-51	.14	320.0 928.6	.01%	25
V	V-52	4.50	1434.0	1ppm	15

A Beckman Model JCF-Z rotor with a B-29 type Norryl core was employed in the zonal centrifuge method. The centrifuge used was a Beckman Model J-21B.

RESULTS AND DISCUSSION

Method development

Separating small amounts of organic matter in the available shale cores (generally <10% organic carbon) from the large amount of mineral matter proved to be extremely difficult. Classical physical methods such as floatation yielded no fraction sufficiently enriched in organic matter. The use of zonal centrifugal techniques to isolate the organic fraction was then investigated. This procedure consists of isopycnic bonding of the shales during centrifugation in aqueous solutions of sucrose with a constant density gradient. A composite sample from the Effingham County core (02IL) with an organic carbon content of 8 percent was used for development of the method (this organic carbon content was representative of the organic carbon content of the available New Albany cores). The sample was pulverized in a ball mill for several days before use.

The general procedures for the addition and removal of gradients and samples are described by Beckman, Inc. (1975). The sample was suspended in distilled water and ultrasonically treated before it was injected into the rotor. Various speeds (5,000 - 10,000 rpm), times of centrifugation (1 - 4 hr), and gradient densities (1.15 - 1.30) were used; however, no separation of the organic fraction was observed with any set of the experimental conditions.

Because the physical methods did not provide an "ash-free" organic fraction, chemical methods were investigated. Hymus and Basak (1949) used a series of acids for the removal of the mineral matter in coals. The ash contents of the separated organic fractions were in the range of 1 to 2 percent.

A variation of the Hymus and Basak method was found to be the most successful means of isolating the organic fraction of shales. The method involved three stages: (1) refluxing with dilute HNO_3 (10% v/v) to remove pyrite; (2) treatment with HF at 50°C to remove the silicates; and (3) treatment with dilute HCl (25% v/v) at 60°C to remove carbonates, sulfates, other sulfides and any residual fluorides from Step 2. The first two isolated organic fractions contained ash contents of .15 and .36 percent. This acid-leaching method was used in the isolation of the organic fractions from the whole shales in this study and was repeated until there was no significant reduction in the ash content of the organic fraction.

A major drawback to this chemical method of isolation is the alteration of the organic material by the acids (Saxby, 1970). It was initially proposed that the organic sulfur content be used as an indicator of the alteration of the organic fraction. Because of the difficulty of isolating the small amount representing the organic fraction from the mineral matrix of the shales, only small amounts of isolated organic matter were obtained—not enough for the determination of organic sulfur in the organic fraction. However, the major alteration of the organic fraction is probably the addition of chlorine (Hickinbottom, 1957) fluorine (Smith, 1961) and nitrogen (Waters, 1964) to the organic matter. The acid treatment may also remove some of the more soluble organic material such as pyridine and aniline derivatives (Dancy and Gredroyc, 1950).

To minimize the chemical treatment and its inherent alteration of the organic matter, use of a combination of the acid treatment and zonal centrifugation was investigated. Two organic samples (isolated by the acid-leaching procedure) with ash contents of 4.09 and 2.33 percent were subjected to zonal centrifugation using the same procedures used in the initial centrifugation work. This approach was unsuccessful in reducing the ash content of the organic fraction.

The samples used for separation of the organic fraction by the acid treatment were chosen on the basis of their gas content as determined by the degassing experiments described in Section XII of this report. It should be emphasized that none of the available cores is from gas producing wells.

Seven samples were chosen from three New Albany cores representing the highest gas contents of the available cores. Four samples were selected from the Wayne County core (13IL), two from the Effingham County core (02IL), and one from the Christian County core (01KY). Two control samples, which contained little or no gas, were taken from the Hardin County core (11IL).

Trace element concentrations in the organic fraction of shales

The data in table 1 indicate that many of the trace elements determined are contained in the separated organic fraction: these elements are Ni, Se, Ta, Yb, Tb, Cr, Lu, Sb, Eu, Ga, Sm, Ce, Co, La, Th, V, U, Mo, and Sc. They are presented in descending order of their percent association with the organic fraction. The percent association calculation normalizes the trace element data of the organic fraction using the trace element concentrations in the

TABLE XI-1. Trace element data for the whole shales and organic fractions.

	02IL05C2			01KY01C1			13IL15C2		
Element	Whole shale	Organic fraction	% Association in org. fraction	Whole shale	Organic fraction	% Association in org. fraction	Whole shale	Organic fraction	% Association in org. fraction
% Ti	.79	ND*	--	.56	--	--	.77	.11	1.26
% Al	13.79	ND	--	10.10	--	--	16.19	.05	.03
% Fe	5.87	.14	.22	6.16	.07	.16	5.04	.09	.16
ppm As	37.	1.0	.25	68.	.6	.12	35.	.9	.23
Ce	67.	2.1	.29	56.	4.4	1.10	82.	14.	1.50
Co	26.	1.6	.57	42.	1.2	.40	33.	2.	.53
Cr	73.	40.	5.05	70.	24.	4.81	84.	68.	7.12
Cs	6.9	.05	.07	5.4	.2	.52	8.1	.2	.22
Eu	1.5	.09	.55	1.6	.23	2.02	1.7	.6	3.10
Ga	24.	1.3	.50	17.	2.9	2.39	21.	2.5	1.05
La	38.	1.1	.27	35.	2.7	1.08	40.	4.	.88
Lu	.4	.2	4.61	.5	.23	6.45	.8	.9	9.89
Mo	89.	5.	.52	170.	15.	1.24	84.	30.	3.14
Ni	92.	142.	14.22	115.	110.	13.42	73.	315.	37.93
Rb	130.	<3.	.21	110.	<5.	.64	160.	9.	.49
Sb	3.7	3.2	7.97	4.9	6.0	17.18	4.0	6.0	13.19
Sc	16.	.2	.12	13.	.6	.65	18.	1.	.49
Se	1.6	6.4	36.84	2.0	4.0	28.06	2.0	.8	3.52
Sm	8.4	.3	.33	5.6	.9	2.26	7.7	2.4	2.74
Ta	1.0	2.3	21.18	.9	2.7	42.09	.96	1.6	14.65
Th	11.	.5	.42	7.1	.9	1.78	11.	3.3	2.64
U	34.	.7	.19	70.	1.6	.32	37.	15.	3.56
V	240.	ND	--	160.	ND	--	82.	24.	2.57
Yb	2.3	.9	3.60	2.3	1.3	7.93	3.0	7.	20.51
Zn	200.	11.	.51	90.	5.	.78	340.	<10.	.26
Tb	.9	.2	2.05	1.1	.5	6.38	1.2	2.0	14.65
% Ash		.15			.36			.48	
% Organic Carbon	9.21			14.03			8.79		
ft^3 gas/ft^3 shale	.37			1.47			1.83		

	02IL06C1			13IL08C1			13IL07C2		
Element	Whole shale	Organic fraction	% Association in org. fraction	Whole shale	Organic fraction	% Association in org. fraction	Whole shale	Organic fraction	% Association in org. fraction
% Ti	.85	.24	2.01	.68	.70	7.25	.55	.70	9.10
% Al	14.62	.04	.02	11.49	.15	.09	10.32	.28	.19
% Fe	5.24	.10	.14	3.05	.12	.28	3.85	.09	.17
ppm As	32.	1.5	.33	32.	6.0	1.32	17.	1.0	.42
Ce	68.	4.	.42	63.	15.	1.68	52.	15.	2.06
Co	25.	1.5	.43	14.	4.	2.01	12.	4.	2.38
Cr	79.	56.	5.05	91.	144.	11.14	87.	110.	9.04
Cs	8.2	.1	.09	6.3	.2	.22	6.2	.2	.23
Eu	1.6	.4	1.78	1.4	.7	3.52	1.3	.8	4.40
Ga	23.	1.3	.40	13.	1.4	.76	14.	1.5	.77
La	43.	2.7	.45	37.	.7	1.33	37.	11.	2.13
Lu	.4	.5	8.90	.9	1.5	11.73	.8	1.4	12.51
Mo	68.	3.	.31	81.	22.	1.91	71.	30.	3.02
Ni	100.	180.	12.81	110.	720.	46.08	100.	550.	39.33
Rb	160.	<10.	.45	120.	<5.	.29	120.	<5.	.30
Sb	3.2	.5	1.11	8.7	2.7	2.19	7.1	6.5	6.55
Sc	19.	1.1	.41	13.	4.	2.17	12.	3.0	1.79
Se	1.0	2.	14.24	10.	2.1	1.48	13.	2.7	1.49
Sm	10.	.8	.57	6.1	2.2	2.54	6.3	2.3	2.61
Ta	1.2	.6	3.56	1.0	2.4	16.90	.9	2.0	15.89
Th	14.	1.5	.76	9.5	3.5	2.59	7.7	3.2	2.97
U	30.	1.0	.24	31.	4.	.91	23.	9.	2.80
V	220.	35.	1.13	360.	130.	2.54	430.	112.	1.10
Yb	2.4	3.4	10.09	3.0	10.	23.47	2.9	10.	24.66
Zn	200.	5.	.02	280.	<5.	.13	570.	20.	.25
Tb	.9	.9	7.12	1.0	2.6	18.30	.8	2.5	22.34
% Ash		.56			2.00			2.21	
% Organic Carbon	7.12			7.04			7.15		
ft^3 gas/ft^3 shale	.54			1.19			2.40		

TABLE XI-1. *Continued*

	13IL06C2			11IL15C1			11IL08C1		
Element	Whole shale	Organic fraction	% Association in org. fraction	Whole shale	Organic fraction	% Association in org. fraction	Whole shale	Organic fraction	% Association in org. fraction
% Ti	.77	.70	4.83	.60	.70	7.58	.86	.10	.06
% Al	14.42	.14	.05	12.65	.07	.04	16.38	.54	.02
% Fe	3.60	.15	.22	4.39	.2	.30	6.51	1.0	.08
ppm As	28.	3.0	.57	66.	4.0	.39	31.	13.	.23
Ce	64.	46.	3.82	76.	11.	.94	71.	12.	.09
Co	13.	4.0	1.63	23.	6.	1.70	19.	8.	.23
Cr	100.	121.	6.43	97.	50.	3.35	84.	100.	.64
Cs	8.1	.14	.09	3.8	.1	.17	5.2	.1	.01
Eu	1.4	1.2	4.55	1.9	.5	1.71	1.4	1.4	.54
Ga	19.	4.	1.12	15.	1.4	.61	20.	1.2	.03
La	43.	13.	1.61	41.	9.0	1.43	43.	4.3	.05
Lu	.6	1.5	13.28	.5	.5	6.50	.6	4.2	3.78
Mo	35.	14.	2.12	150.	40.	1.73	<20.	9.0	.24
Ni	67.	344.	27.26	190.	650.	22.24	66.	270.	2.21
Rb	160.	<5.	.17	170.	2.	.08	170.	<10.	.03
Sb	5.3	6.8	6.81	6.	10.	10.83	1.7	2.	.64
Sc	15.	2.9	1.03	16.	1.6	.65	18.	3.1	.09
Se	10.	4.5	2.39	10.	17.	11.05	<3.	4.0	.72
Sm	6.6	3.2	2.58	7.5	1.9	1.65	6.8	4.3	.34
Ta	1.0	2.2	11.68	.9	3.2	23.11	1.1	1.3	.64
Th	11.	3.9	1.88	11.	3.	1.77	15.	15.	.54
U	17.	7.	2.19	33.	4.7	.93	<7.	7.7	.59
V	270.	60.	1.18	280.	86.	2.00	71.	10.	.08
Yb	3.3	10.	16.09	3.3	3.5	6.89	3.5	25.	3.86
Zn	170.	<2.	.06	150.	ND	--	120.	40.	.18
Tb	.8	2.8	18.59	1.0	.8	5.20	1.2	3.7	.17
% Ash		2.33			2.33			4.09	
% Organic Carbon	5.31			6.50			.54		
ft^3 gas/ft^3 shale	1.26			6.7×10^{-5}			7.2×10^{-5}		

* ND = Not Determined

whole shale and isolated organic fraction plus the organic carbon content of the whole shale. The percentage of association is calculated by the following equation:

$$\text{Percent assoc.} = \frac{(\text{ORG. Frac. Conc.})\ (\text{ORG. C})}{(\text{Shale Conc.})}$$

in which

Percent assoc. = percent association of an individual trace element in the organic fraction

ORG. frac. conc. = concentration of an individual trace element in the organic fraction

ORG. C = organic carbon content of the whole shale (percent)

Shale conc. = concentration of an individual trace element in the whole shale.

The organic carbon content of the whole shale was used as a good approximation of the organic matter concentration in the shales. The true amount of organic matter is slightly larger because of the small amounts of organic hydrogen, nitrogen, sulfur, etc.

The ash content of the organic fraction, however, must be considered in any evaluation of association because mineral matter was never completely removed from the organic fraction of any shale sample. The ash contents of the organic fractions ranged from .15 to 2.33 percent in the samples from the gas-bearing shales. The ash contents of the organic samples from the two non gas-bearing shales were 2.33 and 4.09 percent. Concentrations of Ti, Fe, and Al were at percent levels in the organic fractions, confirming that not all of the mineral matter was removed. Any mineral that had not been removed would be concentrated relative to the organic fraction, and the trace elements associated with that mineral would appear to be present or enriched in the organic fraction.

To determine which trace elements might be present or enriched because of the residual mineral matter, a correlation matrix was calculated using major and trace element data for the whole shales. Details of these calculations can be found in Soupac (1979). The correlation coefficients indicate that many of the trace elements are associated with the major elements of the whole shales. In particular, the elements (correlation coefficients in parenthesis) Ce (.74), Cr (.86), Ga (.79), La (.81), Rb (.82), Sc (.88), Sm (.83), Ta (.80), and Th (.96) show a correlation with the Ti content of the whole shales. The elements Ce (.91), Cs (.93), Ga (.75), La (.79), Rb (.92), Sc (.89), and Th (.82) have a correlation with the Al content of the whole shales. Only Co (.90) and Eu (.76) indicate a correlation with the Fe content of the whole shale.

Since Ti, Fe, and Al are the major mineral matter contaminants in the organic fractions, it is highly probable that trace elements showing a correlation with major elements would, as a result, also be present or enriched in the organic fraction. This could explain the enrichment of Ta and Cr as well as the presence of Sm, Ce, Co, Th, Eu, Ga, and Sc in the organic fraction. Deere, et al. (1966) report the association of Fe, Ta, and Cr with the mineral rutile (TiO_2). Rutile has been observed in the whole shales and is known to be insoluble in acids (Dana, 1932). With the methods used here, it is very difficult to determine if these trace elements are directly associated with the organic matter.

Roaldset (1975) and Cullers et al. (1975) report that clay minerals contain highly variable quantities of rare earths because of their ability to absorb these elements on the crystal surfaces during weathering and sedimentation. The Al content of the isolated organic fraction indicates that not all the original clay material has been removed: therefore, the apparent enrichment of Yb, Tb, and Lu in the organic fraction could be due to their association with the residual clay materials.

The elements Se and Sb are primarily associated with pyrite (Leutwein, 1974). Complete removal of pyrite by leaching with HNO_3 was reported by Saxby (1970), so pyrite should not be a significant source of Se and Sb in the organic fraction. At least a portion of the Se and Sb concentrations could be due to the organic matter.

Nickel, present in all living organisms (Turekian, 1972), shows a consistent enrichment in the isolated organic fractions; it is therefore likely that some of the Ni in the organic fraction is directly associated with the organic matter.

The primary occurrence of Mo in black shales is with pyrite and other metal sulfides, and as minute coatings and impregnations in the organic phase (Manheim and Landergren, 1974). Pyrite and the other metal sulfides have been largely removed from the organic fraction, and at least a portion of the Mo concentration in the organic fraction is due to an association with the organic matter.

The U content of black shales is often associated with organic matter (Swanson, 1960). The amount of enrichment depends on the type of organic matter and the presence of phosphatic minerals. The low abundance of phosphorus in the whole shales eliminates this possible inorganic association for U. The data show a relatively low enrichment for U in the organic fraction; however, Swanson (1960) reports that the humic type of organic matter can concentrate far more U than can the sapropelic type. The gas-bearing samples contain both types of organic matter, but 90-95 percent of it is sapropelic (Barrows et al., 1979). Although U does not appear to be enriched, the U present in the organic fraction is probably organically associated.

Vanadium is important in several biochemical processes. Vanadyl porphyrin complexes are found in oils, sediments, and sedimentary rocks (Landergren, and Evans, 1974), and it is likely that the vanadium in the organic fraction is directly associated with the organic matter.

A correlation matrix was calculated using the trace element concentrations of the organic fraction and the gas and organic carbon content of the whole shales to determine the possible relationship of these elements to gas-bearing potential. None of the trace elements indicated a correlation with the organic carbon content of the whole shales. The lack of correlation may be due to the influence of the residual mineral matter in the isolated organic fraction.

The elements Mo (.92), U (.73), Sb (.75) and Cs (.84) did show a correlation (coefficient in parenthesis) with the gas content of the whole shales. However, there was no significant difference in the relative enrichment of these elements between the gas-bearing and the non-gas-bearing shales. The positive correlations indicated are probably due to the influence of the residual mineral matter also.

Holly Welstein works at the Perkin-Elmer Sigma I gas chromatograph used for released gas analysis.

XII. HYDROCARBON CONTENT AND COMPOSITION

Donald R. Dickerson and Mei-In Melissa Chou

ABSTRACT

Released gas analyses were run on 166 shale core samples taken from seven wells drilled in the Illinois Basin. The volume of hydrocarbon gas released per unit volume of shale was calculated for each sample. The composition of the headspace gas was determined by gas chromatography. The volume of gas released varied from about 0.05 m^3 hydrocarbons/m^3 shale from a Henderson County, Illinois core to about 2.40 m^3 hydrocarbon/m^3 shale from a Wayne County, Illinois core. The released gas contained a higher percentage of ethane and higher hydrocarbons than normally found in pipeline gas.

ANALYSIS OF RELEASED GAS

Samples were collected at each coring site and sealed in airtight, reusable aluminum canisters for released gas analysis. The time that elapsed between coring the samples and sealing them in canisters varied from 4 to 6 hours, depending on the trip-time out of the bore hole and the time required to break down the core barrel, remove the core, and make a brief lithologic description. The time of sealing, the air temperature, and the barometric pressure were recorded; then the sample canisters were transported to the laboratory to be stored at constant temperature (20°C).

The headspace pressure within each canister was monitored weekly until a relatively constant equilibrium pressure was attained. The quantity of gas released by each sample was calculated by Boyles Law using the final, stable headspace pressure. The volume of headspace was determined by weighing the volume of water displaced by the core sample and subtracting it from the known canister volume.

A significant portion of the gaseous hydrocarbons contained within the shale at its normal burial depth was probably lost before the samples were sealed in their canisters (because of the sudden drop in confining pressure as the core was brought up to the surface, and the relatively long period between coring and sealing of the samples). The quantity of gas released from core samples is therefore considered a *minimal* value and the actual in situ gas content is estimated to be two to four times greater.

A small sample of gas was periodically removed by inserting a hypodermic needle through a rubber septum in each canister. Gas compositions for these samples were determined by gas chromatography using a dual phase column (Rendl et al., 1980) for the separations (CTR column, Alltech Associates, Inc.). A Perkin-Elmer Sigma 1 gas chromatograph system was used to analyze the headspace gas. A Perkin-Elmer Sigma 10 data processor was used to integrate peak areas and to calculate both the total headspace gas and the hydrocarbon-only composition of the released gas from a single sample injection.

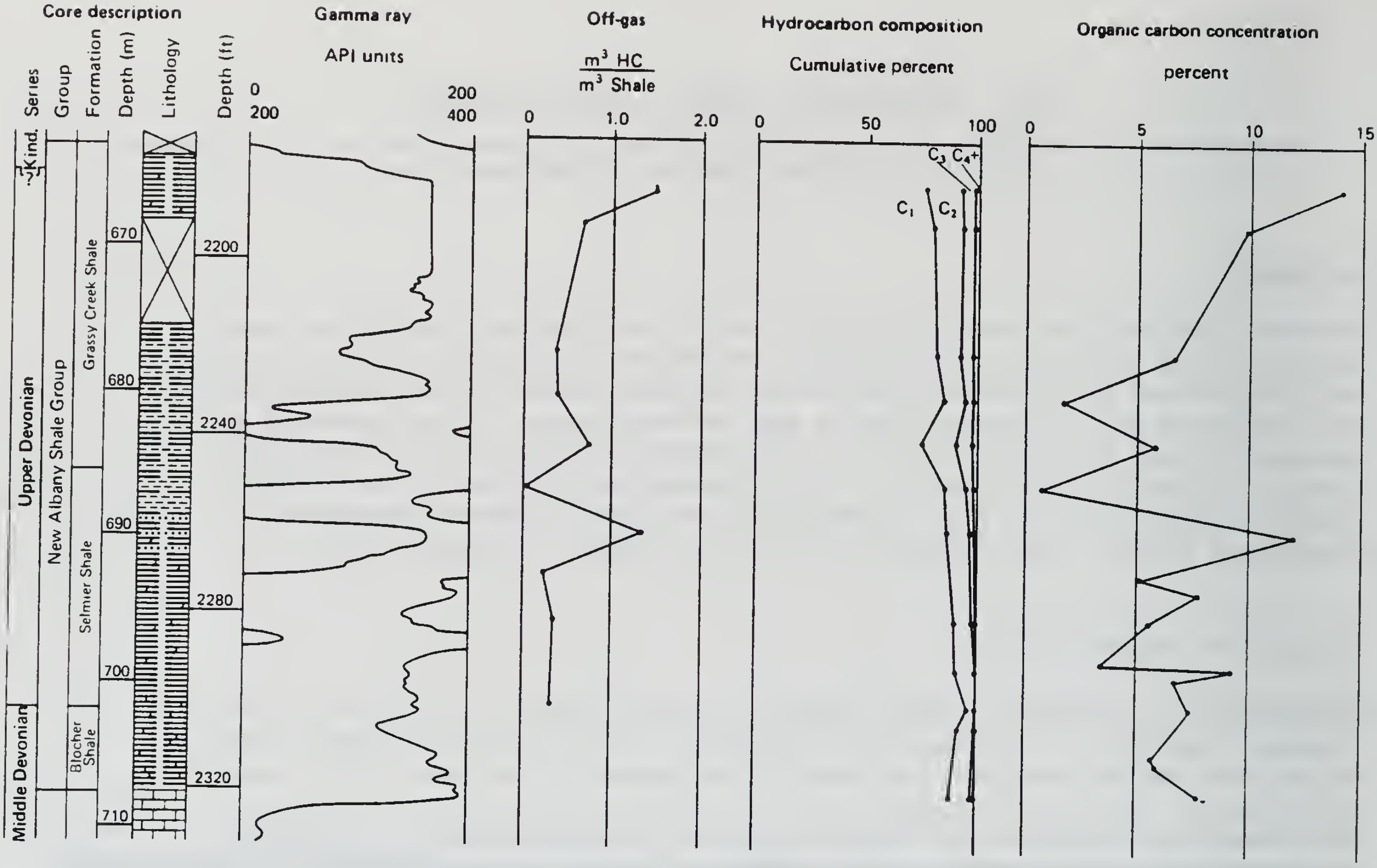


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Figure XII-1. Released-gas analysis and core lithology, Orbit Gas #1 Clark core, Christian County, KY.

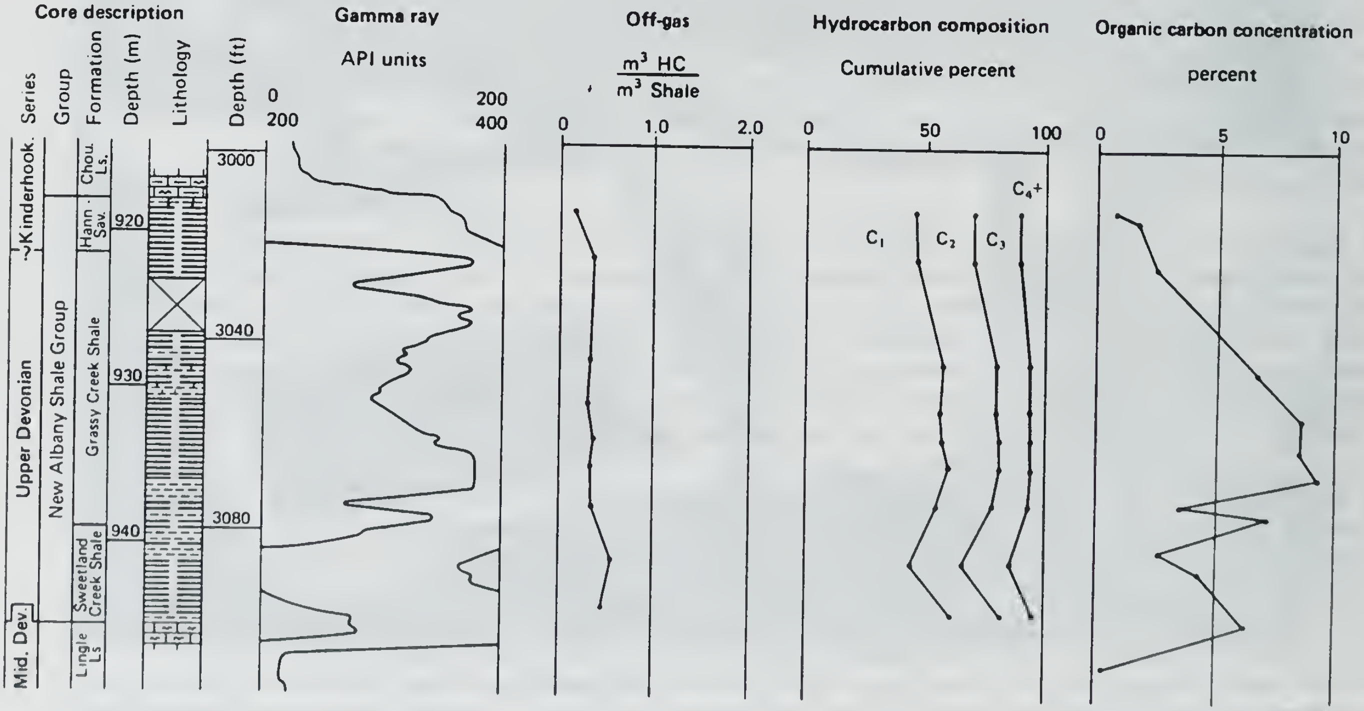

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Figure XII-2. Released-gas analysis and core lithology, Tri-Star Production #1-D Lancaster core, Effingham County, IL.

Orbit Gas #1 Clark Core, Christian County, Kentucky

This was the first core from the Illinois Basin to be analyzed for released gas in the project (Dickerson, 1976). Thirteen shale samples were collected from this core and sealed in fruit juice-size (1500-mL) tin cans for released gas analyses.

The amount of gas released from 10 of the 13 samples ranged from 0.09 m^3 gas/m^3 of shale to .47 m^3 gas/m^3 of shale and averaged 0.6 m^3 gas released/m^3 of shale (fig. XII-1). The average methane content was 92.2 percent identifying this as a relatively dry gas. This well was not completed as a gas producing well.

Tri-Star Production #1D Lancaster Core, Effingham County, Illinois

This core was drilled at the northern edge of the Louden Oil Field in Effingham County, Illinois (Dickerson, 1977). Only nine samples were collected for released gas analysis because the New Albany Shale is thin in this area.

Moderate amounts of gas (generally below 0.5 m^3 gas/m^3 of shale) were released by the core samples (fig. XII-2); however, isotopic analyses suggest the gas is not indigenous to the shale but, rather, migrated upward from the underlying Devonian oil reservoir (Dickerson and Coleman, 1977).

Northern Illinois Gas #1 RAR Core, Henderson County, Illinois and Northern Illinois Gas #1 MAK Core, Tazewell County, Illinois

These two cores of New Albany Shale were acquired in western and central Illinois. For the most part, these cores are representative of a broad area where the New Albany has little or no potential for commercial gas production, rather than an area where gas does occur. Neither of these wells had gas shows, and they released only insignificant quantities of gas in the canisters—less than 0.05 m^3 hydrocarbon/m^3 of shale. Although these quantities were very small, the amount of gas released correlated closely with the gamma-ray intensity (figs. XII-3, XII-4).

Rector and Stone #1 Missouri Portland Cement Core, Hardin County, Illinois

This core was taken in an area known geologically as Hick's Dome (Dickerson, 1979) caused by a cataclysmic upheaval of more than 4,000 feet. Apparently, high temperatures were involved, causing extreme degradation of the organic matter contained within the shale. The top of the New Albany is very near the surface at the point where it was cored, and any gas formed in this shale could easily have been lost to the atmosphere. In fact, this well had no gas shows and released less than 5×10^{-5} m^3 gas/m^3 shale in the canisters. The small amount of gas released did not lend itself to further analyses.

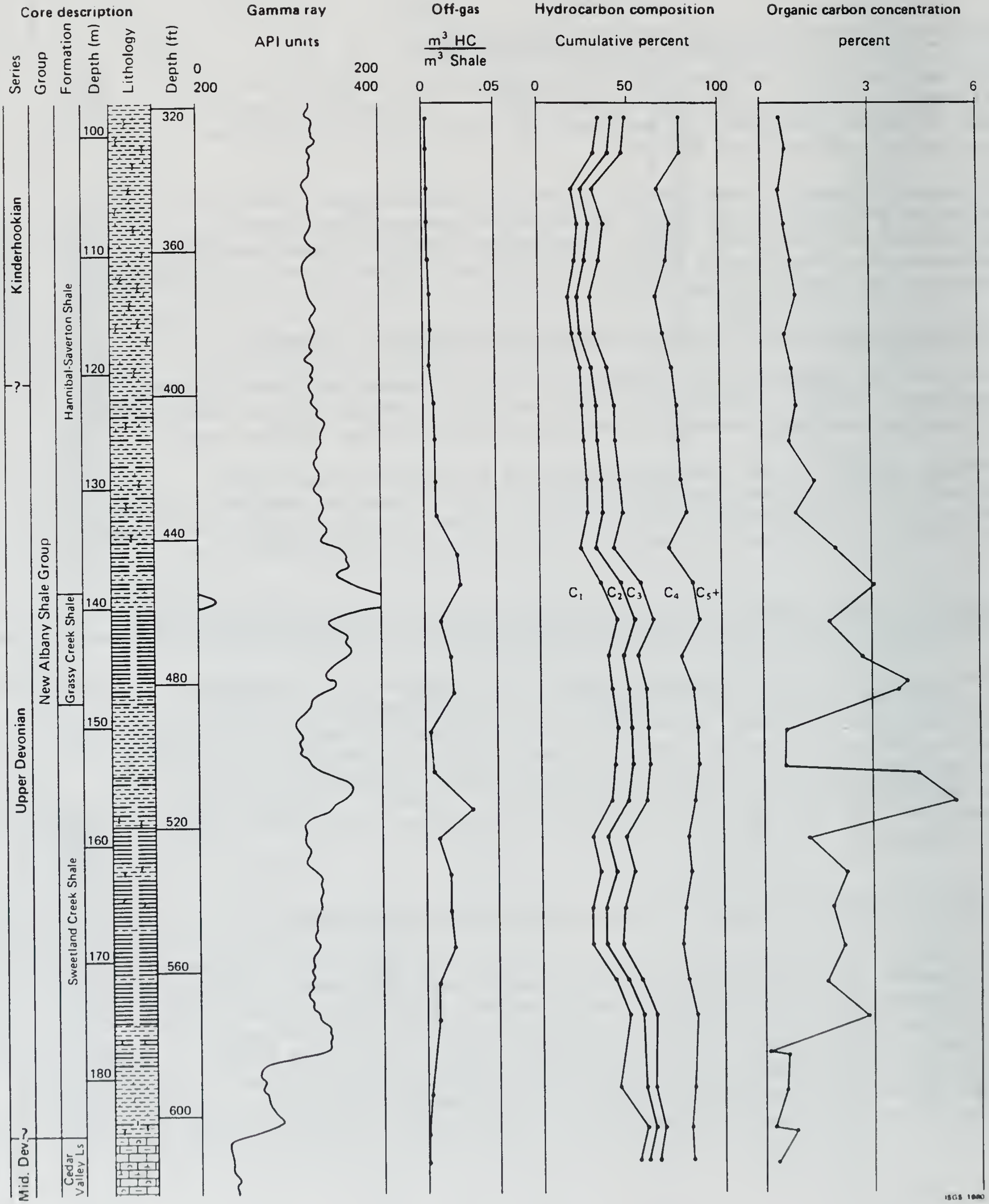

Figure XII-3. Released-gas analysis and core lithology, Northern Illinois Gas #1 RAR core, Henderson County, IL.

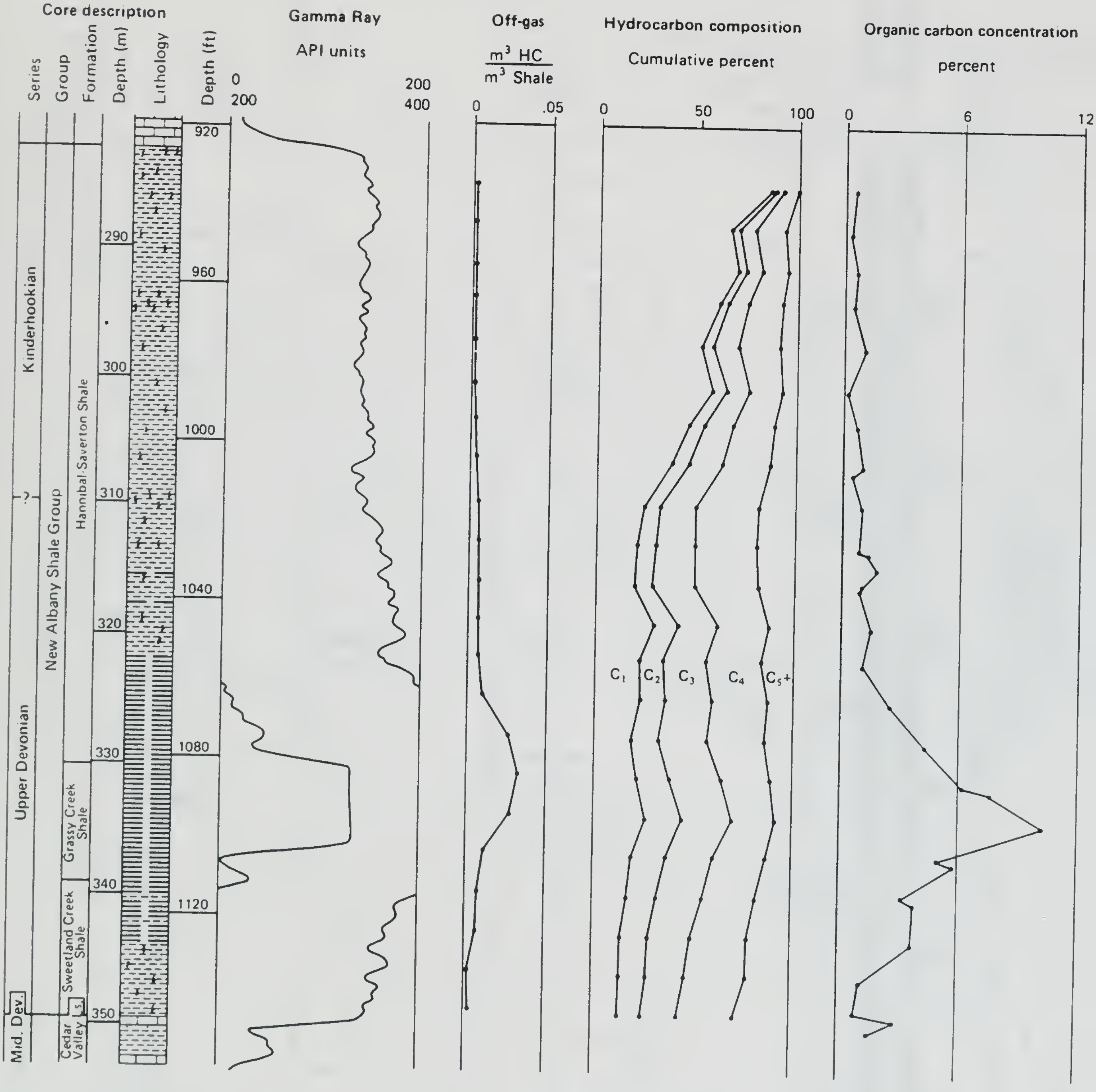

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Figure XII-4. Released-gas analysis and core lithology, Northern Illinois Gas #1 MAK core, Tazewell County, IL.

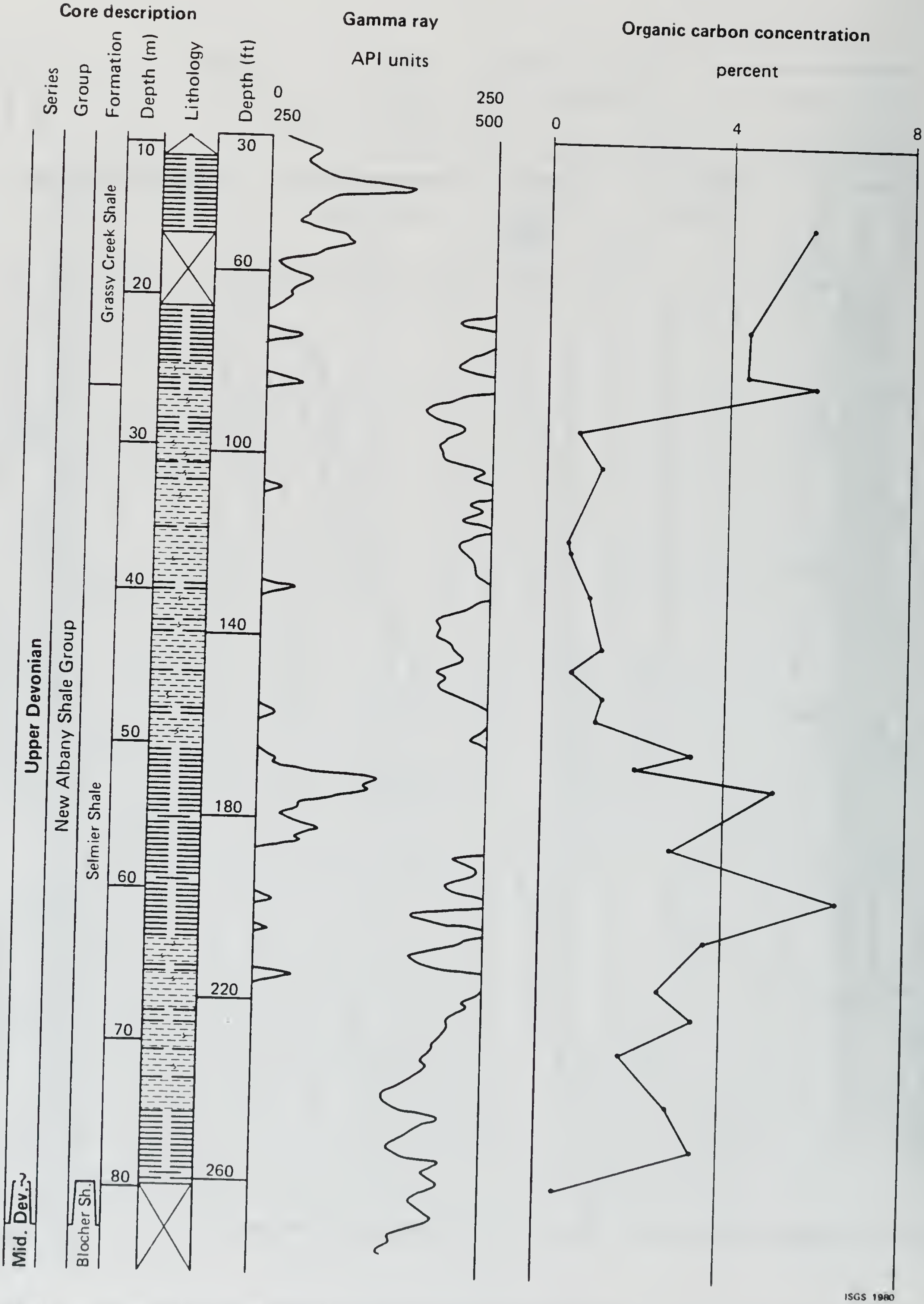

Figure XII-4a. Organic carbon concentration and core lithology, Rector and Stone, #1 Missouri Portland Cement Core, Hardin County, IL.

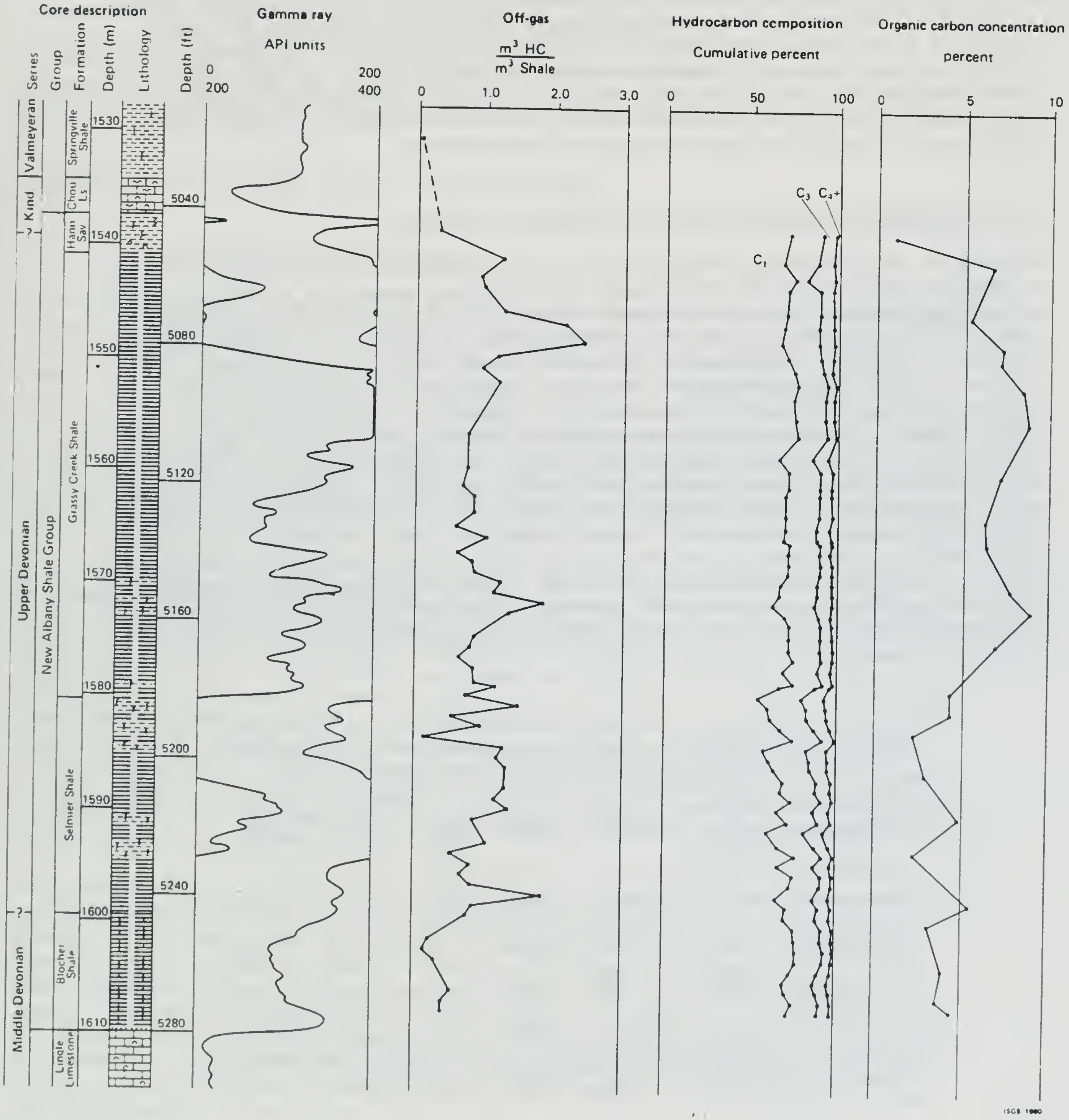

Figure XII-5. Released-gas analysis and core lithology, G. T. Jenkins #1 Simpson core, Wayne County, IL.

Hobson Oil #2 Taylor Core, Wayne County, Illinois

This core provided the first positive evidence that the New Albany Shale contains significant quantities of gas in an area of Illinois (Dickerson, 1979A, 1979B). Five meters of core were recovered from the top of the New Albany Shale Group, all within a dominantly black shale formation known as the Grassy Creek Shale. Unfortunately, the entire length of the core was split by a single near-vertical fracture which resulted in severe jamming of the core barrel and prevented further coring. The gas released from four samples collected from this core ranged from 0.55 to 0.82 m^3 hydrocarbon/m^3 of shale (XII-table 1). The gas was relatively wet, with more than 25 percent ethane and heavier hydrocarbons.

G. T. Jenkins #1 Simpson Core, Wayne County, Illinois

Because of the favorable indications of gas observed in the Hobson Oil well, a complete section of the New Albany (with several meters of overlying and underlying strata) was cored in Wayne County, Illinois. Sixty-six samples taken at approximately 1-meter intervals were collected for off-gas analysis. (Dickerson, 1980). The quantity of gas released after 34 days ranged from 0.16 to 2.40 m^3 hydrocarbons/m^3 of shale. The zones of shale with the highest gas content usually coincided with zones of high gamma-ray county (fig. XII-5). Some of the sample canisters leaked for various reasons; therefore, the gas content of samples within the highest gamma-ray interval of the Grassy Creek Shale (near 5,100 feet; fig. XII-5) could not be accurately determined. Several black shale intervals of the Selmier Shale were relatively gas rich, while the Blocher Shale, a finely laminated, calcareous black shale at the base of the New Albany Group, contained little gas (fig. XII-5). The low gas contents at the base of the New Albany Group suggest that the gas did not migrate into the shale from an underlying, undiscovered hydrocarbon reservoir as was thought to have occurred in the Tri-Star Prod. #1-D Lancaster.

TABLE XII-1. Released gas analysis and hydrocarbon (HC) composition, Hobson Oil #2 Taylor Core, Wayne County, Illinois

Depth to top of sample m (ft)	Off-gas, m^3 HC / m^3 shale	C_1 methane %	C_2 ethane %	C_3 propane %	C_4 butane %	C_5 pentane %
1474 (4834)	0.73	76.81	16.89	4.17	1.28	0.30
1476 (4838)	0.82	72.78	18.30	6.38	1.99	0.55
1477 (4843)	0.66	72.11	18.97	6.39	2.00	0.55
1478 (4846)	0.55	72.57	18.38	6.43	2.04	0.57
Averages	0.69	73.56	18.13	5.97	1.82	0.49

The composition of the released hydrocarbons varied only slightly with stratigraphic position within the shale (fig. XII-5). On the average, the gas comprised 70 percent methane, 19 percent ethane, 8 percent propane, 2 percent butane, and 1 percent heavier hydrocarbons. (This gas is richer in heavy hydrocarbons than typical pipeline gas.) The calculated calorific content of New Albany Shale gas in Wayne County including the four gas analyses from the Hobson Oil core is 46,200 kJ/m^3 (1,240 Btu/ft^3). The actual calorific value of the produced gas would be slightly lower because an unknown percentage of carbon dioxide, nitrogen, and other non-hydrocarbon gases would probably be present. The well was not completed as a gas producer.

CHARACTERIZATION OF THE ORGANIC MATTER IN SHALE

Stepwise pyrolysis-gas chromatography

Stepwise pyrolysis is a valuable technique for the study of complex, naturally occurring organic materials such as those contained in the Eastern Black Shale (Leventhal, 1976). The complex molecules are degraded by heat into smaller species more amenable to analysis by modern instrumental methods. In addition, low-molecular-weight species dissolved in the larger structures are released. Since the type and distribution of pyrolysis products formed is highly dependent on the method used for pyrolysis, identification of the parent species is difficult. However, controlled stepwise pyrolysis-gas chromatography (pyrolysis-GC) analysis provides a simple and direct method for qualitatively characterizing the organic matter contained in shale.

A "Pyroprobe 190" (Chemical Data Systems) and a Perkin-Elmer model 3920B gas chromatograph interfaced with a data processor (Perkin-Elmer Sigma 10) was used in this study (Dickerson, 1978, 1978A). Ten shale samples (01KY07C1, 01KY12C1, 01KY01L1 and 01KY05L1, 04IL04C1, 04IL08C1, 04IL14C1, 06IL19C1, 06IL20C1, 13IL17C3, and S00095) were analyzed for high-volatile, medium-volatile and low-volatile hydrocarbons by pyrolysis-GC. A 3 mm x 3 m stainless steel column packed with 3 percent Dexsil 300 on Chromosorb W, AW was used for the GC separation. The separated hydrocarbons were divided into groups according to their n-alkane chain length (i.e., group A, C_1-C_8; group B, C_9-C_{12}; group C, C_{13}-C_{16}; group D, C_{17}-C_{20}; group E, C_{21}-C_{24}; and group F, C_{25} and greater. The temperatures selected for step-wise heating were 250°C, 350°C, 550°C, and 750°C.

Heating the shale at 250°C and at 350°C yielded the highly volatile group A and medium volatile group B in preference to the less volatile hydrocarbon groups. The hydrocarbon preference at 250°C and 350°C was also dependent upon the organic carbon content of the shale (figs. XII-6 and XII-7). For shales with an organic carbon content greater than 10 percent (01KY07C1) group A was evolved preferentially over groups B through F. For shales with an organic carbon content less than 10 percent (13IL17C3) group B was evolved preferentially over the other groups. Essentially no organic material was evolved during pyrolysis from shales with an organic carbon content of less than 1 percent.

A sample of a shale which had been pre-extracted with benzene-methanol was heated at 250°C. The resulting chromatogram showed no peaks for evolved hydrocarbons, indicating that heating shale at 250°C generally brings about physical desorption of indigenous or weakly bonded highly volatile organic molecules which are also benzene-methanol extractable.

Heating the above shales at 550°C and at 750°C showed group A to be evolved in preference to the less volatile groups (figs. XII-8, XII-9). This result is attributed to the thermal degradation of the low volatile hydrocarbons and to the high temperature release of gas held within the shale matrix.

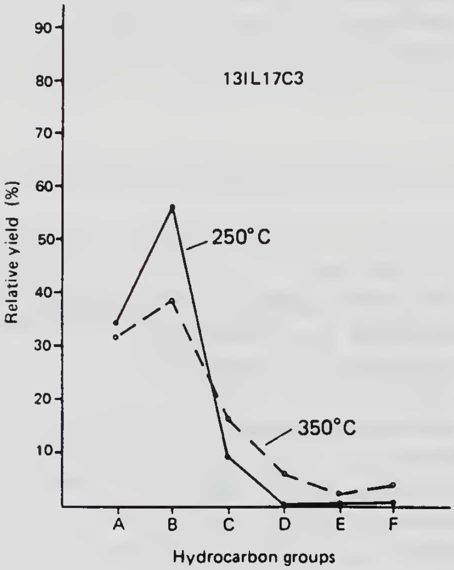

Figure XII-6. Relative yield of volatile hydrocarbons from a shale with less than 10% organic carbon content when heated at 250° C and at 350° C.

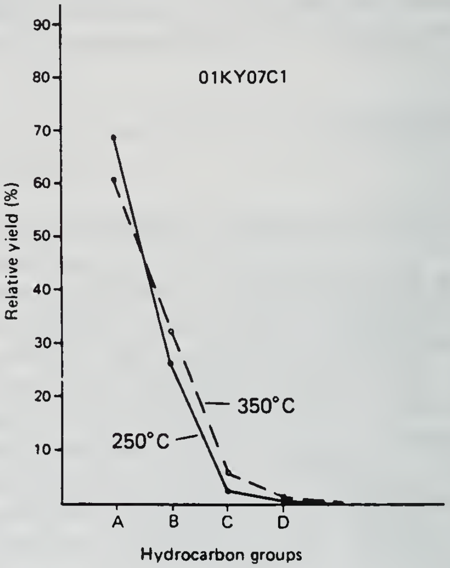

Figure XII-7. Relative yield of volatile hydrocarbons from a shale with greater than 10% organic carbon content when heated at 250° C and at 350° C.

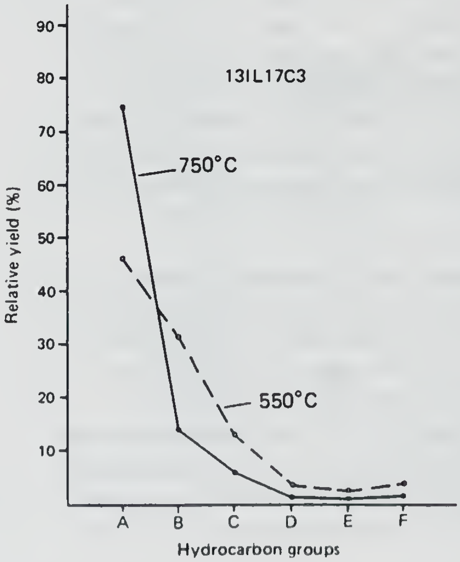

Figure XII-8. Relative yield of volatile hydrocarbons from a shale with less than 10% organic carbon content when heated at 550° C and at 750° C.

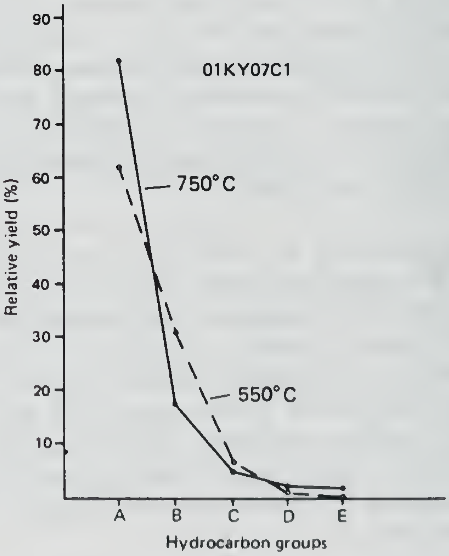

Figure XII-9. Relative yield of volatile hydrocarbons from a shale with greater than 10% organic carbon content when heated at 550° C and at 750° C.

The asphaltene fraction of the organic material extracted from shale (p. 00, this section) with benzene-methanol was analyzed by continuous-stepwise pyrolysis-GC (Dickerson, 1978). In this case the different heating steps followed successively from low temperature to high temperature on the same sample of asphaltene. The evolved hydrocarbon patterns resulting from continuous-stepwise heating varied for asphaltenes from shales from different sources. Typical GC chromatograms at each of six temperatures of an asphaltene are shown in figure XII-10. Medium volatile compounds and possibly weakly bonded components are evolved at the lower temperature steps. The higher temperature steps degraded the non-volatile organic matter into simple molecules such as methane and more complex molecules such as condensed aromatic ring compounds. It is clear from the chromatograms (fig. XII-10) that the temperature required to initiate fragmentation of the non-volatile organic matter was near 550°C.

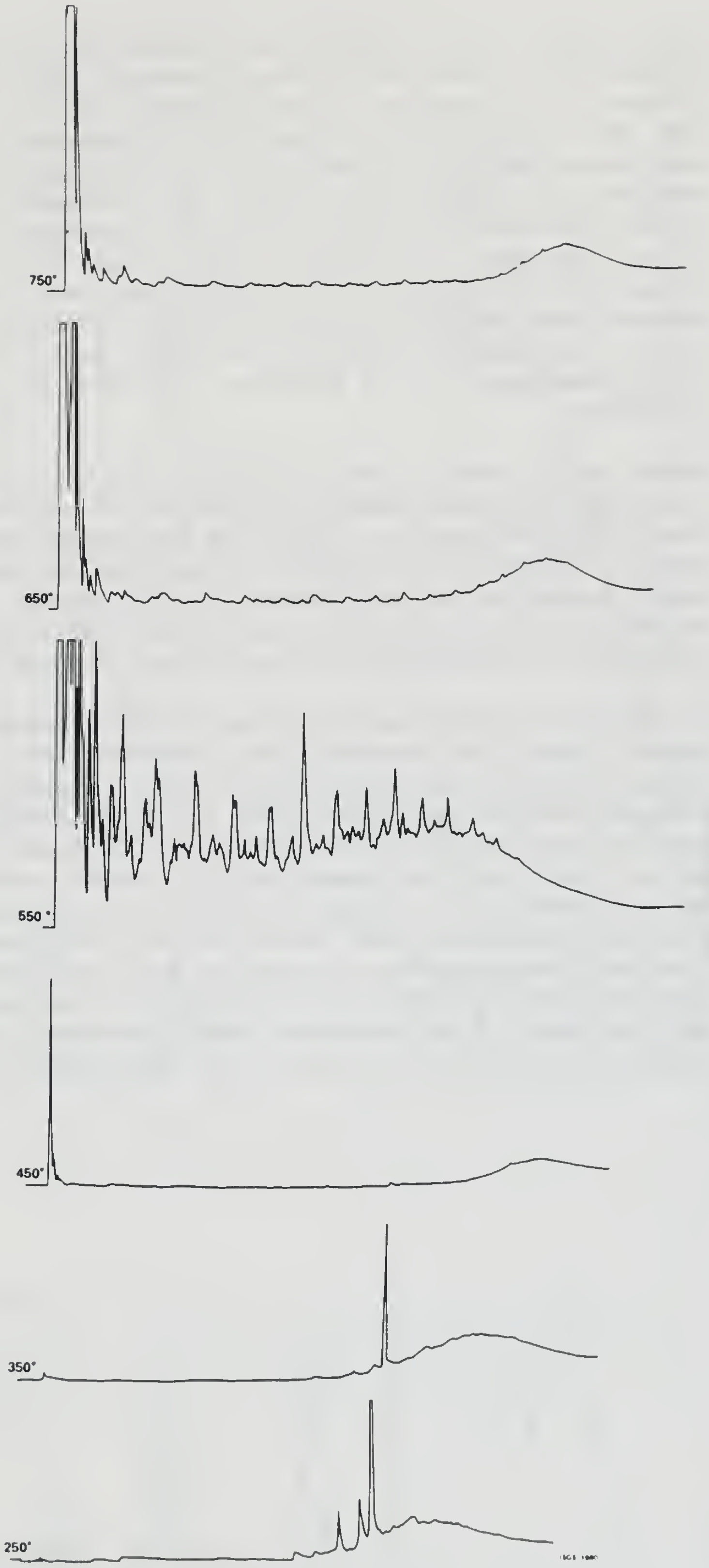

Figure XII-10. Continuous stepwise pyrolysis gas chromatogram of 021L04C1 asphaltene.

Non-condensable hydrocarbons produced by pyrolysis of black shale

The non-condensable hydrocarbons produced by the pyrolysis of shales at two temperatures (450°C and 600°C) were measured quantitatively (Dickerson, 1979). It was found that the quantity of gas produced increased with increased organic carbon content and the increase was even more pronounced with increased temperature (Chou and Dickerson, 1979).

A 250-mg sample of pulverized shale (-100 mesh) was weighed into a pyrex tube (17.5 cm x 1.75 cm ID). The tube was sealed with a rubber serum cap secured with a wire band. The tube was evacuated and then placed in a preheated (450°C or 600°C) electric tube furnace for 5 minutes. A known amount of pure cyclopropane was injected into each sample tube and used as an internal standard. The gases that were noncondensable at 29 ± 1°C were sampled from the headspace and analyzed on a Perkin-Elmer 3920B gas chromatograph equipped with a Flame Ionization Detector (FID) and interfaced with a Perkin-Elmer Sigma 10 data system. A stainless steel column (6 ft x .125 in. [2m x 3mm OD]) 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.

Thirty shale samples were studied. Eight of the samples were from the core from Christian County, Kentucky; six of the 22 Illinois samples were from Effingham County; eight from Henderson County; and eight from Tazewell County. Figure XII-11 shows the gas chromatogram of a representative gas sample separated on the Chromosorb 102 column. The non-condensable hydrocarbons (C_1-C_5) obtained by the thermal treatment of New Albany black shale contain both saturated and unsaturated n-paraffins.

The gas yield from shales heated at 450°C increased with increased organic carbon content for samples from the same core. Although the gas yield always increased as the organic carbon content increased, the amount of increase varied for shales from different geographic locations (fig. XII-12). When the same samples were heated at 600°C an even more pronounced increase in gas yield with increased organic carbon content was obtained (fig. XII-13). For the four cores studied the slopes of the curves for the Kentucky core were the highest at both temperatures. The location from which the Kentucky core was taken appears to have the most potential for gas production of the four locations studied. A difference in the nature of the organic matter or the existence of an anomalous mineral-surface catalytic reaction may partially explain the variation in gas yield among the samples.

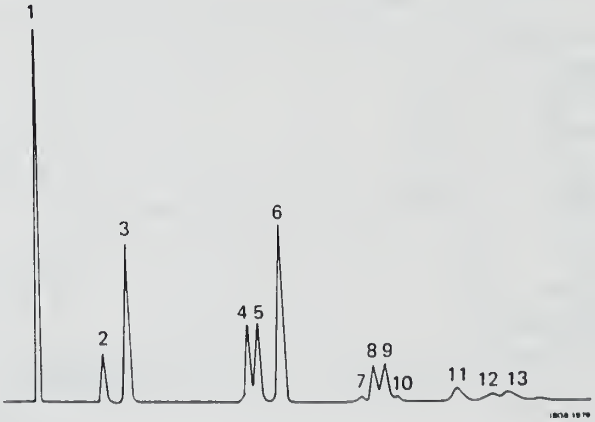

Figure XII-11. Gas chromatogram trace of light hydrocarbon gases from shale pyrolysis. Column: stainless steel 2m x 3mm I. D. Chromasorb 102. Temperature programmed from 40°C to 180°C (held at 180°C for 8 minutes). Hydrocarbon gases: (1) methane; (2) ethylene; (3) ethane; (4) propylene; (5) propane; (6) cyclopropane (std.); (7) iso-butane; (8) 1-butene; (9) butane; (10) 2-butenes; (11) acetone; (12) 1-pentene; and (13) pentane.

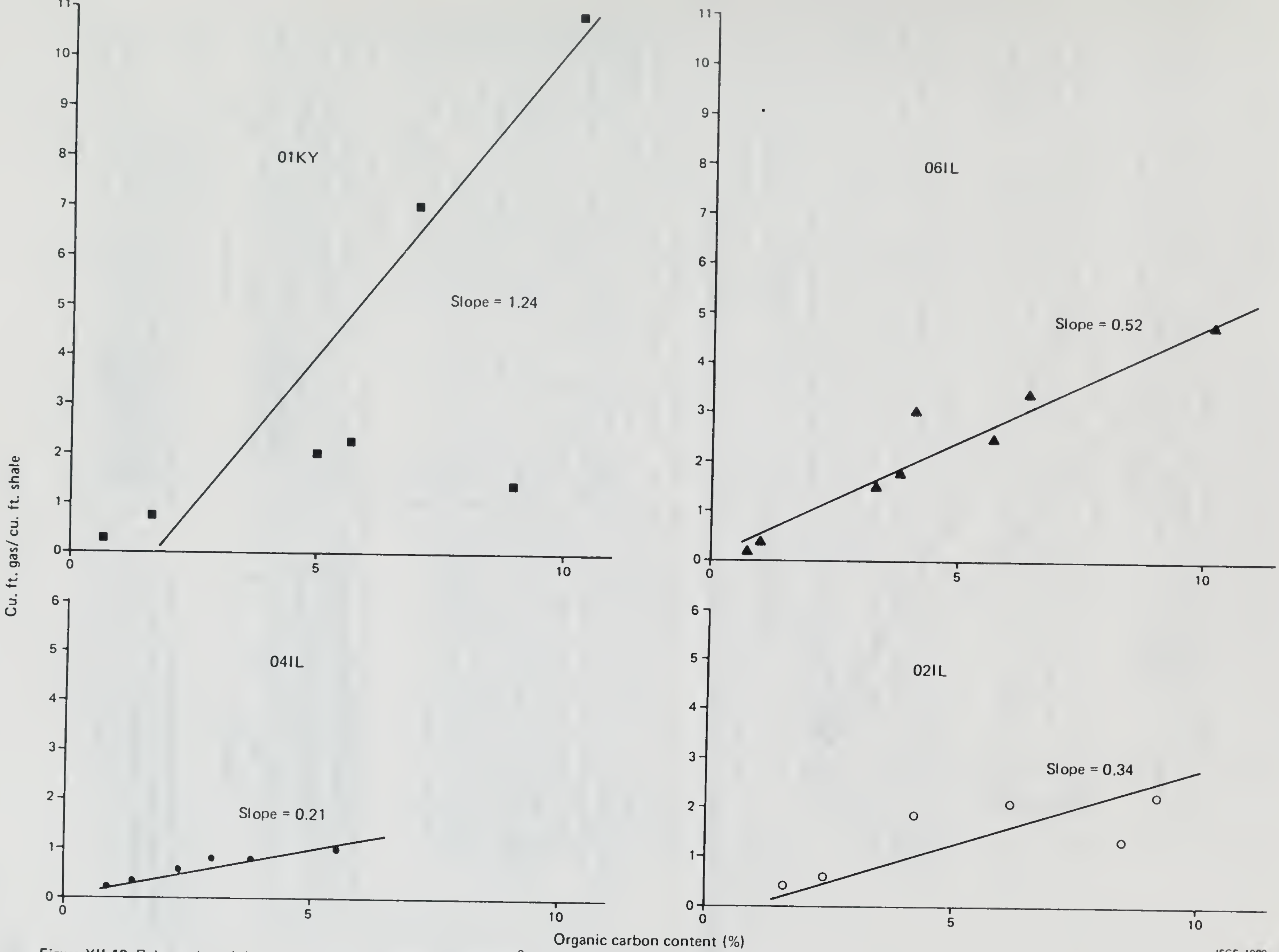

Figure XII-12. Relationship of the gas yield from pyrolysis of shale at 450°C to the organic carbon content of the shale.

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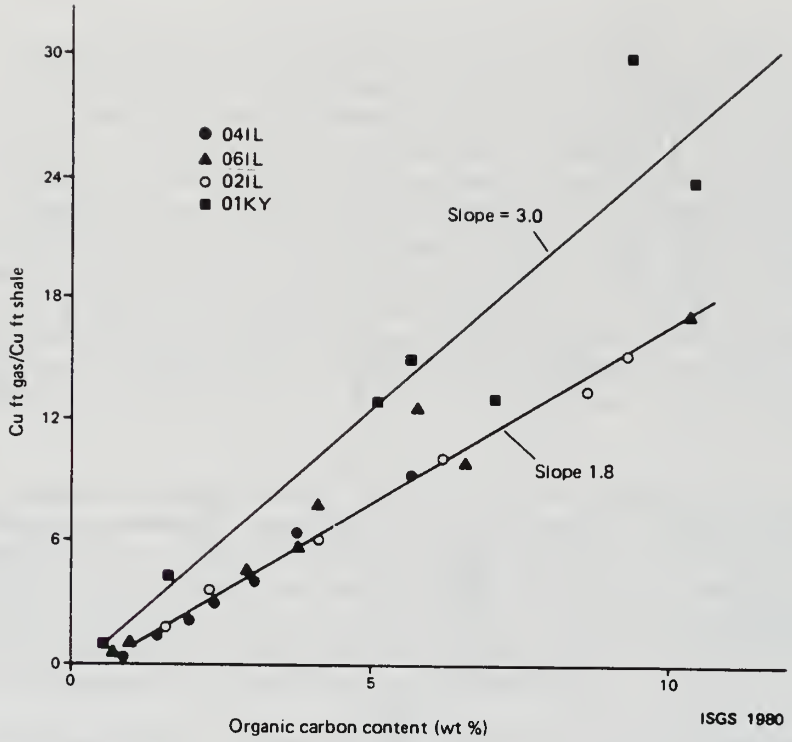


Figure XII-13. Relationship of the gas yield from pyrolysis of shale at 600°C to the organic carbon content of the shale.

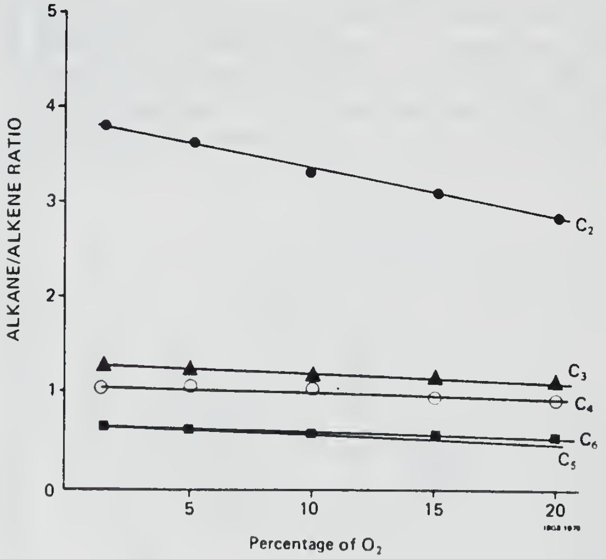


Figure XII-14. Alkane/alkene ratio of hydrocarbons produced by the pyrolysis of shale as a function of the percentage of oxygen in the pyrolysis atmosphere.

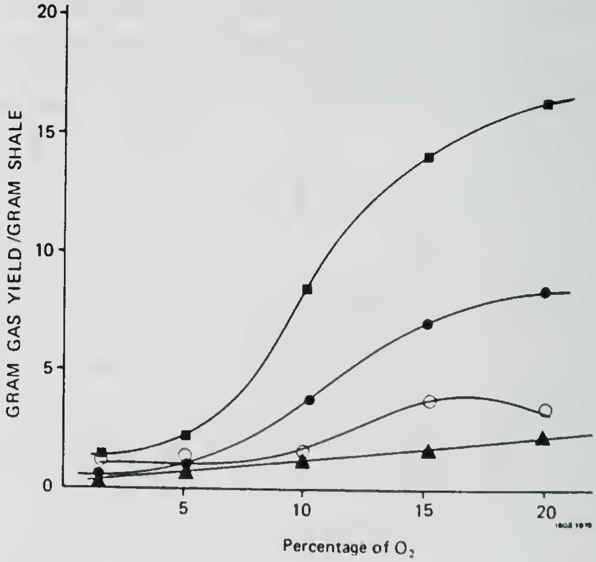


Figure XII-15. Yield (x 10^{-4}) of CO_2, CO, CH_3CHO, and yield (x 10^{-5}) of CH_3COCH_3 produced by the pyrolysis of shale as a function of the percentage of oxygen in the pyrolysis atmosphere.

The effect of molecular oxygen on shale pyrolysis products

A pyrolysis experiment was designed in which the molecular oxygen was the only variable and time, temperature and sample were held constant. The production of non-condensable alkanes, alkenes and oxygenated organic and inorganic gases was monitored quantitatively.

One-gram amounts of the pulverized shale were weighed into pyrex tubes and sealed as described previously. 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.

A shale sample taken from the core from the drill hole in Effingham County, Illinois at 3,053 feet below the surface was used in this study. 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 Carbopack C/0.2 percent CW 1,500 column. A 5Å molecular sieve column was also used for separation of the hydrocarbons and the products of oxidation. Conditions for the molecular sieve chromatography were: injection port at 200°C; column oven with initial hold of 3 minutes at 40°C, then programmed from 40° 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.

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 (fig. XII-14). The quantity of any individual hydrocarbon produced generally increased as the oxygen content increased in the 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 (fig. XII-15). The amount of acetaldehyde formed reached a maximum at an oxygen content of 16 percent. Acetone was found in an order of magnitude less than acetaldehyde, but showed a constant, though small, increase with increased oxygen content (fig. XII-15).

There are indications that the presence of some molecular oxygen in the retort atmosphere could lower the pyrolysis temperature needed to produce a gas of desired composition. Only limited studies were made of the effects of molecular oxygen on the pyrolysis of shale. However, it appears that a knowledge of these effects would be quite helpful in designing a model for in situ retorting of shale for gas production.

Solvent extraction of shale

Solvent extraction of shale was performed in addition to pyrolysis. Because pyrolysis of shale produces a complex mixture containing many organic compounds, it is virtually impossible to identify individual components. In

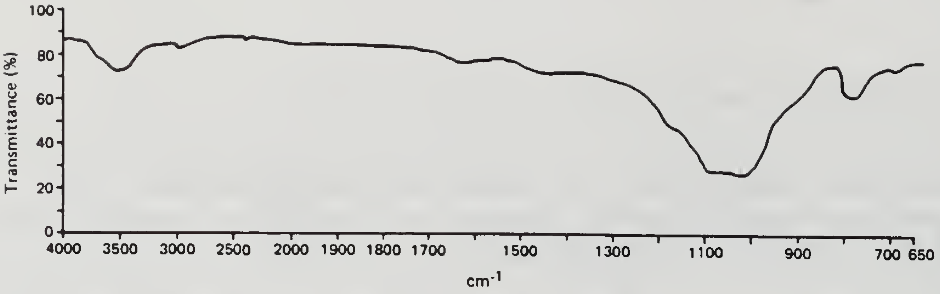


Figure XII-16. Infrared (IR) spectrum of solid shale (-100 mesh) in KBr pellet.

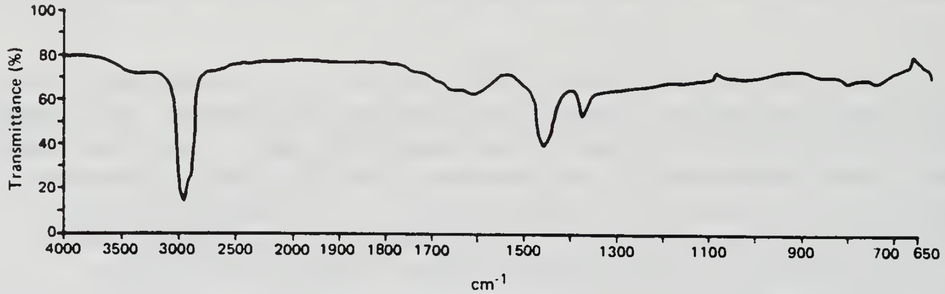


Figure XII-17. IR spectrum of benzene extract from shale (film).

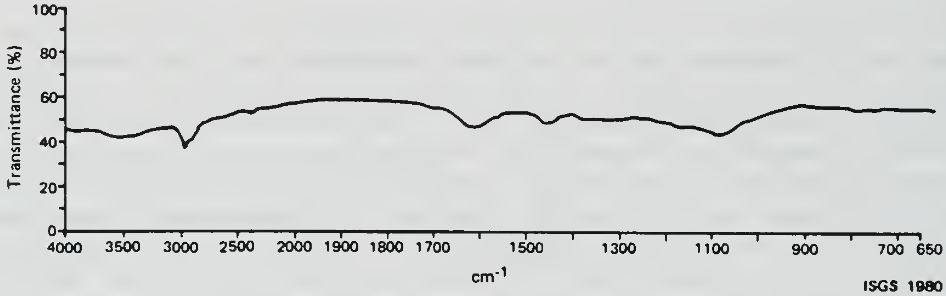


Figure XII-18. IR spectrum of kerogen from shale (KBr pellet).

contrast, solvent extraction yields a smaller and more select number of compounds. Although this does not give a complete picture of the organic matter present, it makes identification of individual compounds less complicated and thus more useful specific information can be obtained.

Samples of shale were extracted in a large soxhlet apparatus using either benzene:methanol (70:30/V:V) or benzene alone as solvent. The extracts were then separated into three fractions: aliphatic, aromatic, and asphaltene. Further separations were made using molecular sieves and high-pressure liquid chromatography. Fractions from the latter separations were analyzed by gas chromatography, mass spectroscopy, and infrared. Elemental analyses (Dickerson, 1980) were run on fractions where feasible.

Shale samples ground to minus 100 mesh were used for soxhlet extraction. The solvent used for extraction was either pure benzene or a mixture of benzene:methanol (v:v/70:30). The amount of bitumen extracted was less than 1 percent of the total shale. The bitumen was separated by silica-gel and alumina column chromatography into three fractions: n-hexane, benzene, and benzene-methanol were used to elute aliphatic, aromatic and asphaltene fractions.

Infrared (IR) spectra taken during and after the application of various chemical treatments were used to ascertain what components in the sample may have been altered by the process and to what extent this alteration may have occurred. Figure XII-16 is a typical IR spectrum of a total shale ground to -100 mesh and dried at 105°C before chemical treatment. The organic matter contribution to the total shale spectrum is relatively small because of the overwhelming contribution of the inorganic matter. The strong bands at 1,015 cm^{-1} and the weak bands at 790 cm^{-1} and 775 cm^{-1} indicate the presence of silicates. The major clay component is illite, as determined by the -OH stretching vibration at 3,597 cm^{-1} and the overall spectrum shape. Figure XII-17 shows the spectrum of a benzene extract, with predominant bands as follows:

(a) 3,010 cm^{-1} aromatic C-H stretching
(b) 2,900 cm^{-1} and 2,975 cm^{-1} aliphatic C-H stretching
(c) 1,625 cm^{-1} olefinic C-H stretching
(d) 1,460 cm^{-1} $-CH_2$ - and $-CH_3$ bending
(e) 1,375 cm^{-1} methyl group bending
(f) 720 cm^{-1} and 900 cm^{-1} aromatic out-of-plane bending

Figure XII-18 is the IR spectrum of the kerogen isolated from shale by acid treatment. The silicate bands were drastically reduced.

In table XII-2 the amount of bitumen extracted is expressed as a percentage of the organic carbon content of shale. The benzene-methanol solvent system (extractability ∿6%) appears to be more efficient than the benzene-only solvent system (extractability 4%) for extracting organic matter from shale. The asphaltene fraction obtained from the benzene-methanol extraction of shale contains more nitrogen and sulfur compounds than does the asphaltene fraction obtained from benzene extraction of the same shale.

TABLE XII-2. Content of the bitumens from benzene and benzene-methanol extraction of Sample 01KY03C2.

	Extract (benzene)	Extract (benzene-methanol)
Extractability	3.9%	6.0%
Aliphatic	41.9%	29.0%
Aromatic	29.0%	27.6%
Asphaltene	21.7%	44.1%
Nitrogen/Carbon ratio	0.0071	0.0167
Sulfur/Carbon ratio	0.0044	0.0065

The aliphatic fraction was further separated into n-paraffins and into branched and cyclic aliphatics by 5Å molecular sieve (O'Connor et al., 1962) Figure XII-19 shows typical GC chromatograms of the two fractions. The GC system used a SP2100 15 m x 0.5 mm WCOT capillary column and a FID detector with an oven temperature program from 50°C to 220°C at 5°C/min and held at 220°C for 16 minutes. In the n-paraffin fraction the predominance of n-alkanes with an odd number of carbon atoms is expressed as a carbon preference index (CPI) (Bray and Evans, 1961); (Dickerson 1979A). The CPI has probably received the greatest attention among methods using chemical composition of bitumen for the study of shale maturity. The distribution of n-paraffins from our shale samples, expressed as the CPI value, is shown in fig. XII-20. The values for 19 samples cluster near 1.0 with a range between 0.91 and 1.25. The distribution of n-paraffins from a Devonian-Silurian crude oil was also measured and found to have a CPI value of 1.01. This study indicates that the New Albany Shale is a source rock of crude oil in the Illinois Basin.

The aromatic fraction (fig. XII-21) from column liquid chromatography of a shale extract was further separated by high pressure liquid chromatography with a reverse phase octadecylsilane (ODS) column, UV detection at 254 nm and a CH_3CN/H_2O solvent system. Ten shale samples which were separated on HPLC showed major differences in the 0 fraction region, but all showed a similar pattern for fractions 1, 2, 3, 4, and 5 (fig. XII-22). The GC/MS analysis (Dickerson, 1980) indicated that the aromatic fraction contains mainly 2-ring and 3-ring aromatics substituted with combinations of 1, 2, 3, or 4, methyl, ethyl or propyl side chains.

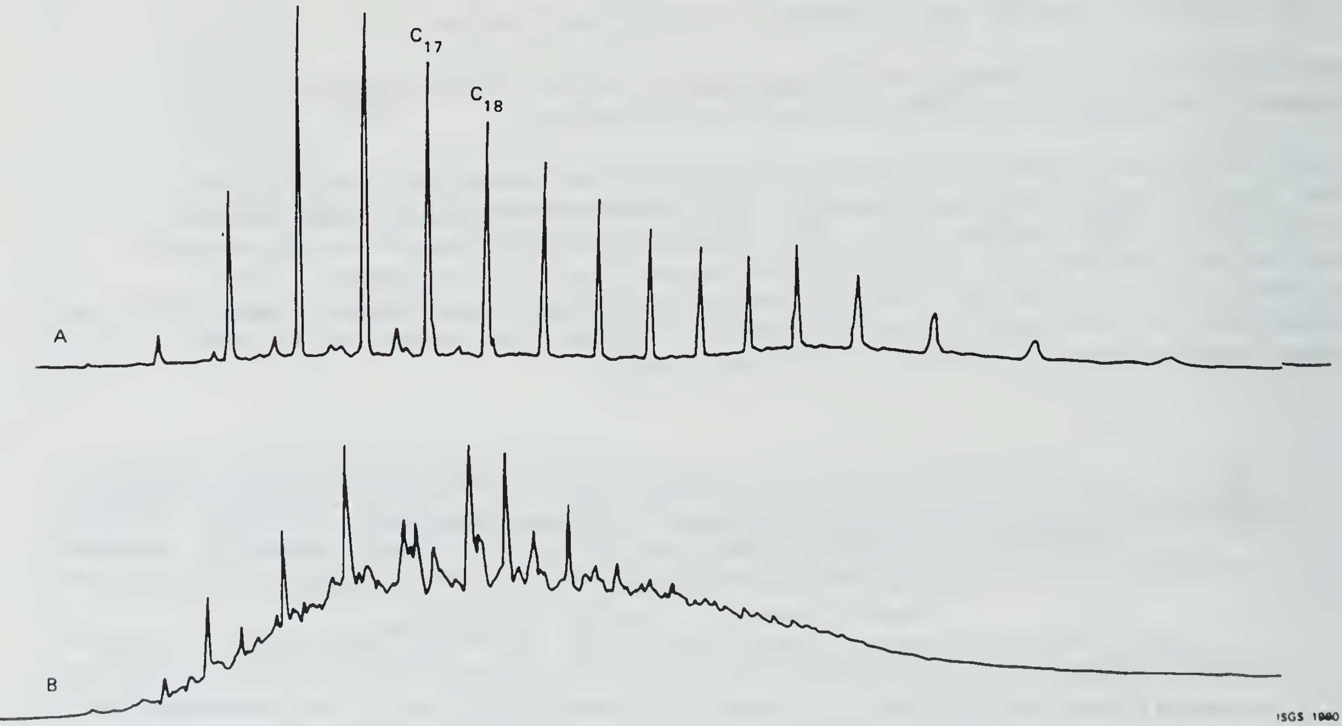


Figure XII-19. Typical gas chromatogram of (a) n-paraffins and (b) branched and cyclic aliphatics from shale extract.

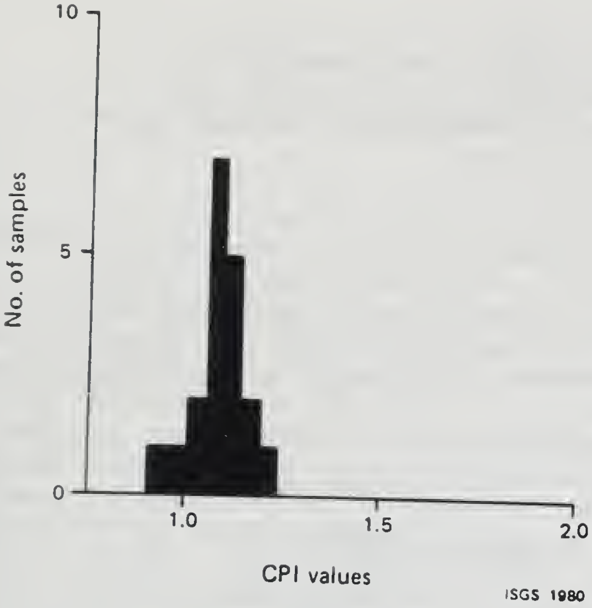


Figure XII-20. N-paraffin distribution in Devonian shale extracts as expressed by Carbon Preference Index (CPI) values.

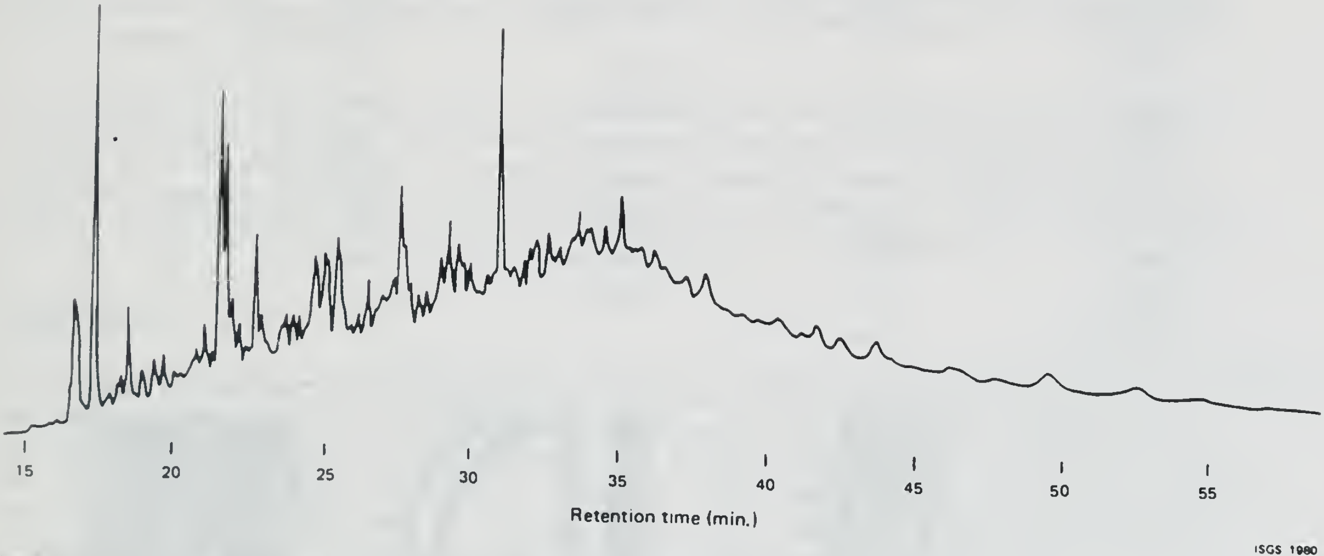


Figure XII-21. A typical chromatogram of an aromatic fraction from shale extraction.

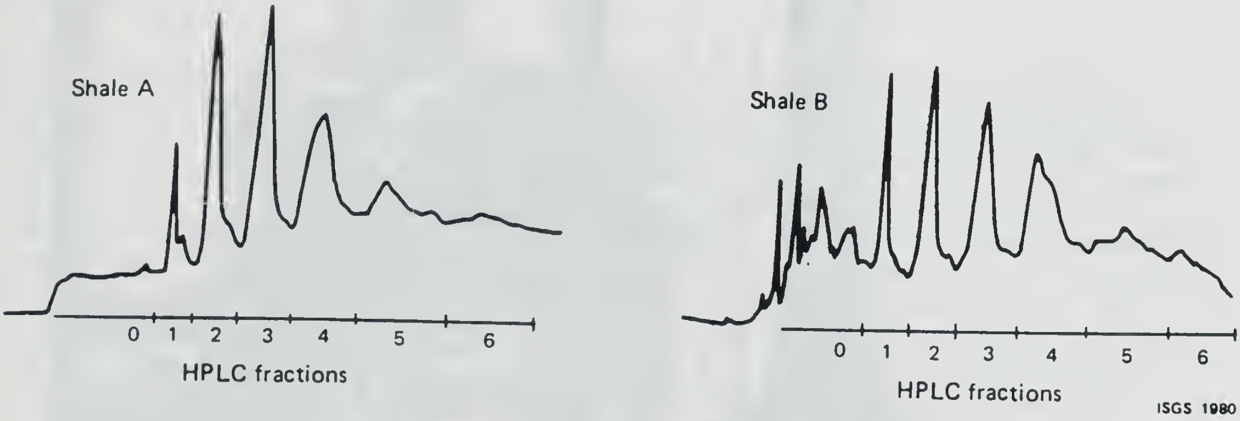


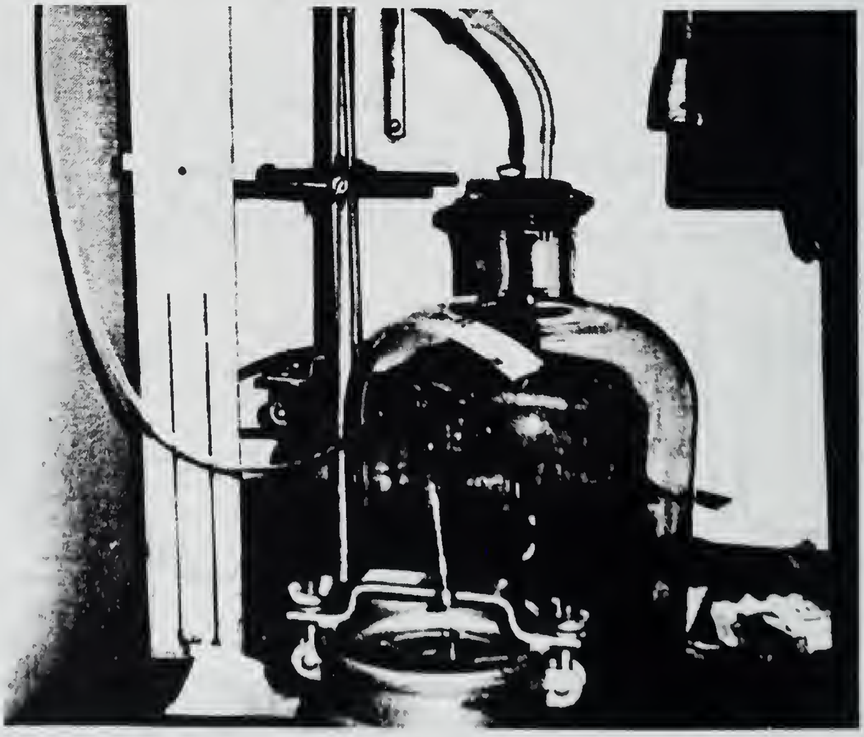
Figure XII-22. Typical high pressure liquid chromatography separations of aromatic fraction from shale extract. Reverse phase ODS column, uv detection at 254 nm and CH_3CN/H_2O solvent system.

The asphaltene fractions obtained from column liquid chromatography had an average molecular weight ranging from 400 to 1,400 as determined with a vapor pressure osmometer (table XII-3). The analysis of the asphaltene fractions by continuous-stepwise pyrolysis-gas chromatography has been discussed previously.

The fragmentation temperature and the molecular distribution from both heating of the shale and solvent extraction of the shale can provide information about the structure of the organic matter which can be related to the source, depositional environment, and degree of diagenesis of the shale. Data obtained in this study can also be used to develop the most efficient methods for the production of hydrocarbons from the black shale by retorting.

TABLE XII-3. Average molecular weights of the asphaltene fraction from shale extracts

Benzene-methanol extracted		Benzene extracted	
Sample number	Average molecular weight	Sample number	Average molecular weight
S00087-89	436	01KY03C2	624
S00007	486	S00010-5	602
S00109	779	06IL20C2-2	760
S00094	658	13IL06C2	1412
02IL04C1	784	06IL20C2-1	743
S00060	906	01IN04C1-4	502
06IL19C1	429	13IL09C2	1156
01KY03C2	546		



Mercury manometer used to measure released gas pressure build-up on canned samples of shale.

XIII. CARBON ISOTOPE ANALYSIS OF OFF-GASES

Dennis D. Coleman

ABSTRACT

Interpretations based on the analyses of off-gases from shale cores require the assumption that the off-gas that collects in the canister has the same composition as the gas originally present in the shale. To test the validity of this assumption, a laboratory study was conducted to evaluate the extent of isotope fractionation which occurs during the outgassing of shale. Shale samples were degassed, pressurized with natural gas of known composition and allowed to equilibrate. The samples were degassed under controlled conditions and variations in the composition of the released gas were monitored. Study results suggest that although isotopic fractionation does occur, the effects will probably not be significant if the core samples are sealed in canisters very quickly after they are collected and then outgassed until the outgassing rate becomes negligible.

The carbon isotopic composition of methane from four New Albany Shale cores was determined. Results indicate that the gases are of low-grade thermal origin with no significant contribution of bacterial gas. Comparison of the isotopic composition with other data available on the core samples adds information about the origin and history of the gas in the shale.

INTRODUCTION

The primary goal of this study was to determine the isotopic composition of the methane released from canned core samples and relate that information to the origin and history of the natural gas in the shale. To investigate whether the composition of this off-gas is sufficiently close to the composition of the gas originally present in the shale to allow accurate interpretations to be made, laboratory study was undertaken to evaluate the effects of fractionation on the composition of gas as it migrates out of a shale core.

METHODS

In the first phase of the fractionation experiments, a segment 4 inches in diameter from core 01KY was sealed in a high-pressure vessel and evacuated for 96 days to remove all of the gas originally present. The vessel was then filled to a pressure of 965 psi with natural gas of known chemical and isotopic composition. After 76 days, uptake of gas appeared to have stopped and it was assumed that equilibrium had been achieved. The gas was then gradually released over a period of 2 hours, simulating the gradual decrease in pressure that occurs as a core sample is removed from a well. The pressure was then maintained at atmospheric pressure for another two hours, simulating the time during which a core is described and segmented for canning. Samples of the gas released were collected periodically and analyzed. After the initial 4 hours of gas release, the sample was sealed and the pressure allowed to build up, simulating the canning of a core sample. Gas samples were again collected periodically and analyzed.

Because of the problems encountered in achieving equilibrium within such a large sample of shale within a reasonable length of time, the second phase of the fractionation experiment was done with plugs .75 inches in diameter by 2.9 inches long cut with a diamond core bit from a larger piece of shale. To remove any original gas present, the plugs were baked out in a vacuum oven at 80°C for 72 days, then placed in individual high-pressure vessels and attached to a high-vacuum system for an additional 20 days.

The samples were then pressurized to 600 psig with natural gas of known chemical and isotopic composition. Five pressure vessels were used; one contained a brass blank, similar in size to the shale plugs, to evaluate container effects; four contained shale plugs. One of the four vessels containing shale plugs was found to leak and therefore was discarded.

The gas was allowed to equilibrate with the shale for varying lengths of time, then released from the vessels. The pressure was gradually dropped to atmospheric pressure over a period of about 2 hours; during this time gas samples were periodically collected for analysis. The vessels were then sealed and the "off-gas" allowed to accumulate.

Samples for isotopic analysis were prepared by removing CO_2 and hydrocarbons heavier than methane cryogenically, then oxidizing the methane to CO_2 over hot cupric oxide. This CO_2 was then sealed in ampoules and transported to the mass spectrometer. Two different vacuum systems were used for sample preparation in this study: one a circulating system using a toepler pump, the other a flow-through system using helium to flush the gases through the various traps and furnaces.

Isotopic analyses were performed at the University of Illinois Department of Geology. In the early part of the study analyses were performed on a double-collector Nuclide 6-60 mass spectrometer which was later replaced with a triple-collector Varian MAT 250 mass spectrometer. All isotopic results are given as δC^{13} values where

$$\delta^{13}C_{\text{sample}} = \frac{(C^{13}/C^{12})_{\text{sample}} - (C^{13}/C^{12})_{\text{standard}}}{(C^{13}/C^{12})_{\text{standard}}} \times 1000.$$

All values are relative to the internationally accepted PDB standard.

RESULTS AND DISCUSSION

Fractionation experiments

In the first phase of the fractionation experiments in which a 4-inch-diameter core was used, gas release rates were controlled so as to match the conditions occurring when a core is collected in the field. The canister pressure was first decreased from the initial pressure of 965 psig to atmospheric pressure over a 2-hour period. The first methane released was isotopically heavier (more positive δC^{13} value, enriched in C^{13}) than the methane initially injected by about 0.8 °/₀₀. During the bleed-down the methane became progressively lighter and at the end of the 2-hour bleed-down period attained an isotopic composition similar to that of the starting gas. During the next 2-hour period, the pressure was maintained at atmospheric pressure, simulating the normal time required for a core to be described and cut into segments. The methane released during this time continued to become isotopically lighter. The canister was then closed, and the composition of the off-gas accumulated was monitored for 195 days. The gas continued to become isotopically lighter until about the 5th day when the trend reversed slightly for about 10 days. Then once again the gas continued to become isotopically lighter. The composition of the methane in the off-gas after 195 days of accumulation in the canister was about 4 °/₀₀ lighter than composition of the methane originally injected.

The variation in the methane to ethane composition of the gas showed a similar variable trend, but in the reverse direction (the initial gas was enriched in the lighter component, the final gas enriched in the heavier component).

The variable results obtained in this experiment were interpreted as indicating that the gas injected had not totally equilibrated with the core. The more mobile components would have migrated farther into the core whereas the less mobile components would have been concentrated near the outside of the core. When the core was degassed there would then be two factors controlling the composition of the off-gas: the concentration gradient which had been established, and the different migration rates of the various components. These two factors would have opposite effects on the composition of the off-gas.

In an attempt to overcome the lack of equilibration observed in the first experiment, we used smaller shale samples (.75-inch-diameter plugs) and longer equilibration times during the second phase of this study. Because there were much smaller amounts of gas involved in this study, we could not monitor the composition of the gas as frequently as in the previous case. Results of these experiments are summarized in table XII-1.

If total equilibration had occurred between the gas and the shale, the composition of the gas present in the head space of the vessel would be exactly equal to the composition of the gas injected. The first sample taken during the bleed-down is almost entirely from the head space; therefore the data indicate that vessel #2 had most closely achieved equilibrium, although vessel 4 had a much longer equilibration time. The reason for this is not known.

Although none of the shale plugs appears to have completely achieved equilibrium, the data on the off-gas are consistent, indicating that the first gas released during the outgassing is enriched in the light isotope, C^{12}, and the last gas released is enriched in the heavy isotope, C^{13}.

TABLE XIII-1. Summary of results of isotope fractionation experiment

		Gas released during bleed down $\Delta\delta C^{13}$(°/oo)*		off-gas	
Vessel #	Equilibration time days	initial	final	Accumulation time** days	$\Delta\delta C^{13}$ (°/oo)
1	130	+0.5	+0.4	0 to 14	-2.4
				14 to 154	-2.4
				154 to 388	+1.1
2	287	+0.2	0	0 to 26	-5.0
				26 to 145	-1.1
				145 to 231	+3.7
4	440	+2.6	+.1	0 to 65	-4.3

* $\Delta\delta C^{13}$ is the difference in δC^{13} value between the sample and the gas initially injected.

** The vessel was quickly evacuated after each sample was taken and therefore the data apply to the gas which diffused out of the shale during each time period shown and not to the total gas which would have accumulated in the vessel had no samples been taken.

Although at least one of the vessels appears to have approached isotopic equilibrium, the chemical data indicate that none of the vessels approached chemical equilibrium. The reason for this may be that in the migration of different isotopic species the only significant factor is the small difference in molecular weight, whereas in the migration of different chemical species, variations in molecular size and adsorptivity may also be significant (see Section XIV).

The data obtained from this set of experiments are interpreted as indicating that outgassing of shale cores does result in isotopic fractionation. However, the rate at which shale outgasses is relatively slow; therefore, if the cores are sealed into canisters very soon after the core has been cut and are allowed to outgas for a sufficient length of time (until outgassing has reached a negligible rate) the isotopic composition of the accumulated off-gas is probably sufficiently close to the composition of the gas originally present in the shale to allow valid interpretations. The isotopic composition of that gas lost prior to sealing the core in the canister differs from the composition of the total gas in a direction opposite to that of the gas which remains in the core after the normal outgassing period; these two effects would therefore tend to cancel each other.

Isotopic analysis of off-gases

Only four cores had samples which released sufficient amounts of methane for isotopic analyses. The cores studied and the ranges of isotopic compositions observed are summarized in table XIII-2. The δC^{13} values of three of the samples from core 01KY range from -48.5 to -49.4 °/₀₀ and are similar to those obtained on samples of gas from wells in southern Illinois (Coleman, 1976; Coleman and Meents, 1978). These values are typical of gas of low-to-moderate maturity, formed by thermal degradation of organic matter. One sample, however, is isotopically much heavier (i.e., has a higher C^{13}/C^{12} ratio and a more positive δC^{13} value) than the others, and the δC^{13} value obtained is typical of relatively mature gas such as that produced in the Gulf Coast region and the south-central United States. This value appears to be anomolous when compared to the others from the same core.

The sample with the anomalous δC^{13} value was obtained from near the top of the shale in core 01KY. The chemical data show that there is a consistent decrease in the amount of methane relative to heavier hydrocarbons in going from the bottom of the shale upward to the top. A possible explanation for the variations in chemical and isotopic composition observed in this shale may be that part of the gas originally present in the shale has been lost through upward migration. If gas has been migrating from the shale very slowly over a long period of time, one would expect the gas remaining to be enriched in the heavier components (i.e., $C^{13}H_4$ relative to $C^{12}H_4$; C_2H_6 relative to CH_4; etc.). Also, if the migration were upward, the upper portion of the shale would be more affected than the lower portion.

Isotopic determinations were made on methane from nine samples from core 02IL. There is little variation between the samples, and no trends are apparent. Oil is produced from immediately beneath the New Albany Shale

TABLE XIII-2. Summary of isotopic data on off-gas samples.

Core	Depth range feet	Number of core samples	Number of analyses	δC^{13} CH_4 °/₀₀ range
01KY		4	4	-41.7 to -49.4
02IL		9	9	-52.3 to -56.0
12IL	4834 to 4847	4	14	-49.0 to -52.9
13IL	5046 to 5271	67	132	-49.0 to -53.1*

* One sample, which was from a canister that leaked was outside of this range.

in this area and analysis of solution gases from several of these oil wells shows that these gases have approximately the same chemical and isotopic compositions as the gases from the shale core. The data therefore indicate that the formation of the oil beneath the New Albany Shale and the formation of the gas within the shale are closely related. However, the data do not provide any information as to whether the gas has migrated from the underlying units into the shale or whether the oil has migrated out of the shale.

Gases were analyzed from four samples from core 12IL. Gases were collected four times from each of the canisters during outgassing (from 17 to 67 days after the core was collected). Two of the canisters showed no significant variations with time, one showed a change of +2.1 °/oo, and the other a change of -3.0 °/oo. However, instrumental difficulties encountered during the time these samples were analyzed may be responsible for some of the variations observed. The isotopic values obtained on these samples indicate that the gas is of slightly greater thermal maturity than that from core 02IL.

Gases were analyzed from 65 samples of core 13IL; most were sampled twice. These gas samples were taken 10 and 40 days after the core was collected. In most cases, the two splits from each canister were within analytical error (±.2 °/oo) of each other; however, some splits showed significant differences (up to 4.2 °/oo). More than half of the samples showing significant differences between the two analyses were from canisters which, on the basis of the outgassing data, were suspected of having leaked. Probably the rest of the samples showing significant variations between the two analyses were also from leaking canisters which had not been identified as leaking. The isotopic composition is summarized as a function of depth on figure XIII-1. Data for the canisters suspected of leaking has been omitted. The gas content of the shale is also shown on figure XIII-1 for purposes of comparison; although the two sets of data do not match perfectly, there are similarities. in general, those samples with higher gas contents contained heavier methane, and vice-versa. The uppermost sample is an exception to this trend and may have been affected by loss of gas from the top of the shale (as suggested for core 01KY).

The range of isotopic compositions for core 13IL is almost identical to that for core 12IL, indicating a similar degree of thermal maturity. The apparent similarity between gas content and δC^{13} values could be explained by at least three different theories. Differences in the types of organic materials from which the gas was produced could explain the variations observed (Section VIII). It is also possible that local compositional differences within the shale could have resulted in slight differences in maturity. For example, differences in the concentrations of certain minerals could result in different catalytic properties: those zones which had better catalytic properties would produce more gas, and this gas would tend to be isotopically heavier. Another possibility is that all core samples contained about the same composition and amount of gas originally but that some samples released a greater proportion of their gas. The fractionation studies conducted implied that there is some fractionation which accompanies outgassing and that the residual methane is isotopically heavier

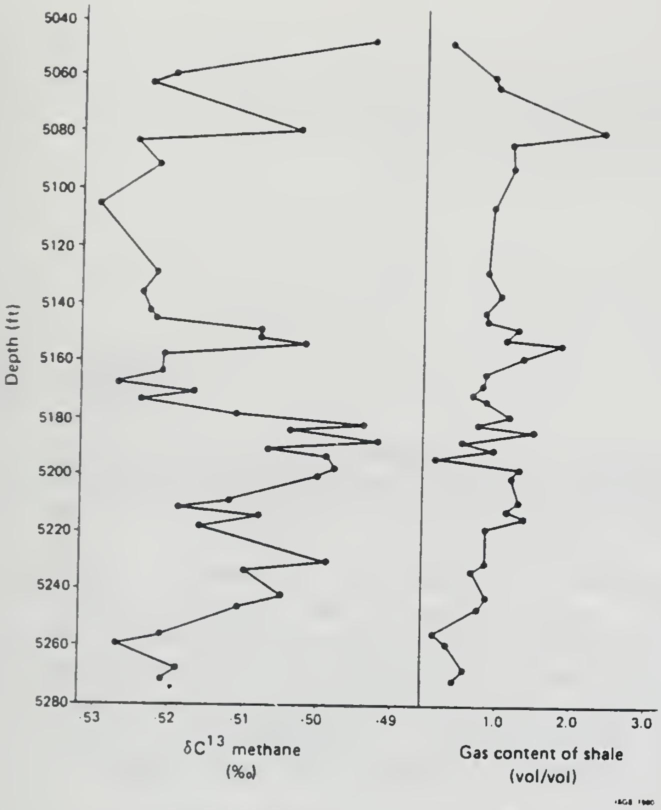


Figure XIII-1. Variations in the isotopic composition of methane and the gas content of core 13IL.

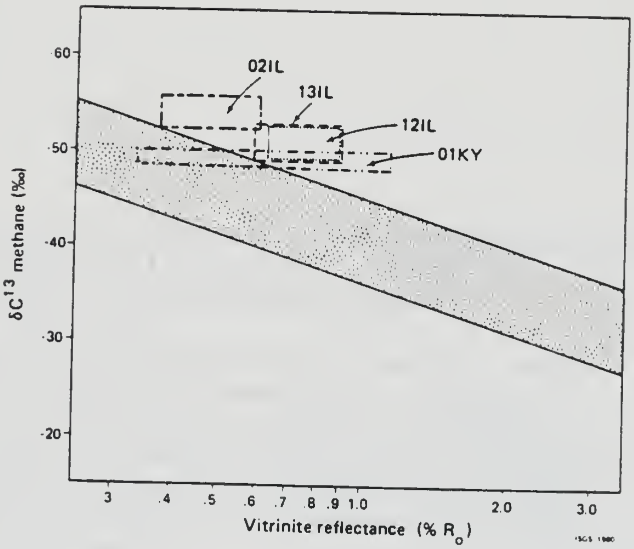
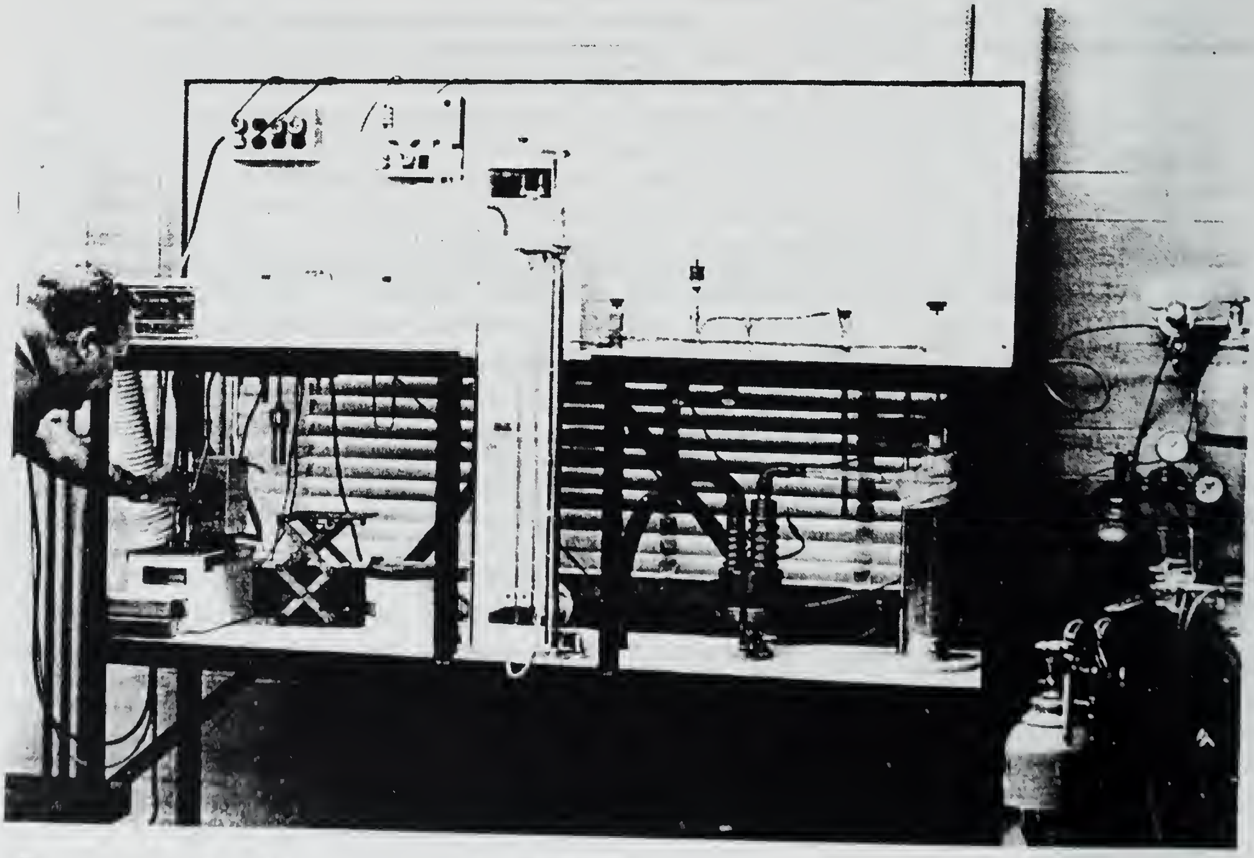


Figure XIII-2. Comparison of the isotopic composition (C^{13}) and vitrinite reflectance (R_o) for the shale cores studied. The stippled area represents the data of Stahl (1977).

than the initial methane. Therefore, those samples which released the greatest proportion of their gas would produce the heaviest methane. The relatively large differences in isotopic composition observed between core samples, in comparison with the small differences between different splits from the same sample, however, imply that this second possibility is the least likely.

Stahl (1977) and Stahl and Carey (1975) have shown that there is a direct relationship between the vitrinite reflectance of organic matter and the isotopic composition of the associated methane. The stippled region on figure XIII-2 shows the range of compositions observed by Stahl (1977) for natural gas formed from sapropelic source material. Increasing maturity would result in a progression from left to right.

The boxes drawn on figure XIII-2 show the ranges of C^{13} values and vitrinite reflectance values (including probable errors) determined for the cores studied. The vitrinite reflectance data is discussed in Section VIII of this report; in general, the trend followed by this data is parallel to that observed by Stahl, but the gas is isotopically lighter than that analyzed by Stahl (possibly because of differences in the compositions of the organic precursors).



Laboratory-constructed apparatus used for high-pressure gas adsorption/sorption isotherms and methane release-rate measurements.

XIV. ADSORPTION/DESORPTION STUDIES OF GASES THROUGH SHALES

Josephus Thomas, Jr. and Robert R. Frost

ABSTRACT

This section is concerned with the nature of the porosity in the low-permeability New Albany Shale Group (Devonian-Mississippian) of the Illinois Basin as related to possible future production of gas from gas-bearing shales.

Shale porosity is influenced by three major variables—depth of burial, carbonate content, and organic content. Low-temperature adsorption (sorption) of N_2 and CO_2 by shale samples shows that much of the porosity in the more-deeply buried black shales is associated with ultramicropores having diameters less than 5 Å. Shales with such small pores have molecular-sieve characteristics; the diffusion of gases within such structures is activated and, thus, is temperature dependent and pressure independent.

Methane adsorption (sorption) at high pressures (up to 100 atmospheres) and methane release-rate measurements from laboratory-pressurized samples also reflect the molecular-sieve nature of the black shales. The methane release rates are lower as the degree of ultramicroporosity increases. The release rates are also dependent upon particle size and orientation. As particle size increases, the release rate decreases. The release rate from slabs cut perpendicular to the bedding planes is greater than that from slabs cut parallel to the bedding planes. In addition, however, there is indirect evidence from methane adsorption isotherms that some of the methane is sorbed and pressure-solubilized within the organic portion of the matrix. This greatly complicates the modeling of gas-release mechanisms.

INTRODUCTION

Porosity is a fundamental characteristic of a compacted particulate material. A study of the gas-producing potential of extremely low-permeability black shales must necessarily include an evaluation of the nature of the porosity within the shales and its influence on gas diffusion. Our part of the overall study of the New Albany Shale Group in the Illinois Basin addresses this task.

In studies of porosity in highly compacted materials such as the black shale, experimental methods based on gas adsorption (sorption) generally yield the most useful interpretive data. We have used such methods in our study. In the preliminary section of this paper we will discuss some of the theoretical principles on which these studies are based so that our findings can be more easily understood.

THEORETICAL BACKGROUND

Compaction of sediments

Gravitational compaction of sediments is accompanied by a decrease in porosity. Although change in porosity is mainly a function of overburden stress and time, it is also influenced by lithology, depositional environment, overpressured fluid zones, diagenesis, and tectonic stress. All these factors form complex interrelationships which have brought about some pronounced variations in porosity-depth curves for porous sedimentary rocks from different geographic locations. An excellent text by Rieke and Chilingarian (1974) provides references on the subject.

Coarse-grained sediments (sandstone and limestone) exhibit the least change in porosity with increased compaction; fine-grained (colloidally-derived) argillaceous sediments change the most. (Coal actually shows the greatest change. Coal, however, is a transformation product and not a sediment, per se.)

Müller (1967) pointed out that once a sediment has been compacted by a certain overburden pressure, the process is irreversible. Even after a later uplift and erosion of the upper layers, with the attendant release of pressure, the porosity attained at the maximum burial depth does not change. This is a necessary assumption in any porosity-depth studies involving geologic samples in the laboratory.

The Illinois Basin, with its essentially passive underlying basement, provides an excellent geologic environment to observe compaction differences. In proceeding from the northwest to the southeast portions of the Illinois Basin, the sediments thicken and are more deeply buried. A study by Thomas and Damberger (1976) on the high-volatile bituminous coals (Pennsylvanian) in Illinois showed that the porosity for the same seam of coal (Illinois No. 6) gradually decreases from a value of more than 20 percent in the northern part to less than 5 percent in the southern portion. It was anticipated at the beginning of the present study that the New Albany Shale Group in the Illinois Basin would show a similar relative change in porosity.

Porosity in highly-compacted structures

The porosity of an aggregate is readily approximated from the difference in two density measurements: (1) the absolute density, determined by the displacement of helium, which is assumed to fill all the pores; and (2) the bulk density (particle density) determined by the displacement of mercury, which is assumed to fill none of the pores. Such measurements, however, reveal nothing about the pore-size distribution, and nothing about the internal surface area (a very important parameter insofar as the adsorption of gases or liquids are concerned).

Although such substances as bone, coal, and shale differ markedly in chemical composition, they share an important physical characteristic: they were deposited, or formed, chiefly from colloidal-size particles. As the particles became compacted and partially cemented through contact in the fluid medium, the fluid was continually exuded, bringing about an aggregate structure with an inherent tortuous porosity, occupied by the fluid medium and any degradation products, formed around and between the individual crystallites, or grains.

In highly-compacted structures of colloidal-size particles, an ultramicroporous network is formed in which the diameters of the pores, or passageways, are well below 10-angstrom units (Å), or approaching molecular dimensions. The diffusion of gases in such small pores is severely retarded, a fact well-recognized by those working with natural and synthetic zeolites (Barrer, 1978). Although the total pore volume within these ultramicropores is not necessarily large, the internal surface area (ISA) around the walls of the microcapillary system is quite large, measured in the hundreds of square meters per gram (m^2/g) of material in some cases. Large surfaces play an important role in gas adsorption, in ion exchange, and in catalysis, when that surface is available to the diffusing species.

Electron microscopy, mercury intrusion, line broadening from high-angle x-ray diffraction, and the low-angle scattering of x-rays all provide useful and supplementary information concerning porosity and ISA; but these methods do not adequately characterize the availability of that surface. Gas adsorption (sorption) affords the only method for doing this.

Gas adsorption (sorption) methods for studying ultramicroporosity

We use two methods in our laboratories for studying ultramicroporosity. The well-known BET method (Brunauer, Emmett, and Teller, 1938) is used for determining the internal surface area (together with the external surface area, a very small fraction of the total surface). In this method, nitrogen is considered the standard adsorbate at liquid nitrogen temperature (-196°C) and usually is the gas of choice for surface area measurements. However, other gases—particularly carbon dioxide at dry ice temperature (-77°C)—can be used to advantage, as will be shown. The second method involves the introduction of a gas at high pressure (in increments up to 100 atmospheres) into the pore structure. An adsorption (sorption) isotherm is obtained. After equilibrium is established at the highest pressure desired, the pressure is suddenly reduced to atmospheric, and the rate of gas-release from the sample is measured at constant pressure.

Studies on molecular sieves in the late 1950s and early 1960s have shown that nitrogen at -196°C is unable, in a reasonable time period, to penetrate pores with diameters less than about 5 Å, as the N_2 molecule is not sufficiently activated to overcome the repulsive forces near the pore openings. Carbon dioxide, on the other hand, is sufficiently activated at its much higher adsorption temperature of -77°C to penetrate pores having diameters down to about 3.5 Å. Thus, used in conjunction with the standard N_2 adsorption method, carbon dioxide is a valuable gas probe for determining whether or not a given substance possesses molecular-sieve characteristics (i.e., for determining the presence and extent of ultramicropores and passageways with diameters less than about 5 Å). This combination of adsorbates is being used in the study of coals, shales, clays, zeolites, and activated carbons (see Thomas and Bohor, 1968; Thomas and Damberger, 1976; Thomas and Frost, 1978; Frost and Thomas, 1978; and references listed in those reports).

While not providing a direct measurement of porosity, the CO_2 and N_2 ISA measurements do provide a measure of the nature of the porosity, or of the change in porosity, in highly-compacted substances. If the total porosity is known from density measurements, the proportion of the total porosity within the ultramicropores can be approximated from the CO_2 and N_2 ISA determinations. If only external surface area is involved, or the pores which are present have diameters greater than 5 Å, the surface area values determined from both N_2 and CO_2 adsorption are the same (within an experimental error of about 5 percent). But if ultramicropore structure is present the CO_2 ISA values are significantly larger, since CO_2 "sees" the same surface as N_2, in addition to that surface within the ultramicropores. It is useful to compare the CO_2/N_2 ISA ratios; the larger this ratio, the more extensive is the molecular-sieve nature of the sample.

EXPERIMENTAL PROCEDURES

Surface area measurements

Data for internal surface area (ISA) measurements with N_2 and CO_2 as adsorbates at -196°C and -77°C, respectively, were obtained by a dynamic sorption method. Laboratory-constructed apparatus in use is similar in design to that first described by Nelsen and Eggertsen (1958) and later refined by Daeschner and Stross (1962).

Shale core samples were crushed and screened. The 40 x 120 mesh sieve fractions were used for the ISA measurements. Samples of 0.5 to 1.0 g were outgassed at 110°C in a stream of helium for 3 hours. Initially, 3-point BET plots were used with N_2 as the adsorbate at -196°C. It was found that no additional N_2 was adsorbed in 10 minutes at a constant relative pressure (p/p_o) of about 0.25. Thus, an equilibrium time of 10 minutes was used with a single-point BET plot passing through the origin. With CO_2 as the adsorbate at -77°C, however, several hours adsorption are required to approach equilibrium. An adsorption period of 16 hours (overnight) was selected for convenience at a p/p_o of about 0.15. The saturation vapor pressure (p_o) under the conditions used was 1,450 mm. The area occupied by the CO_2 molecule under these conditions is 22.1 Å, based on calibration with standards of known surface areas. Again, a single-point BET plot was used.

High-pressure methane adsorption (sorption) and gas release measurements

Laboratory-constructed apparatus similar to that described by Dubinin et al. (1958) was used for the measurement of high-pressure (up to 100 atmospheres) methane adsorption/sorption isotherms and for the measurement of gas release rates. A block diagram of the apparatus and a detailed description of its operation are given by Frost and Thomas (1978).

With a shale sample of about 50 g of 6 x 12 mesh particles in the sample chamber (heated to about 100°C), the apparatus was evacuated until a pressure of about 5 x 10^{-3} mm was attained (12 to 48 hours). Methane was introduced at pressures greater than atmospheric through a valving system by condensing appropriate quantities of methane at liquid nitrogen temperature and then allowing it to expand at the desired temperature (most data were collected at 28°C) into the high-pressure part of the apparatus. After a suitable length of time (1 to 36 hours) for sorption equilibrium to be achieved (as evidenced by no further pressure changes within the high-pressure system), the procedure was repeated for the next datum point. After the last sorption datum point for a particular sample was obtained at the highest desired pressure, the methane pressure surrounding the sample was reduced to atmospheric by bleeding it off through a valve over a period of about 1 minute. The amount of methane released by the sample into gas burets was then measured as a function of time (for up to 3 days) at constant pressure (atmospheric). In cases in which methane was still being released after 3 days, the plots of volume released versus time were extrapolated to obtain the final volume of methane released from the sample.

The method of calculation for isotherms depends upon whether adsorption isotherms or total sorption isotherms are desired. According to the classical definition of adsorption, the amount of methane adsorbed by a sample at pressure P is the difference between the amount of methane introduced to produce pressure P and the amount of methane that would produce pressure P in the helium dead-space volume if the sample were not present. The total methane sorbed by a sample at pressure P is defined as the amount adsorbed at pressure P, plus the amount of methane required to produce pressure P in the sample pore volume, which is calculated from the difference in helium and mercury sample densities. Thus, sorption isotherms represent the maximum methane capacity of the shale samples if methane were the only gas occupying the pore volume. A methane compressibility curve (cc methane at STP/cc helium dead-space versus absolute pressure) was determined using the empty sample tube.

Total porosity

When total porosity was evaluated, helium (absolute) densities were determined with a Model 1302 He-Air Pycnometer (Micromeritics Instrument Corp., Norcross, GA). Mercury densities were determined with a macro-filling device accessory for mercury intrusion porosimeters (American Instrument Company, Silver Spring, MD).

RESULTS AND DISCUSSION

Two-hundred eleven shale samples from 13 cores in the Illinois Basin were studied along with another 27 samples from Eastern Kentucky, Ohio, and Virginia. Internal surface area values were obtained for all samples. About 45 samples were selected (on the basis of their ISA values) for high-pressure methane adsorption (sorption) and gas release-rate studies. The samples we evaluated represent a good cross-section of samples that might be found anywhere within the Illinois Basin. A number of older core samples and well cuttings from the Illinois State Geological Survey storage files evaluated by other methods in the overall program were not evaluated in this portion of the study. These older samples were not deemed satisfactory for our purposes as the partial removal of organic matter through oxidative degeneration alters the pore characteristics.

Internal surface area

Changes in the pore characteristics of the New Albany Shale Group in the Illinois Basin are quite marked as one proceeds geographically from the shallower horizons in the northwestern part of the Basin to the deeper part of the Basin in the southeast. Table XIV-1 presents data for a few selected samples from four cores representing the near-minimum to the near-maximum present-day burial depths of the New Albany Shale Group. Internal surface area data for samples evaluated by the high-pressure methods are included in tables appearing later in this report. The CO_2 and N_2 ISA values for all the samples studied are included with the Analytical Chemistry data.

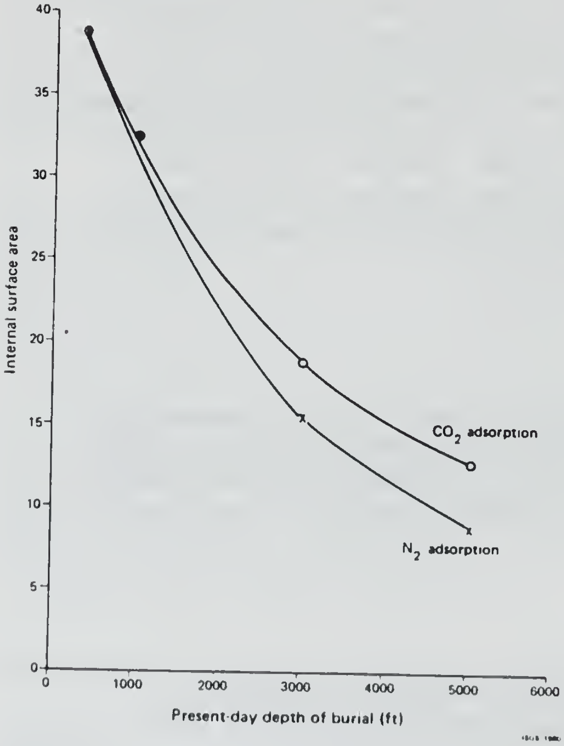


Figure XIV-1. Relationship of CO_2 and N_2 internal surface area with present-day depth of burial for shale of low organic content and low carbonate content.

Study of all the data shows that inherent shale porosity is altered by three major variables: (1) depth of burial; (2) carbonate content; and (3) organic content. To study the effects of each variable, it is first necessary to examine the data for those samples in which the effects of the other two variables are minimized.

A plot of CO_2 and N_2 ISA values versus present-day depth of burial for four samples of relatively low carbon content (from both organic matter and carbonates) takes the form of that shown in figure XIV-1. At the shallower depths, the ISA values from N_2 and CO_2 sorption are closely comparable. The pore structure is equally accessible to both CO_2 and N_2. The porosity of the shallower samples is relatively high, ranging up to 16 percent for samples from 04IL. As the depth of burial increases, the compaction produces decreased total porosity (well below 5 percent in samples from core 13IL) and decreased pore sizes. The ISA becomes less available to both CO_2 and N_2 at their respective adsorption temperatures, but N_2 is excluded to a greater extent, since many of the pore diameters decrease to less than 5 Å. The two curves in figure XIV-1 diverge, producing a CO_2/N_2 ISA ratio of about 1.5 for the more-deeply buried samples.

TABLE XIV-1. Internal surface area (ISA), organic-carbon content, and carbonate-carbon content of selected shale core samples from the Illinois Basin

Sample	Depth to top of sample (ft)	Total Carbon %	Organic carbon %	Inorganic carbon %	Porosity %	ISA, m^2/g		CO_2/N_2 ISA
						CO_2	N_2	
Core 04IL—Henderson County, Ill								
*07C1	383.45	2.41	0.65	1.76	-	38.9	38.8	1.0
10C1	413.45	1.90	0.74	1.16	15.7	45.4	42.1	1.1
14C1	453.05	4.12	3.07	1.05	-	35.1	31.2	1.1
17C1	482.35	3.98	3.75	0.23	-	23.5	16.7	1.4
20C1	513.35	5.65	5.60	0.05	13.4	26.4	17.0	1.6
27C1	583.4	6.91	0.60	6.31	-	14.5	14.1	1.0
30C1	613.3	10.70	0.32	10.38	-	6.7	7.3	0.92
Core 06IL—Tazewell County, Ill								
04C1	933.4	2.18	0.57	1.61	-	29.0	27.7	1.1
*11C1	1003.2	1.60	0.99	0.61	-	32.5	32.8	1.0
18C1	1073.3	4.50	4.14	0.36	-	33.7	25.8	1.3
19C1	1083.2	6.37	6.11	0.26	11.3	37.6	23.1	1.6
20C1	1093.35	10.33	10.20	0.13	6.8	38.0	13.1	2.9
24C1	1133.5	2.80	1.08	1.72	-	20.0	18.4	1.1
Core 02IL—Effingham County, Ill								
*01C1	3011.4	1.62	1.61	0.01	7.0	18.9	15.7	1.2
05C1	3056.3	9.45	9.21	0.24	-	24.5	2.1	11.7
06C1	3073.4	7.25	7.12	0.13	3.4	19.4	2.3	8.4
08C1	3096.5	6.36	6.17	0.19	6.6	22.8	6.0	3.8
Core 13IL—Wayne County, Ill								
*04C1	5046.3	3.53	0.95	2.58	-	12.8	8.8	1.5
08C1	5082.2	7.09	7.04	0.05	-	16.9	3.6	4.7
09C1	5090.3	9.23	8.36	0.87	2.2	22.3	1.6	13.7
10C1	5100.3	9.44	8.67	0.77	-	25.0	1.6	16.1
25C3	5258.4	9.71	4.01	5.70	4.3	9.7	1.0	9.7

*Data for these samples were used in figure XIV-1.

It is interesting to note that numerous studies on porosity-depth relationships (Rieke and Chilingarian, 1974; Chapter 2) for clays and shales from various basins indicate that the greatest porosity loss occurs in the first few hundreds of feet of burial. However, it is estimated that a burial depth of at least 2,500 feet is required to reduce the porosity to a value of 15 percent. Sample 04IL10C1, which is low in carbon content, has a porosity of 15.7 percent. Its present-day burial depth is about 413 feet. Thus, it is likely (judging from this sample and others with similar porosity values from this core) that at least an additional 2,000 feet of overburden existed over that location in the geologic past. We cannot determine to what extent the additional overburden existed over the entire Illinois Basin, since changes in porosity at levels less than 5 percent become quite small over large intervals of burial depth. Published curves indicate that as much as 5,000-12,000 feet of overburden are required to reduce porosities to less than 5 percent.

Carbonates appear to behave as an intergranular cement which prevents the diffusion of CO_2 and N_2 into a part of the pore structure. Core 04IL, which was not particularly rich in organic matter but did contain a rather wide

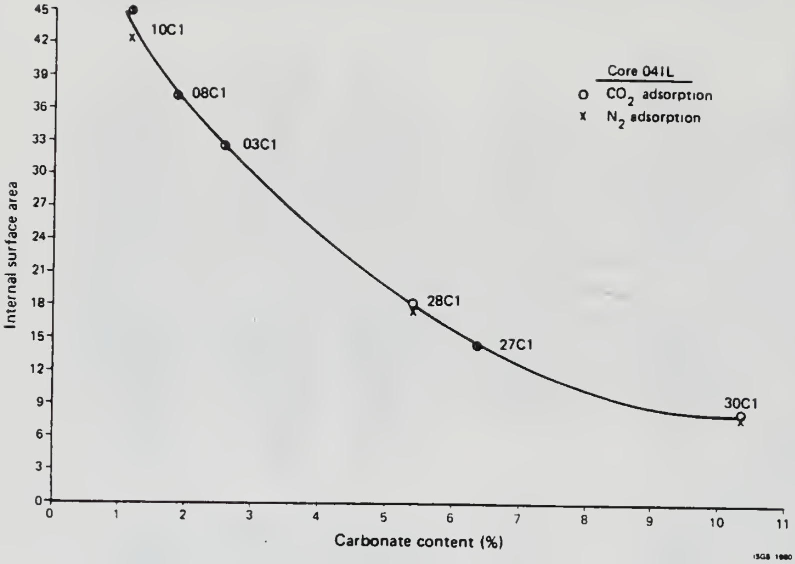


Figure XIV-2. Relationship between internal surface area and carbonate content of shale samples from core 04IL. Samples selected have organic carbon contents of less than 1%.

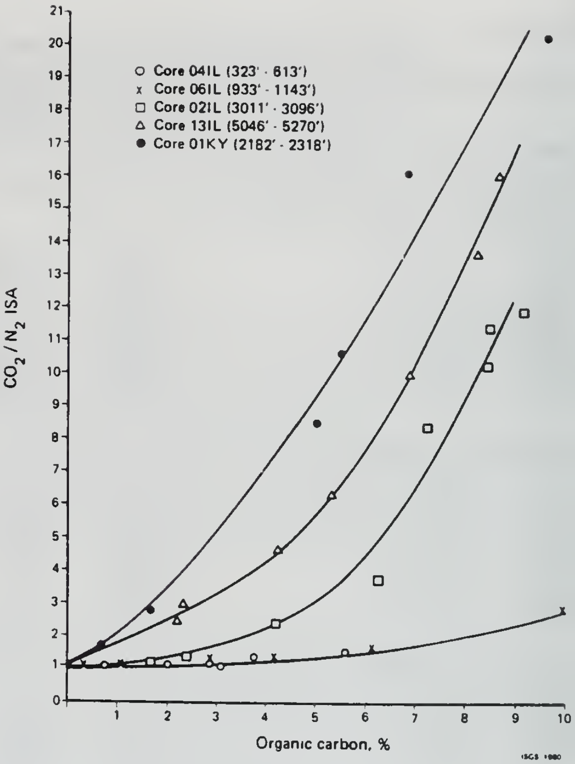


Figure XIV-3. Relationship between the CO_2/N_2 ISA ratio, organic carbon content, and depth of burial for the New Albany Shale Group in the Illinois Basin.

range of carbonate content, yielded the most samples for the evaluation of this variable. Figure XIV-2 is a plot of ISA versus carbonate content. Changes in porosity due to depth-of-burial differences are not significant here since the six samples are from an interval of only 270 feet.

The ISA values from both N_2 and CO_2 sorption decrease drastically as carbonate content increases. The ISA values from N_2 and CO_2 sorption are essentially the same for each sample; thus, the same surface is available to both gases, and molecular-sieve properties are not evident. Free silica (as "amorphous" or opaline silica) would also behave as a cementing agent. Since it was assumed that free silica was not present in significant quantities, its influence on porosity was not evaluated.

Organic matter plays a very important and somewhat complex role in altering the inherent shale porosity. As the organic carbon content increases, the partial occupation of the shale pores by the organic matter reduces the pore diameters so that an increasing proportion of the porosity is associated with pores, or passageways, having diameters less than 5 Å. This is apparent in a comparison of the larger CO_2 ISA values relative to those obtained by N_2 sorption on the same samples. The largest difference we have measured is with sample 01KY01C1 (containing about 14 percent organic carbon), in which the CO_2 ISA value is 39.3 m^2/g, and the N_2 ISA value is only 1.5 m^2/g, giving a CO_2/N_2 ISA ratio of about 26. The porosity of this sample is about 3.6 percent. About 60 percent of the pore volume within this shale sample is associated with pores having diameters less than 5 Å.

The organic matter in the higher-porosity samples from the shallower depths does not appear to contribute much to the internal surface area, but does contribute to the surface area in the more deeply-buried samples. Whether this phenomenon reflects some change in the nature of the organic matter (i.e., more carbon-like in the thermally-degraded deeper samples) is not known at present. In the more-deeply buried samples, both CO_2 and N_2 ISA values decrease as porosity is closed off, but the N_2 ISA values decrease much more markedly. The CO_2/N_2 ISA ratios remain large. This is apparent (table XIV-1) when one compares the ISA data for samples from core 13IL with those from the shallower cores.

We have found the CO_2/N_2 ISA ratio useful in this study since this ratio reflects the degree of pore closure and molecular-sieve characteristics. In plots of organic carbon content versus CO_2/N_2 ISA ratios for samples from five cores (fig. XIV-3) it is evident that an increase in organic content brings about an increase in ultramicroporosity for samples from the same core. It is also evident that there is a further increase in ultramicroporosity when an increase in organic content is coupled with increased depth of burial. The CO_2/N_2 ISA ratio is significantly larger for more-deeply buried samples of comparable organic contents.

The plot for core 01KY has a greater slope at corresponding organic carbon contents than that for core 13IL. This would indicate that, in the absence of additional compaction from tectonic stresses, the samples for core 01KY were more deeply buried in the geologic past than those from core 13IL, although present-day burial depths would not indicate this.

Samples from core 11IL, from a faulted zone in extreme southern Illinois (in the fluorspar-producing district), reflect the effects of additional tectonic stresses. Samples from this core, today only 48-260 feet below the surface, were the most compact, low-porosity samples studied. (Most samples had a porosity of less than 2 percent.) Some mineralization also was apparent as indicated by the relatively high fluoride contents of samples from this core.

High-pressure adsorption (sorption) of methane

The characteristics of samples selected for the high-pressure methane adsorption (sorption) studies are given in table XIV-2. Typical adsorption isotherms at 28°C for some of these samples are shown in figure XIV-4, and the total sorption isotherms are shown in figure XIV-5. Pertinent adsorption data at given pressures for all the samples studied (from which the isotherms can be plotted) are given in the computer tape provided with this contract report.

The molecular diameters of CO_2 (4.1 Å), N_2 (4.05 Å), and CH_4 (4.0 Å) are equal for all practical purposes. At 28°C, each gas should reach the same available surface. Thus, the volume of methane adsorbed at 28°C at increasing pressures should be a function of the available surface area, as determined by CO_2 adsorption at -77°C. A comparison of the adsorption isotherms (fig. XIV-4) shows that the amount of methane adsorbed at a given pressure does correlate reason-

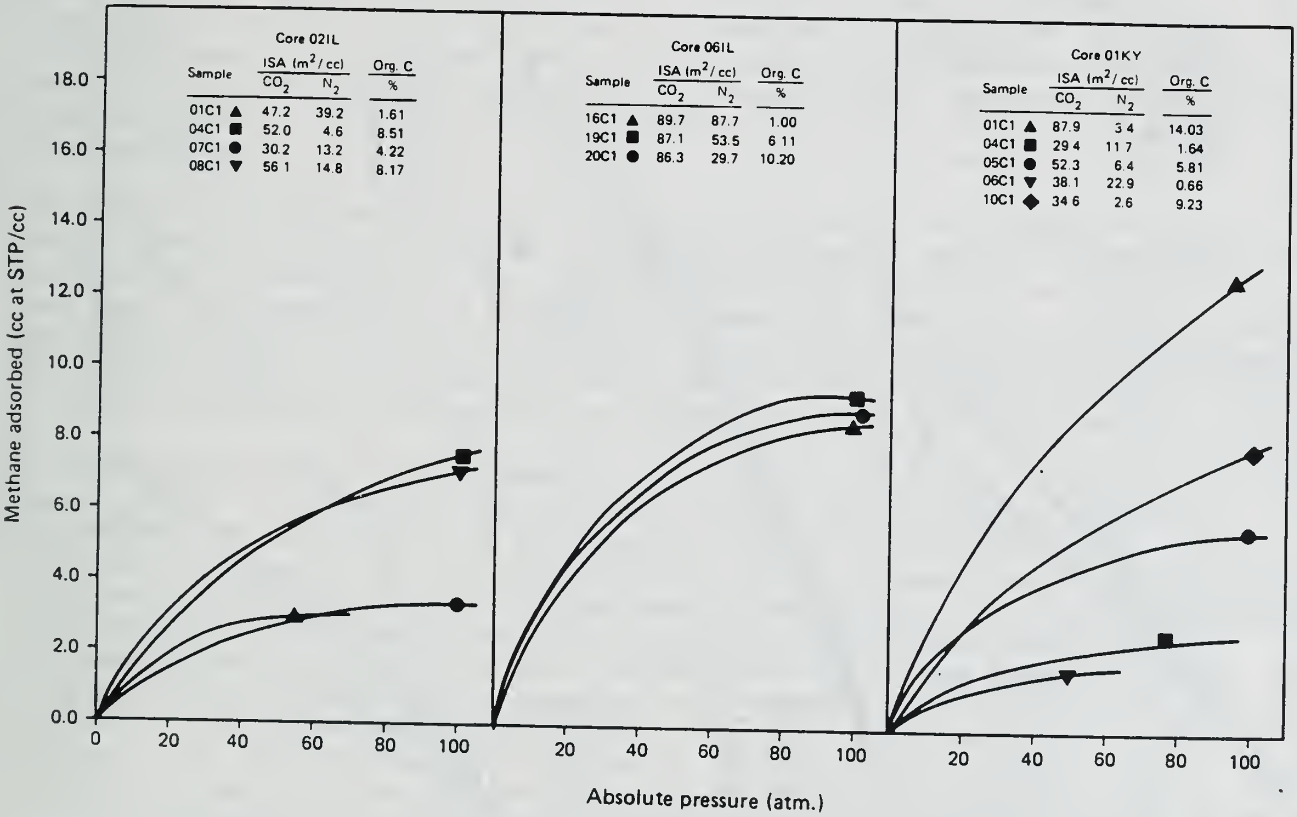
TABLE XIV-2. Characteristics of samples selected for high-pressure methane adsorption (sorption) studies and gas-release rate measurements

Core and sample no.	Depth to top of sample (ft)	ISA CO_2 (m^2/g)	ISA N_2 (m^2/g)	Helium density (g/cc)	Mercury density (g/cc)	Porosity (%)	Organic carbon (%)
02IL-01C1	3011.4	18.9	15.7	2.678	2.495	7.0	1.61
04C1	3053.0	21.5	1.9	2.553	2.420	4.6	8.51
06C1	3073.4	19.4	2.3	2.518	2.433	3.4	7.12
07C1	3085.5	12.1	5.3	2.686	2.498	7.0	4.22
08C1	3096.5	22.8	6.0	2.637	2.460	6.6	6.17
04IL-10C1	413.45	45.4	42.1	2.766	2.322	15.7	0.74
20C1	513.35	26.4	17.0	2.605	2.259	13.4	5.60
26C1	573.0	21.9	19.1	2.747	2.358	14.2	2.84
29C1	604.5	6.3	6.5	2.851	2.588	9.1	0.82
05IL-01L1	655.9	25.7	12.9	2.604	2.372	9.0	4.74
01L2	660.2	28.4	15.9	2.572	2.355	8.5	4.39
01L3	662.2	29.0	16.5	2.566	2.355	8.2	4.99
06IL-16C1	1053.15	37.1	36.3	2.742	2.417	11.8	1.13
19C1	1083.20	37.6	23.1	2.609	2.316	11.3	6.11
20C1	1093.35	38.0	13.1	2.435	2.270	6.8	10.20
10IL-01L1	2892.2	28.1	5.6	2.442	2.393	2.2	6.67
01L3	2898.2	5.7	5.3	2.818	2.651	5.8	0.87
01L6	2902.9	11.2	5.2	2.748	2.540	7.6	1.69
11IL-02C1	48.0	18.4	6.5	2.593	2.328	10.2	5.77
04C1	83.0	13.6	2.5	2.543	2.477	2.7	5.86
10C1	141.35	3.4	0.8	2.660	2.627	1.3	1.28
15C1	195.6	15.2	2.2	2.495	2.452	1.7	6.50
18C1	230.0	5.6	2.0	2.663	2.614	2.1	1.81
20C1	251.4	10.3	1.7	2.613	2.585	1.0	3.41
12IL-02C1	4838.0	10.1	1.4	2.530	2.454	2.9	
13IL-07C2	5078.1	14.2	3.2	2.500	2.379	4.8	7.16
09C1	5090.3	22.3	1.6	2.490	2.432	2.2	8.36
11C2	5115.4	19.5	2.5	2.520	2.433	3.4	7.11
16C2	5164.1	19.9	2.0	2.518	2.436	3.2	6.87
17C4	5178.2	13.5	3.4	2.574	2.525	2.0	4.35
18C2	5184.1	10.4	2.2	2.544	2.508	1.5	4.30
23C4	5239.6	8.2	1.6	2.518	2.484	1.3	5.48
24C2	5245.5	4.2	1.0	2.603	2.552	1.4	3.14
25C3	5258.4	4.3	1.0	2.554	2.445	4.3	4.01
01KY-01C1	2182.5	39.3	1.5	2.318	2.237	3.6	14.03
04C1	2230.2	11.3	4.5	2.714	2.605	4.2	1.64
05C1	2240.1	21.1	2.6	2.545	2.477	2.7	5.81
06C1	2250.0	14.5	8.7	2.712	2.631	2.9	0.66
10C1	2290.75	14.7	1.1	2.404	2.355	2.0	9.23
02KY-02C1	45.0	53.0	6.4	2.201	2.155	2.1	15.55
04C1	65.0	25.8	10.1	2.536	2.383	6.0	6.01
08C1	105.0	27.7	4.6	2.341	2.275	2.8	9.32
01IN-04C1	2531.4	31.3	1.3	2.351	2.286	3.0	11.08
07C1	2561.8	10.9	2.5	2.682	2.513	6.3	2.93
13C1	2622.8	14.7	1.4	2.541	2.451	3.4	6.30
SDO-1	-	36.4	4.6	2.386	2.308	3.2	
Wise Co., VA	4916.5	24.4	20.2	2.601	2.458	5.5	

ably well with the CO_2 ISA values and is relatively independent of the porosity of the samples. The ISA values are given in figure XIV-4 as m^2/cc of shale rather than in m^2/g as this provides a more convenient comparison with other reported data on the gas content of shale (generally expressed on a volume-to-volume basis as cubic feet of gas per cubic foot of shale).

The total sorption data presented in figure XIV-5 represent the maximum quantities of methane the outgassed samples are capable of containing at any given pressure; they do not represent the quantity of methane actually present in the shale lithologies from which the samples were obtained.

The methane sorption capacity of a particular sample is dependent upon two factors. The first factor is methane adsorption by the surface within the pore space. For a given pore volume, as the average pore diameter decreases, the total surface area within the pores increases, leading to the adsorption of more methane. The second factor is the simple filling of the pore volume, or void space, with gaseous methane. As the pressure is increased, methane in the void space is continually compressed, and the total sorption of methane will continue to increase.



Core 02IL

Sample	ISA (m^2/cc) CO_2	ISA (m^2/cc) N_2	Org. C %
01C1 ▲	47.2	39.2	1.61
04C1 ■	52.0	4.6	8.51
07C1 ●	30.2	13.2	4.22
08C1 ▼	56.1	14.8	8.17

Core 06IL

Sample	ISA (m^2/cc) CO_2	ISA (m^2/cc) N_2	Org. C %
16C1 ▲	89.7	87.7	1.00
19C1 ■	87.1	53.5	6.11
20C1 ●	86.3	29.7	10.20

Core 01KY

Sample	ISA (m^2/cc) CO_2	ISA (m^2/cc) N_2	Org. C %
01C1 ▲	87.9	3.4	14.03
04C1 ■	29.4	11.7	1.64
05C1 ●	52.3	6.4	5.81
06C1 ▼	38.1	22.9	0.66
10C1 ◆	34.6	2.6	9.23

Figure XIV-4. Methane adsorption isotherms at 28°C for selected samples from Effingham County, IL (core 02IL); Tazewell County, IL (core 06IL); and Christian County, KY (core 01KY). Note that the ISA values in this figure are given on a m^2/cc bulk shale basis instead of the m^2/g basis as for table 1.

Menon (1969) has discussed the adsorption of gases at high pressures in some detail. A limiting value for the volume of gas adsorbed (but not for the volume of gas totally sorbed) should be reached at some pressure at any given temperature. The pressure at which this occurs depends upon the sizes of pores within the structure. For methane at 28°C, the limiting value should occur at pressures less than 120 atmospheres. For many of the samples studied, a limiting adsorption value is approached within the pressure range to 100 atmospheres, the upper pressure limit of the apparatus. However, from the inspection and extrapolation of some of the adsorption curves (in particular those for the more-deeply buried samples of high organic content) there is anomalously large adsorption and an indication that the limiting value is considerably greater than 120 atmospheres. This is best exemplified by sample 01KY01C1 (fig. XIV-4). The CO_2 ISA value of this sample is 87.9 m^2/cc, a value not as large as that (89.7 m^2/cc) for sample 06IL16C1, yet the adsorption of methane is much greater for the sample from the Kentucky core.

There are two possible explanations for this behavior. First, the average pore size in the more highly compacted, high organic content samples is quite

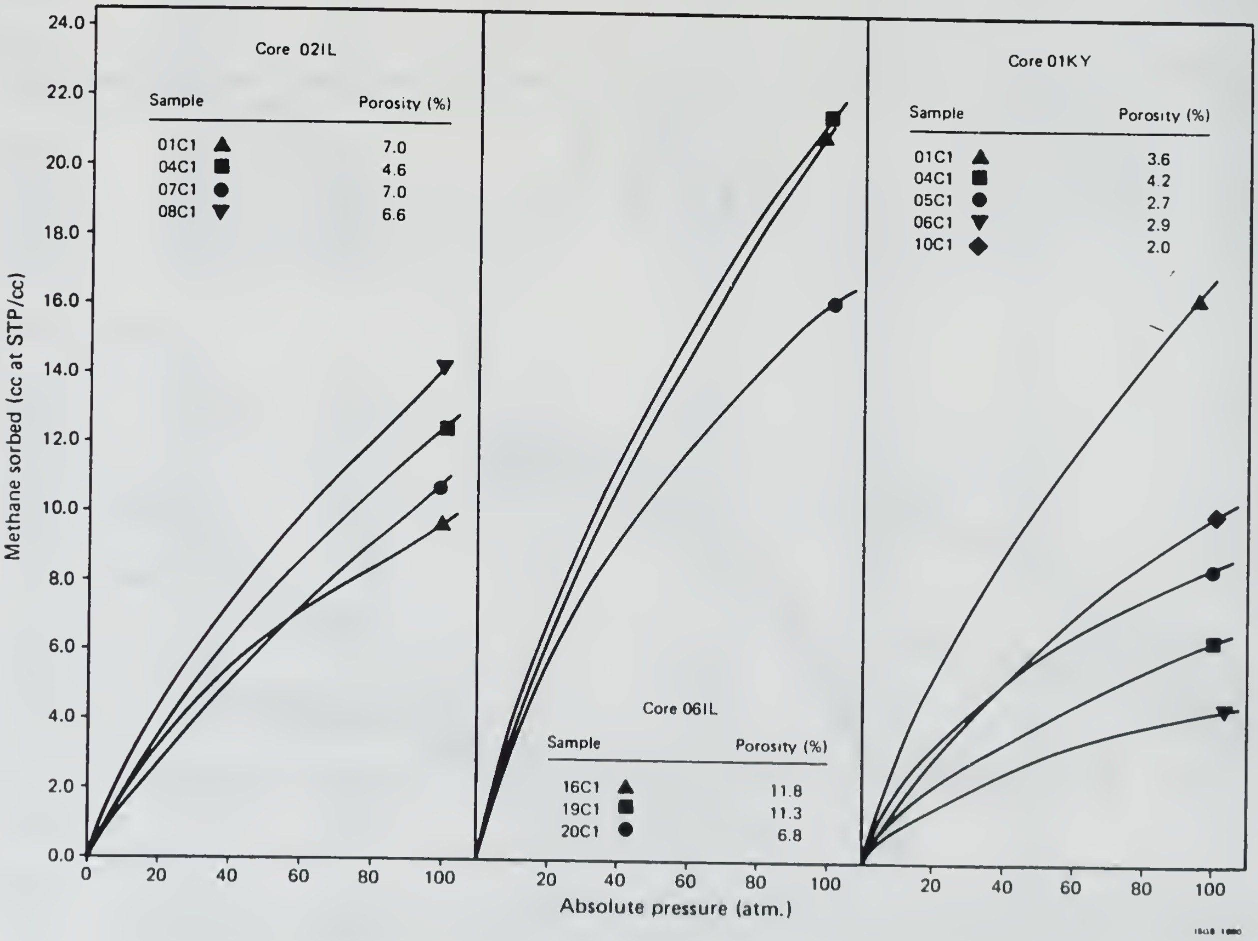


Figure XIV-5. Methane sorption isotherms at 28°C for selected samples from Effingham and Tazewell Counties, IL, and Christian County, KY.

small, as shown by the large CO_2/N_2 ISA ratios. As the pore sizes decrease to molecular dimensions, the methane adsorption potential increases (because of wall forces within the ultramicropores), thereby producing greater methane adsorption for a given amount of surface area. Supporting this explanation is the fact that sample 06IL20C1, shown in figure XIV-4, has a CO_2 ISA value of 86.3 m^2/cc, comparable to that of 01KY01C1 under discussion, and also a high organic carbon content (10.2 percent). It does not have nearly as much ultramicroporosity as the sample from the Kentucky core, as their respective CO_2/N_2 ISA ratios indicate. A limiting adsorption value is reached with sample 06IL20C1 within the range of pressure studied.

The second explanation, one that has serious implications for modeling attempts, is that methane is being sorbed and solubilized within the organic material. In this case, the nature of the organic material would influence the amount of methane contained within it. In the deeper sediments where methane is generated by thermal degradation, other longer-chain aliphatics also are present in measurable quantities. Solubilization of methane at high pressures in such material would be large. Its slow release from this state at reduced pressure, coupled with the inhibited diffusion from within the ultramicropores, makes modeling a formidable task. Although sample 06IL20C1 contains more than 10 percent organic carbon, it is from a shallow depth where little gas was found in the core. Significant thermal degradation to form methane and other aliphatics has not occurred, although some methane, long since gone, was no doubt generated by bacterial degradation (see Section VIII). Thus, the differing nature of the organic matter remaining in the two cores may account for some of the differences observed in the methane adsorption isotherms.

The sorption isotherms show that the shales are capable of holding much more methane than is typically found. A maximum pressure of only 100 atmospheres was used in these studies. As a rule of thumb, each foot of overburden increases the pressure on an underlying sediment by about 1 psi. One hundred atmospheres pressure thus is equivalent to only about 1,470 feet of burial depth. The total sorption of methane by some of the more-deeply buried shales studied would be even greater at pressures equivalent to their depths of burial.

In this context (from a consideration of porosity alone), the porosity of a shale sample of low organic content from a given core is greater than the porosity of an adjoining shale lithologic unit rich in organic matter. Thus, the sorption capacity of the former should be greater than that of the latter. It seems unlikely that in a given gas-bearing shale column only the organic-rich lithologies are gas bearing and the organic-poor lithologies sandwiched between are not. Diffusion of gas from organic-rich shales where the gas originated into the organic-poor shales to reach some equilibrium state throughout the column seems more likely. Yet, data from canned core samples indicate that much more gas is released by the organic-rich shales. This finding may be partly attributable to methane which is pressure-solubilized in the organic matrix, as suggested above. However, as discussed in the next section, the diffusion of methane from organic-poor shales with little ultramicroporosity is extremely fast in comparison with diffusion from the organic-rich shales containing a greater proportion of pores less than 5 Å in diameter. The sampling procedure involves bringing the core to the surface, examining, cutting, and canning it. During this time a much greater proportion of the

TABLE XIV-3. Data pertinent to discussion of methane release results.

Core and sample no.	ISA			Release parameters		Recoverable methane
	CO_2 (m^2/cc)	N_2 (m^2/cc)	CO_2/N_2	Initial slope[a] (S_I)	V_∞ (cc at STP) cc	(cc at STP) cc
02IL-01C1	47.2	39.2	1.2	1.0	-	9.33
04C1	52.0	4.6	11.4	0.068	9.17	12.94
06C1	47.2	5.6	8.4	0.078	7.90	7.68
07C1	30.2	13.2	2.3	0.8	2.69	11.33
08C1	56.1	14.8	3.8	0.155	8.17	14.85
04IL-10C1	105.4	97.8	1.1	1.0	-	28.82
20C1	59.6	38.4	1.6	1.0	-	21.17
26C1	51.6	45.0	1.1	1.0	-	19.50
29C1	14.8	15.3	0.97	1.0	-	10.74
05IL-01L1	61.0	30.6	2.0	0.99	-	14.11
01L2	66.09	37.4	1.8	0.99	-	14.20
01L3	68.3	38.9	1.8	0.99	-	15.38
06IL-16C1	89.7	87.7	1.0	1.0	-	20.50
19C1	87.1	53.5	1.6	1.0	-	20.98
20C1	86.3	29.7	2.9	0.99	-	15.66
10IL-01L1	67.2	13.4	5.0	0.144	8.21	11.92
01L3	15.1	14.0	1.0	1.0	-	8.51
01L6	28.4	13.2	2.2	0.99	-	10.46
11IL-02C1	42.8	15.1	2.8	1.0	-	14.71
04C1	33.7	6.2	5.4	1.0	-	6.19
10C1	8.9	2.1	4.4	1.0	-	2.13
15C1	37.3	5.4	6.8	0.99	-	5.10
18C1	14.6	5.2	2.8	0.99	-	3.24
20C1	26.6	4.4	6.0	0.99	-	2.64
12IL-02C1	24.8	3.4	7.2	0.059	4.56	13.33
13IL-07C2	33.8	7.6	4.4	0.120	5.59	8.68
09C1	54.2	3.9	13.7	0.070	7.10	8.71
11C2	47.4	6.1	7.9	0.067	6.84	8.20
16C2	48.5	4.9	10.0	0.063	7.38	10.33
17C4	34.1	8.6	4.0	0.104	6.14	11.77
18C2	26.1	5.5	4.7	0.093	5.46	5.85
23C4	20.4	4.0	5.1	0.055	5.74	5.76
24C2	10.7	2.6	4.2	0.041	2.76	4.16
25C3	10.5	2.4	9.7	0.056	3.42	7.56
01KY-01C1	87.9	3.4	26.2	0.058	10.09	16.08
04C1	29.4	11.7	2.5	0.184	3.07	6.28
05C1	52.3	6.4	8.1	0.085	6.54	8.35
06C1	38.1	22.9	1.7	0.369	1.47	4.53
10C1	34.6	2.6	13.6	0.045	5.56	10.03
02KY-02C1	114.2	13.8	8.2	0.122	11.87	11.34
04C1	61.5	24.1	2.6	0.99	-	11.15
08C1	63.0	10.5	6.0	0.168	7.80	10.78
01IN-04C1	71.6	3.0	23.6	0.075	7.91	12.32
07C1	27.4	6.3	4.3	0.113	3.59	8.59
13C1	36.0	3.4	10.5	0.058	4.39	7.60

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[a] Initial slope of V_t/V_∞ versus time$^{1/2}$ plots.

[b] Total methane released during slow gas release phase.

[c] The difference between methane sorption at maximum and atmospheric pressures.

gas would have diffused from the organic-poor shales than from the organic-rich shales. Thus, the question pertaining to the relative gas contents of the various lithologies within a given gas-bearing core still remains unanswered. Only the retrieval and proper handling of samples from a pressurized core can bring a satisfactory answer.

Methane release from high-pressure sorption

This section is concerned with the cause-effect relationship between the presence and extent of ultramicroporosity in shale, which gives the shale enhanced molecular-sieve properties, and the rate of release of contained gases.

Unless otherwise noted, the methane-release data presented in this report specifically represent the release of methane sorbed in the range of 80 to 102 atmospheres from 6 x 12-mesh shale particles. The methane-release data were plotted in the reduced form of V_t/V_∞ (vs. $t^{\frac{1}{2}}$ where V_t/V_∞) is the fraction of total gas released at time t. Selected reduced-form methane-release curves are shown in figure XIV-6. As the curves in this figure indicate, the initial slopes of the curves largely determine the relationship of one curve to another. Therefore, the initial slopes (S_I) of V_t/V_∞ vs. $t^{\frac{1}{2}}$ plots will be used in this report as the parameter for comparison and discussion of methane-release results. S_I values are presented in table XIV-3, along with other data pertinent to the discussion.

The S_I values for samples listed in table XIV-3 can be divided essentially into two groups. The first group of values for samples from cores 04IL to 11IL are representative of samples from the northern part of the Illinois Basin. Although the samples from these cores sorb significant amounts of methane, the release of the sorbed methane is very rapid and probably occurs simultaneously with depressurization of the sample bomb. With one exception, S_I values for this group of samples are either 0.99 or 1.0.

S_I values of 1.0 indicate that no appreciable methane was measured after the initial depressurization, while a S_I value of 0.99 indicates that only a small amount of methane was measured after the initial depressurization. These shale samples have moderate total porosity that is easily accessible to methane, as indicated by similar CO_2 and N_2 ISA values which result in CO_2/N_2 ISA ratios near unity.

The second group of values are for samples from cores 02IL, 12IL, 13IL, 01KY, 02KY, and 01IN from the southern part of the Illinois Basin. Most of these samples appear to exhibit two phases of methane release; that is, a portion of the total recoverable sorbed methane (total methane sorbed at maximum pressure minus the methane sorbed at about 1 atmosphere) is released during depressurization of the sample bomb, followed by a slow release of methane from the ultramicropores. V_∞ is usually less than the total recoverable sorbed methane (table XIV-3). Previously, we (Frost and Thomas, 1978) assumed that all this difference was due to the loss of methane during the initial depressurization of the sample bomb. However, indirect evidence suggests that, at least for some samples in this group, some sorbed methane may remain trapped within the shale particles after the slow methane-release phase is apparently completed.

The slow methane release from shale particles is a two-step process because of the presence of both ultramicropores (<5 Å) and micropores (>5 Å). The gas transport mechanism indicated by comparing S_I values and corresponding CO_2/N_2 ISA ratios (table XIV-3) involves activated diffusion of methane from the ultramicropores to the particle surface or into the micropores, followed by Knudsen diffusion, or molecular diffusion, or simple forced flow due to the pressure gradient, to the particle surface. Although there is not a good numerical correlation between S_I and CO_2/N_2 ISA ratio values, small S_I values are associated with the presence of significant ultramicroporosity as indicated by the CO_2/N_2 ISA ratios. A reasonable correlation obtained from a comparison of S_I and N_2 ISA values indicates that the micropores (those with diameters >5 Å), as represented by the N_2 ISA, play a very significant role in the release of methane from within a shale particle.

It would be desirable to be able to calculate diffusion coefficients from the methane release curves (fig. XIV-6) and from the data in table XIV-3, for use in modeling potential gas production from gas-shale reservoirs. Such coefficients, based on several assumptions, can be readily calculated but have little meaning. For example, we have not been successful (nor has anyone else we know of) in calculating a single diffusion coefficient which can be used to model the gas release curves for the three different "particles" of the same shale sample, exemplified by the release-rate curves shown in figure XIV-7. In the figure it is seen that the release rates differ markedly for 6 x 12-mesh particles, and for thin slabs cut either perpendicular or parallel to the bedding planes from the same core sample. Although we know that ultramicropores, micropores, cracks, and other discontinuities exist within a shale particle, we cannot know the precise pore structure (exact size, length, number, and arrangement of pores) necessary to determine a unique diffusion coefficient applicable to different-sized shale "particles".

In general, we know that in shales with low total porosities and low N_2 ISA values which contain significant ultramicroporosity (as shown by the large CO_2/N_2 ISA ratios) the release of sorbed methane or other contained gases will be very slow, and the release rates will decrease as shale particle size increases.

It has been shown elsewhere in this report that the black shales in the southern part of the Illinois Basin do contain significant amounts of methane and other hydrocarbons. Recovery of methane (at reasonable production rates) would appear to be dependent upon the existence of abundant natural fractures within the shale strata and/or the ability of an artificial fracturing technique to induce significant numbers of fractures within the shale strata.

SUMMARY

The principal findings of this investigation are:

1. The porosity of a shale depends on three major factors: depth of burial, carbonate content, and organic content.

2. Increasing depth of burial, combined with increasing organic content, produces shales having molecular-sieve characteristics, in that much of the

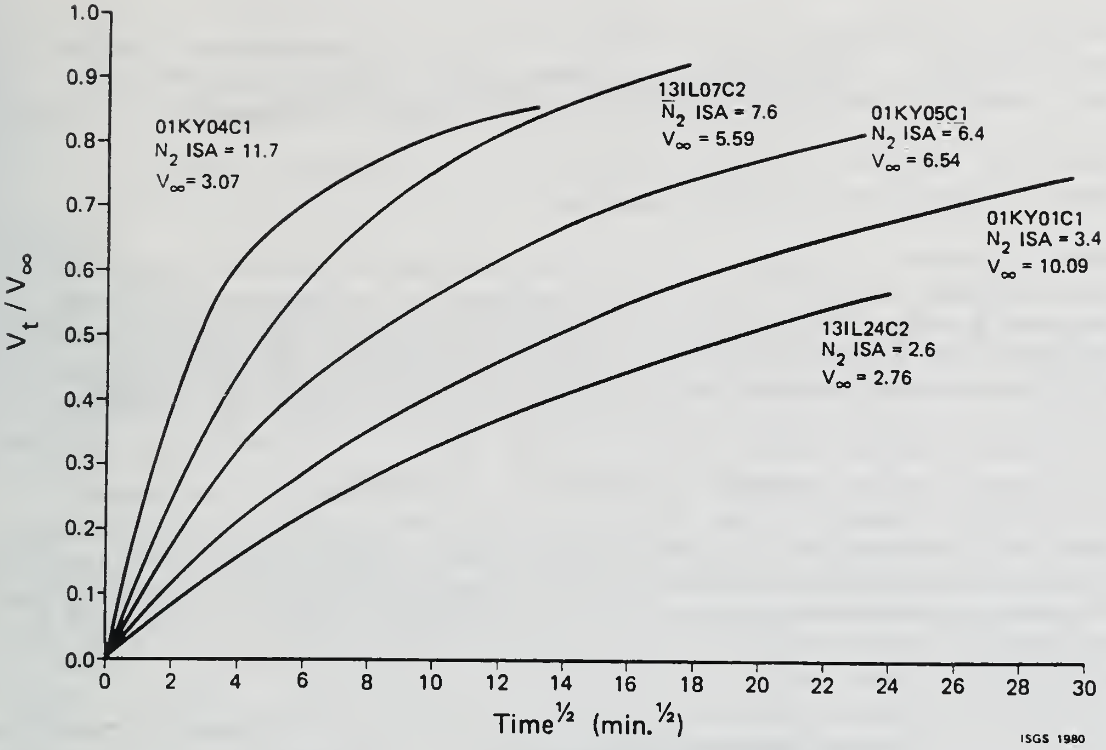


Figure XIV-6. Rate of release of methane from similarly pressurized samples. V_t/V_∞ is the fraction of gas released as a function of time$^{1/2}$. N_2 ISA values are given in m^2/cc of shale.

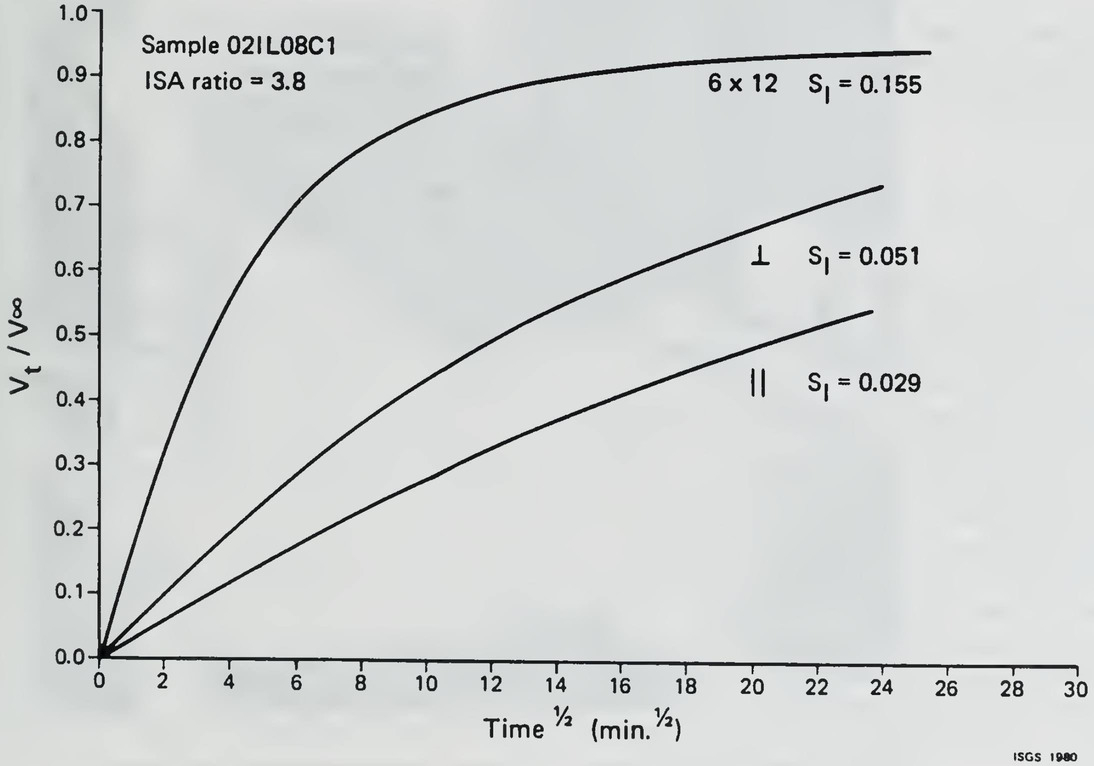


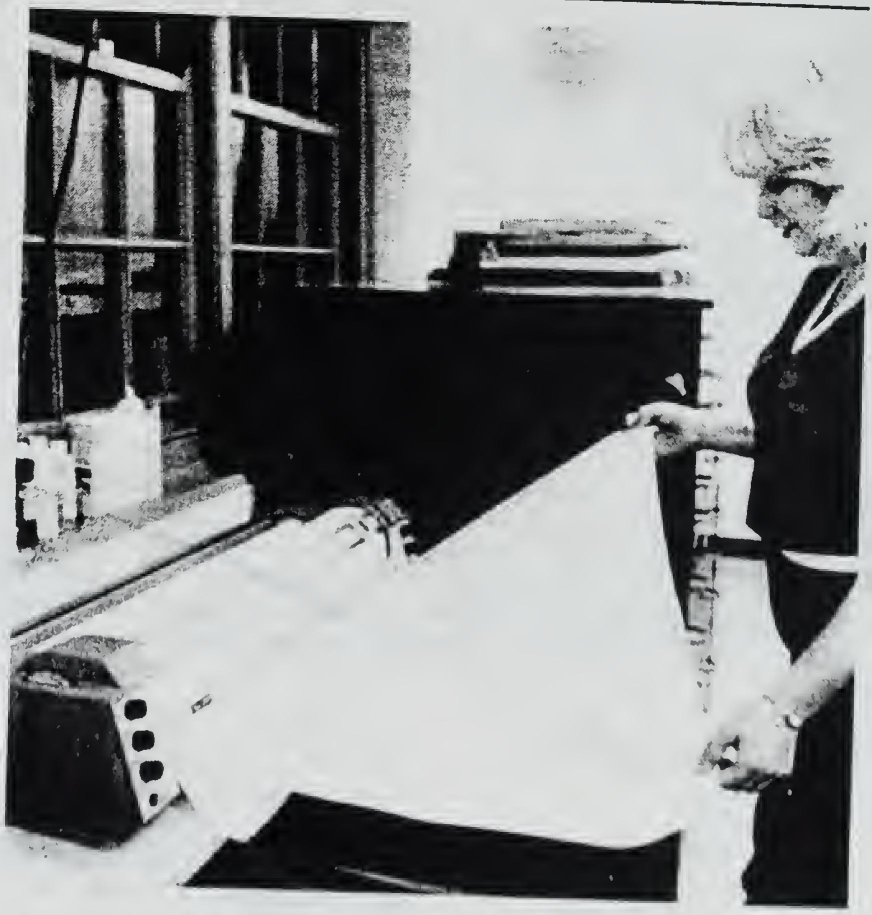
Figure XIV-7. Methane release-rate curves for thin slabs split parallel (||) to bedding planes, slabs cut perpendicular (⊥) to bedding planes, and for 6 x 12-mesh particles.

total pore volume is associated with ultramicropores, or passageways, having diameters less than 5 Å. The diffusion of gases within such structures is activated and, thus, is temperature dependent and pressure independent.

3. Shales are capable of holding appreciably more methane than is typically found in gas-producing core samples.

4. There is indirect evidence that in the more-deeply buried shales of relatively high organic content, some of the methane is pressure-solubilized within the organic portion of the matrix. When this possibility is considered in conjunction with the activated diffusion occurring in the ultramicropores, the modeling of gas-release mechanisms for gas-production estimates becomes a formidable task.

5. The release-rate of methane from shale is a function of the degree of ultramicroporosity present in the shale, and is also a function of shale "particle" size and orientation. The two factors which apparently contribute the most to methane generation—increased burial depth (for thermal degradation) and increased organic carbon content—unfortunately work together to produce a very low-permeability structure detrimental to rapid gas release.



Deborah Gaines checks a computer-drawn base map prepared using ILLIMAP and the Survey's CALCOMP plotter.

XV. MINERAL RESOURCES EVALUATION SYSTEM (MINERS)

L. H. Van Dyke

ABSTRACT

MINERS, a comprehensive information and management data system designed to process and retrieve geological, geophysical and chemical data required in the evaluation of mineral resources in Illinois, was constructed for use with data gathered and generated in the New Albany Shale project. The system was designed to accommodate various types of data bases, since mineral data can relate to borings, to mines, to individual horizons, etc.

MINERS is a batch-oriented system consisting of four modules: (1) file generation and maintenance; (2) retrieval; (3) processing of data, using special purpose programs (GEOMAPS); and (4) a base-map drawing, data plotting section for data display. The system is designed to meet the need for fast, efficient retrieval of geologic and related data. The special purpose program section includes routines for construction of numeric surfaces, mathematical operations between the numeric surfaces, trend surface calculations, areal extent, and volumetric calculations—operations all useful in evaluating mineral resources. Other routines may be added or substituted for those now in MINERS, as desired by the user. Designed to run on an IBM 360/75, the system contains many routines written in IBM Assembler language.

The MINERS system has been extended to handle and display data from the entire Illinois Basin; this extension has necessitated considerable change in the file generation and maintenance section, as well as construction of two new map-drawing data bases for Indiana and Kentucky.

INTRODUCTION

The purpose of this project was to develop a Mineral Resources Evaluation System (MINERS) with the capability of: (1) storing data related to ISGS studies of gas-bearing Devonian Shales; (2) retrieving selected data (related or unrelated) from one or all data files; (3) processing data by constructing numerical surfaces and performing operations between surfaces, such as trend and isopach surfaces, volume and areal calculations, contouring, and intersurface and intrasurface operations; (4) processing data according to classification of area; (5) processing data by statistical routines; (6) processing data by input to special purpose programs; and (7) displaying a wide variety of data on plotter maps, graphs, diagrams, printer maps and overlays and producing maps which could include structure contours, isopachs and iso-concentrations of parameter and trend surfaces. Although the system was developed to process data collected on the New Albany Shale Group in the Illinois Basin, the system can easily be adapted to most types of geologic data and to almost any geographic area.

DISCUSSION

MINERS has been designed rogrammed, tested, and put into use. All data gathered or generated by e Illinois Survey for this project have been put into files, and the ies and programs used to build and operate MINERS have been transfer d to a magnetic tape. When all the Illinois Basin data generated or gather for this project have been processed at ISGS and transferred to the magne tape, the tape will be sent to the Morgantown Energy Technology Center per instructions from Jan Downey on May 1, 1980. More detailed informatio MINERS appears in the final report included in the July 1-September 30, Quarterly Report to DOE. A user's manual to aid in building and oper the MINERS system accompanies this report as a separate enclosure. T anual explains the system in basic terms and describes operations fam to anyone with an introductory background in computers. It is assume t any person implementing and operating the system will have some kno dge of computers and programming.

A basic assumption in the sign of MINERS was that manual processing of data is impractical in geologi esearch, particularly that oriented toward mineral resource evaluat which involves the handling of large amounts of data. Experience gain from processing ISGS data has indicated that data necessary for vario nds of research are usually related geologically, chemically, or ge ically but not structurally insofar as computer files are concerned. The ore, any data storage and manipulation system must be able to handle di rent data bases as well as large amounts of data. MINERS can file, maintain nd retrieve data from many different data bases; the only restriction is t the total number of files in all data bases cannot exceed 4,096. (No that this number refers to files, not data items.) Limitation to the usage o he full capabilities of MINERS would probably result from hardware rest tions rather than from the system itself.

Users who have their own puter may not wish to optimize any of the routines in MINERS. Howeve hose who must purchase computer time may want to improve operations som at. For instance, file generation and maintenance can be speeded up eably, and some of the checking and message-writing routines can be ced, but inasmuch as data should be loaded only once, we have left intac l the bookkeeping and checking procedures in MINERS to insure that the ta are placed where they should be. Removing these procedures will lowe the cost of file generation. Retrieval processes will be used more often th file generation and maintenance operations, hence require the most ef ent operation. Maximum efficiency of retrieval operation can be obtained n all items in a retrieval criteria expression are contained in three or wer files.

If each separate file in data base contains only closely-related data items, searching for des data items can be speeded up substantially, since most retrieval req involve the inspection of only a very small percentage of the total er of data items in a data base. If each file contains only closely-re d items, most retrieval requests will only need to access one, two or thr of these small files.

The file generation and retrieval portions of MINERS have been designed with the concept of careful file construction in mind (as a key factor in fast retrieval). It is not necessary that this concept be followed in order for MINERS to work; however, all the data items in a data base can, if desired by the user, be put into one large file and searched on every retrieval request.

The principal aim in the design of MINERS was to allow users to retrieve data, process this data, using GEOMAPS routines, and receive final output on a plotter through ILLIMAP—all in the same processing run. This sequence can be carried out in several steps. Data may be retrieved and printed out immediately, or may be used for additional processing. It is possible to retrieve information based on certain criteria, then display data items in the record that were not part of the retrieval criteria. In addition, it is possible to output values of some of the data items in a file if the correct retrieval condition is met, then, during the same retrieval run, to output the data item values to a file from records not meeting the retrieval criteria. It is also possible to use the output from one retrieval run as the file to be searched in a subsequent run.

MINERS allows a wide range of options after data have been retrieved. The data can be displayed on a printer or a plotter and can be input to GEOMAPS or to programs developed or provided by a user for special processing. All but the special processing option can be accomplished in the same run as the retrieval request. However, if a user has a series or package of programs frequently used to process data, these routines might possibly be linked to MINERS as a replacement for (or an addition to) GEOMAPS, and become a continuous operation so that retrieval, processing of retrieved data, and display by use of ILLIMAP can be accomplished.

As long as a user works with Illinois Basin data, the base map drawing capabilities of ILLIMAP will suffice. However, if MINERS is used to store and process data in other parts of the country (which it is capable of doing) ILLIMAP cannot produce the required base maps unless a MAPDATA base of X-Y coordinates of every section corner in the area desired has been prepared. Measuring the values of every section corner and county and state boundaries is a time-consuming task, but worth the effort if many maps are to be drawn of this area in the future. Measuring values from topographic sheets of areas surveyed in the section-township-range manner is the easiest way to do this. ILLIMAP was designed to accept data and to draw maps using this type of data. Building a data base of another state or of a selected area could probably be done by using programs we have already established for this purpose. Some alterations might be required; but for the most part, programs that worked in Illinois and Indiana should form at least the framework for building a mapping base in states surveyed with the section-township-range system. (Areas that have not been surveyed with this system can still be mapped by ILLIMAP, under certain conditions.)

The Illinois Basin lies beneath portions of three states—Illinois, Indiana, and Kentucky. In order to display data in the Illinois Basin for the current study it was necessary to extend ILLIMAP into both Indiana and Kentucky. Indiana was surveyed with the section-township-range system and therefore presented no problems in building a mapping data base; Kentucky, however, has not been surveyed by the section-township-range system. Since ILLIMAP can be converted so that it can produce maps in areas having a consistent rectangular mapping system and still draw maps accurately in the polyconic or Lambert conformal conic projections, the Carter Grid could be used in Kentucky. The Carter Grid is a system based on latitude-longitude, in which 1 minute of arc on a side forms an area roughly the size of a section. Twenty-five of these areas, five wide and five deep, form a grid. It is possible for ILLIMAP to treat each 1-minute square area as a section and a grid as a township. Other areas can be treated similarly, whether or not a rectangular grid has already been established for an area.

It may not always be practical, or desirable, to use the Lambert Conformal Conic Projection for mapping an area. Texas, for instance, is probably an inappropriate candidate for ILLIMAP. It covers such an extensive east-west distance that the degree of inaccuracy of location of section corners on the east and west edges of the state would most likely be unacceptable. The use of two or more Lambert surfaces in the state would help solve the problem; but there may be better solutions. Another problem for ILLIMAP in states such as Texas would result from the inconsistent township sizes: many "special cases" would be required to process the numerous railroad blocks that have inconsistent numbers of sections. Most other areas in the United States could probably be handled if the amount of work and time required to build a data base were considered acceptable.

Hydraulic fracturing of the New Albany Shale Group, Hobson Oil #2 Taylor well, Wayne County, IL (June, 1979).

XVI. NATURAL GAS POTENTIAL IN ILLINOIS

R. M. Cluff

ABSTRACT

Data from geologic and geochemical studies of the New Albany Shale Group indicate that a 19-county area of southeastern Illinois is a favorable area to explore for gas in Devonian shale. Devonian shale in this area is characterized by: (1) predominance of organic-rich, finely laminated, black shale; (2) total shale thickness of more than 150 feet (46 m); (3) sufficient thermal maturation of organic matter for gas generation; and (4) the presence of natural fracturing and faulting. Although gas shows have been encountered in several wells in this area which penetrate the Devonian shales, there has been no commercial production of gas from shale in Illinois. Until 1979, no attempts had been made to complete or fully evaluate a shale gas well.

Core samples were taken in May, 1979 from 16 feet (5 m) of the upper New Albany Shale in the Hobson Oil #2 Taylor well (34-1S-7E, Wayne County) and in September-October, 1979 from 72 m of New Albany Shale (a complete section) in the G. T. Jenkins #1 Simpson well (17-3S-8E, Wayne County). Seventy core samples were removed on site at 3-foot (1 m) intervals throughout both cores and were sealed in airtight metal canisters for off-gas analysis. The quantity of gas released after 34 days ranged from 0.16 to 2.40 m^3 hydrocarbons/m^3 shale. These are minimal values; the actual in situ gas content of the shale may be two to four times greater. The highest gas contents were observed in the Grassy Creek Shale and in black shale intervals throughout the Selmier Shale. These gas-bearing intervals generally correspond with high radioactivity intervals on gamma-ray logs. Olive-gray and greenish-gray shales in the New Albany contained only moderate amounts of gas, as did the calcareous, laminated, black Blocher Shale at the base of the New Albany.

The quantities of gas in core samples of New Albany Shale from southeastern Illinois compare favorably with those in core samples from gas-producing areas of Devonian shale in the Appalachian Basin; however, because the New Albany Shale is much thinner than its Appalachian Basin equivalents, the total gas resource is probably much smaller. Conventional rotary drilling with mudbased drilling fluids commonly causes extensive formation damage and accounts for the paucity of gas shows and completion attempts in the Devonian shales; therefore, commercial production of shale gas in Illinois will probably require novel drilling and completion techniques not commonly used by local operators.

INTRODUCTION

Previous studies of gas bearing shales have shown that areas of gas production are related, at least partly, to four characteristics: (1) regional facies patterns; (2) areas of thick shale accumulation; (3) the degree of thermal maturation of the organic matter in the shale; and (4) the presence of extensive fracturing or faulting. Other factors may also be important, but have not been well-documented. Our preliminary evaluation of the New Albany Shale in Illinois, using these four criteria, indicates that southeastern Illinois is the most favorable area for gas production (Cluff and Dickerson, 1980).

Depositional facies

Shale gas production in the Appalachian Basin is usually from black to brownish-black, laminated, organic-rich shales (Hunter and Young, 1953). The gas in these shales originated from the thermal transformation (maturation) of the sedimentary organic matter dispersed throughout the shale matrix. Minor gas production from gray shales with low organic contents has been reported, but geologists generally believe that the gas originated in the black shales and has migrated through natural fractures into the other zones.

As previously discussed (Sections IV, VI), the distribution of New Albany Shale facies forms a roughly concentric pattern around the depositional center of the basin. The cumulative thickness of organic-rich black shales is greatest near the center of the ancestral Illinois Basin in southeastern Illinois and adjacent western Kentucky (fig. VI-3), while organic-poor greenish-gray and olive-gray shales predominate away from the basin center and are thickest in western and west-central Illinois. A broad transitional zone, where these two major facies belts interfinger and grade laterally into one another, trends northeast-southwest across central Illinois.

Shale thickness

Harris, de Witt, and Colton (1978) documented a close correlation between areas of thick black shale accumulation and gas production in the Appalachian Basin. They found that the best producing areas occurred in areas where the black, organic-rich shales exceeded 150 m in thickness.

The entire New Albany Group attains a maximum thickness of approximately 470 feet (143 m) in the Illinois Basin (fig. IV-2). Clearly, if a minimum thickness of 150 m is essential for commercial production of shale gas, then the entire Illinois Basin must be considered unattractive. Two broad regions of moderately thick shale accumulation are found in the Illinois Basin, however, and improved completion techniques might permit recovery of gas from such areas. The western depocenter (fig. IV-2) is not considered a likely area for gas accumulation because of the paucity of black shale (fig. VI-3). The southern depocenter (fig. IV-2) is the area of greatest black shale accumulation and is a much more favorable area to explore for gas. The central thin (fig. IV-2) is the transitional facies region discussed previously and is believed to have a low, or at best, marginal, potential for gas.

Thermal maturation

Numerous studies on the origin of petroleum and natural gas have established that there is a time-temperature dependence in the transformation of sedimentary organic matter to mobile hydrocarbons. As discussed in Section VIII, one of the best measures of thermal maturation is vitrinite reflectance. Generally, a vitrinite reflectance level of 0.5 percent corresponds to the minimum attainment of the mature stage (mainly oil generation), and a level of 1.2 percent corresponds to the attainment of the super-mature stage (mainly gas generation). Figure VIII-4 is a map of isoreflectance values in the New Albany Shale Group, based on samples from over 100 wells in Illinois. Only the areas on this map with a reflectance greater than 0.5 percent are likely to have significant potential for gas production, and those areas with the highest reflectance are probably the most favorable. Note that the area where reflectance exceeds 0.5 percent coincides with the area of thickest New Albany sediments and the area of greatest accumulation of black shale.

Fracturing and faulting

Most major fault systems in Illinois occur in the extreme southern and southeastern portions of the state (fig. V-2). Extensive natural fracturing is known to occur in the same general area as these faults.

Area of greatest gas potential

Evaluation of these four major geologic criteria—depositional facies, shale thickness, thermal maturation, and known faulting and fracturing—indicates that a 19-county area of southeastern Illinois is geologically the most favorable area in Illinois for shale gas resources (fig. XVI-1). Although numerous oil and gas tests penetrate the Devonian shales in this region, especially in the northernmost counties, relatively few shows of gas have been reported (fig. XVI-2), and there has never been any known commercial production of gas from the shale. There are several possible reasons for the apparent lack of gas shows in Illinois:

1. Virtually all Devonian tests in southern Illinois are drilled with rotary tools. In Indiana and western Kentucky most reported gas shows have resulted from cable tool holes, in which the shows are more noticeable.

2. Mud logging units are not widely employed in Illinois.

3. Operators in Illinois tend to show little interest in Devonian shales; therefore, there probably have been many shows that have not been reported. The marginal economics of shale gas production and the lack of production in Illinois may account for this lack of interest.

4. The Devonian shales beneath Illinois might not be gas bearing.

Except for a few inconclusive or negative drill stem tests of the Devonian shales in wells with gas shows, the producing potential of the shale in southeastern Illinois region was essentially untested until very recently. No gas release data from shale cores were available to use for estimating the quantity of gas in place (if any) or determining the most favorable stratigraphic zones for gas production. Without additional data on gas content or gas production, a geological evaluation must be limited to identifying broad areas that may be favorable for finding gas resources; any quantitative analysis or commercial evaluation of the gas potential would be purely speculative.

Summary of gas release data

In May 1979, Hobson Oil Company, an independent operator based in Flint, Michigan, cored 16 feet (5) of the uppermost New Albany Shale in their #2 Taylor test (section 3 IS-R7E, Wayne County, Illinois). Four samples were removed on-site from is core for off-gas analysis. In September and October of 1979 the U. . Department of Energy funded coring of the entire New Albany Shale Group in ne Gordon T. Jenkins #1 Simpson test (Section 17 T. 3 S., R. 8 E., Wayne Co ty, Illinois). Sixty-six samples were removed for off-gas analysis from e 238 feet (72 m) of Devonian shale recovered.

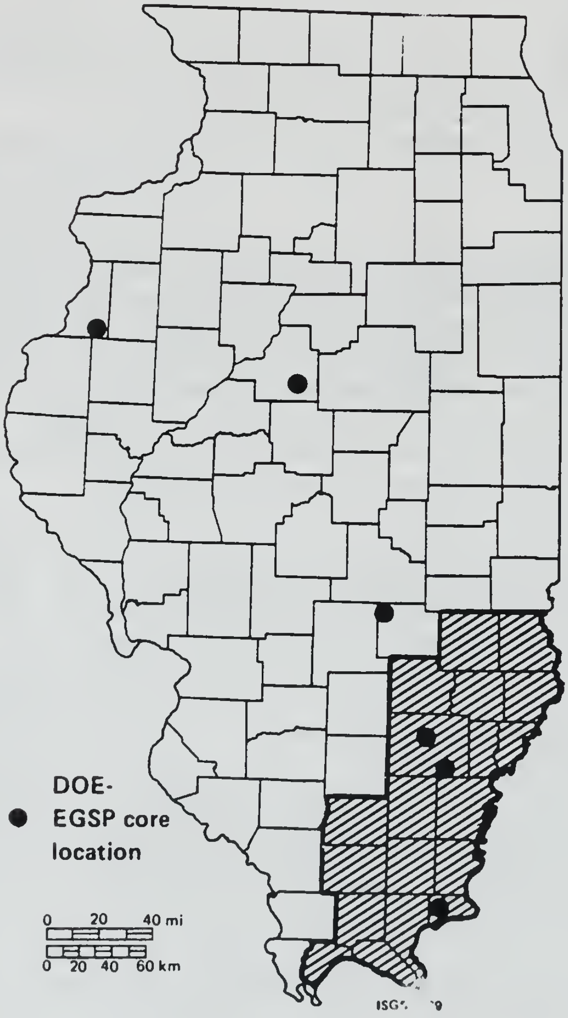


Figure XVI-1. The 19-county area of mo obable Devonian shale gas resources in Illinois, with ions of cores sampled for off-gas analysis.

Figure XVI-2. Locations of known gas shows in the New Albany Shale as of February, 1980.

These two cores provided the first data upon which a more definitive assessment of the gas potential of the New Albany Shale in southeastern Illinois could be made.

As discussed in Section XII the gas released by four samples collected from the Hobson Oil core ranged from 0.55 to 0.82 m^3 hydrocarbons/m^3 shale. The gas was very wet, with more than 25 percent ethane and heavier hydrocarbons (table XII-1).

The quantity of gas released by samples from the G. T. Jenkins core ranged from 0.16 to 2.40 m^3 hydrocarbons/m^3 shale, with the zones of highest gas content generally coinciding with high radioactive intervals (fig. XII-5).

The composition of the released hydrocarbons varied only slightly with stratigraphic position within the shale, averaging 70 percent methane, 19 percent ethane, 8 percent propane, 2 percent butane, and 1 percent heavier hydrocarbons.

Three New Albany Shales had been previously acquired in western and central Illinois as part of this research program. For the most part these cores confirmed the geologic evaluation that in several broad areas of Illinois the New Albany has little or no potential for commercial production. The northernmost two cores, located in Henderson and Tazewell Counties, released insignificant quantities of gas—less than 0.05 m^3 hydrocarbon/m^3 shale. Although the quantities released were very small, the amount of gas released correlated rather closely with the gamma-ray intensity (figs. XII-3, XII-4).

The third core was drilled at the northern edge of Louden Oil Field in Effingham County, Illinois. This core, located in an area where the New Albany is thin, is just outside the 19-county area previously outlined as having favorable geologic characteristics for gas. Although moderate amounts of gas were released by the core samples (generally below 0.5 m^3/m^3 shale; fig. XII-2) isotopic analyses suggest the gas is not indigenous to the shale but rather migrated upward from the underlying Devonian oil reservoir.

CONCLUSIONS

The analysis of two cores from southeastern Illinois demonstrated that: (1) the New Albany contains gas in at least some areas of southeastern Illinois; and (2) the quantity of gas released compares favorably with gas-producing areas in the Appalachian Basin, where gas contents approaching 1.0 m^3 hydrocarbon/m^3 shale are typical. Broad areas of the Devonian shales in Illinois probably have little or no potential for commercial production of gas, on the basis of both geologic data and off-gas analysis of three cores from these outlying areas. The total in-situ gas resource in Illinois is probably much less than a similar sized area in the Appalachian Basin would contain because the New Albany is much thinner and the level of thermal maturation is generally lower; however, the total resource may still be appreciable. In our estimation a quantitative assessment of the resource is still premature because of the very limited data available.

An economic evaluation of the potential for commercial development of this resource is outside the scope of this report. However, the widespread use of conventional rotary drilling with high-density mud-based drilling fluids in Illinois is a major problem in evaluating the commercial potential for gas production from the New Albany Shale. Drilling muds apparently cause extensive formation damage to ultra-low permeability reservoir rocks such as shale, where even minor blockage of the few high-permeability pathways available (including natural fractures) may be disastrous. The gas trapped within shales is released rather slowly and at low pressures; thus the reservoir lacks the energy necessary to clean itself of drilling-induced damage. Unpublished studies in Kentucky and Indiana have shown that the proportion of natural gas shows in the Devonian shales is very much higher in holes drilled with cable tools than in rotary tool holes. This suggests the possibility that drilling with cable tools and water, or, better yet, drilling with air, may be the most satisfactory methods for drilling Devonian shale tests. Because of the numerous water-saturated porous zones in the overlying Mississippi and Pennsylvanian, such techniques would probably require that a casing string be set prior to drilling into the New Albany Shale. Furthermore, conventional drill-stem testing of shales is probably of little value. Drill-stem tests are of short duration and involve very limited quantities of fluids; they are most satisfactory when evaluating rocks with high porosity and permeability. Production testing lasting several days (or even weeks) and involving some type of stimulation technique such as massive hydraulic fracturings would be necessary for any accurate assessment of the commercial viability of a prospect in the Devonian shales. The expense and risk of setting casing and stimulating the shale to evaluate its producing potential will undoubtably be major barriers to the development of this potential but as yet untapped resource.

Natural gas flare.

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