Analysis of the Devonian Black Shale in Kentucky for Potential Carbon Dioxide Sequestration and Enhanced Natural Gas Production (U.S. DOE/NETL DE-FC26-02NT41442)

Keywords: CO_2, adsorption, methane, enhanced recovery

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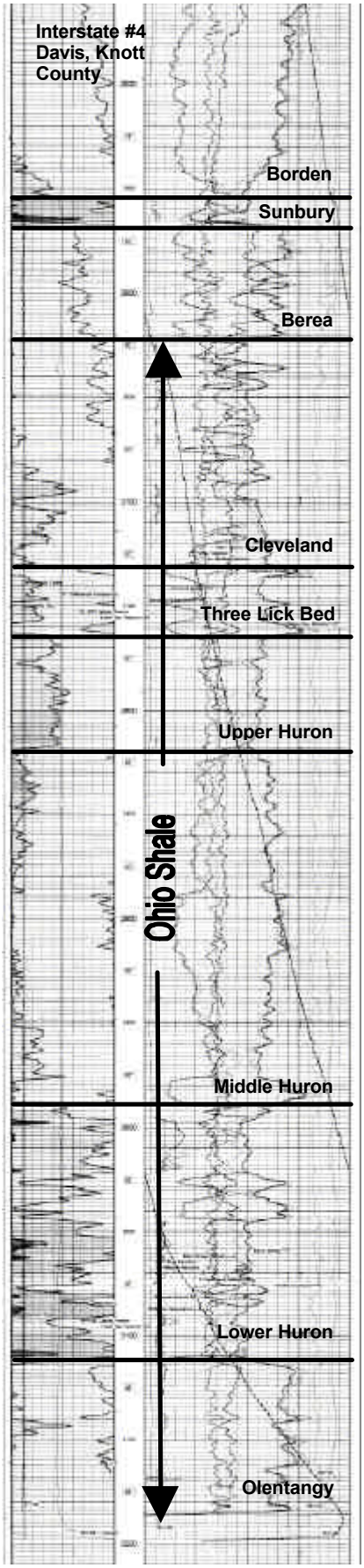
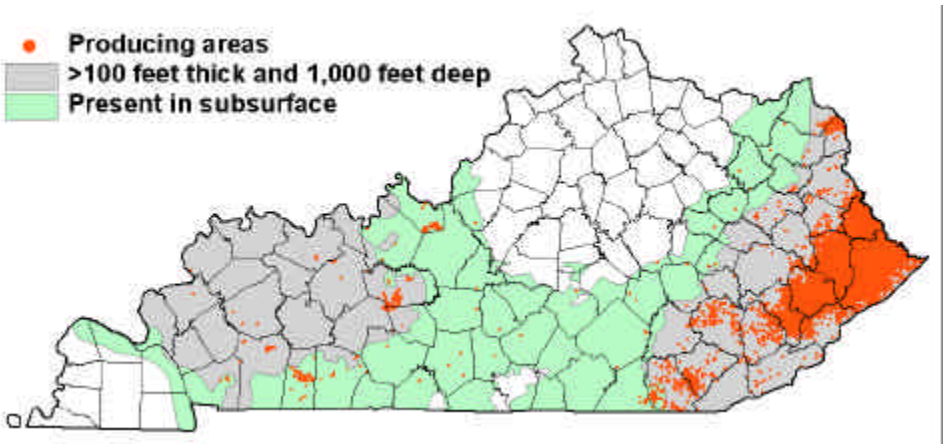
Emissions of CO_2, especially from the combustion of fossil fuels, are being linked to global climate change. One group of proposed carbon management technologies involves geologic sequestration of CO_2. A possible, but untested, sequestration strategy is to inject CO_2 into organic-rich shales of Devonian age. Devonian black shales underlie approximately two-thirds of Kentucky and are generally thicker and deeper in the Illinois and Appalachian Basin portions of Kentucky than in central Kentucky. The Devonian black shales serve as both the source and trap for large quantities of natural gas; total gas in place for the shales in Kentucky is estimated to be between 63 and 112 trillion cubic feet. Most of this natural gas is adsorbed on clay and kerogen surfaces, analogous to the way methane is stored in coal beds. In coals, it has been demonstrated that CO_2 is preferentially adsorbed, displacing methane at a ratio of two to one. Black shales may similarly desorb methane in the presence of CO_2. If this is the case, black shales may be an excellent sink for CO_2, and have the added benefit of serving to enhance natural gas production.

This untested concept that black, organic-rich Devonian shales could serve as a significant geologic sink for CO_2 is the subject of current research. To accomplish this investigation, drill cuttings and cores will be selected from the Kentucky Geological Survey Well Sample and Core Library. Carbon dioxide adsorption analyses will be performed in order to determine the gas-storage potential of the shale and to identify shale facies with the most sequestration potential. In addition, new drill cuttings and sidewall core samples will be acquired to investigate specific black-shale facies, their potential CO_2 uptake, and the resulting displacement of methane. Advanced logging techniques (elemental capture spectroscopy) will be used to investigate possible correlations between adsorption capacity and geophysical log measurements.

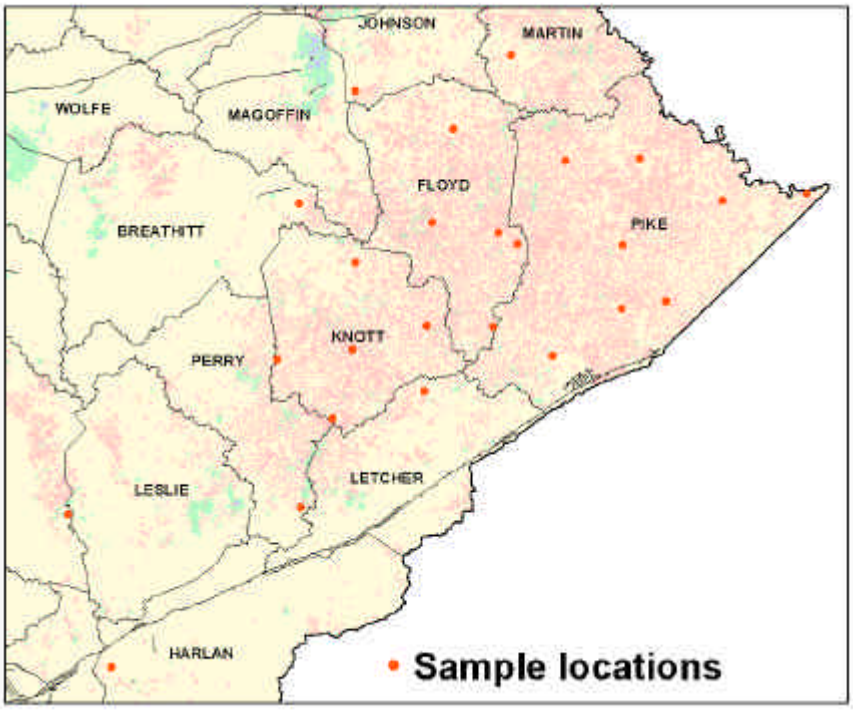
Should the Devonian black shales of Kentucky prove to be a viable geologic sink for CO_2, their extensive occurrence in Paleozoic basins across North America would make them an attractive regional target for CO_2 storage and enhanced natural gas production.

Research sponsored by the National Energy Technology Laboratory, U.S. Department of Energy





Distribution of the Devonian black shale in Kentucky



Wells to be sampled for petrographic and CO_2 adsorption analysis

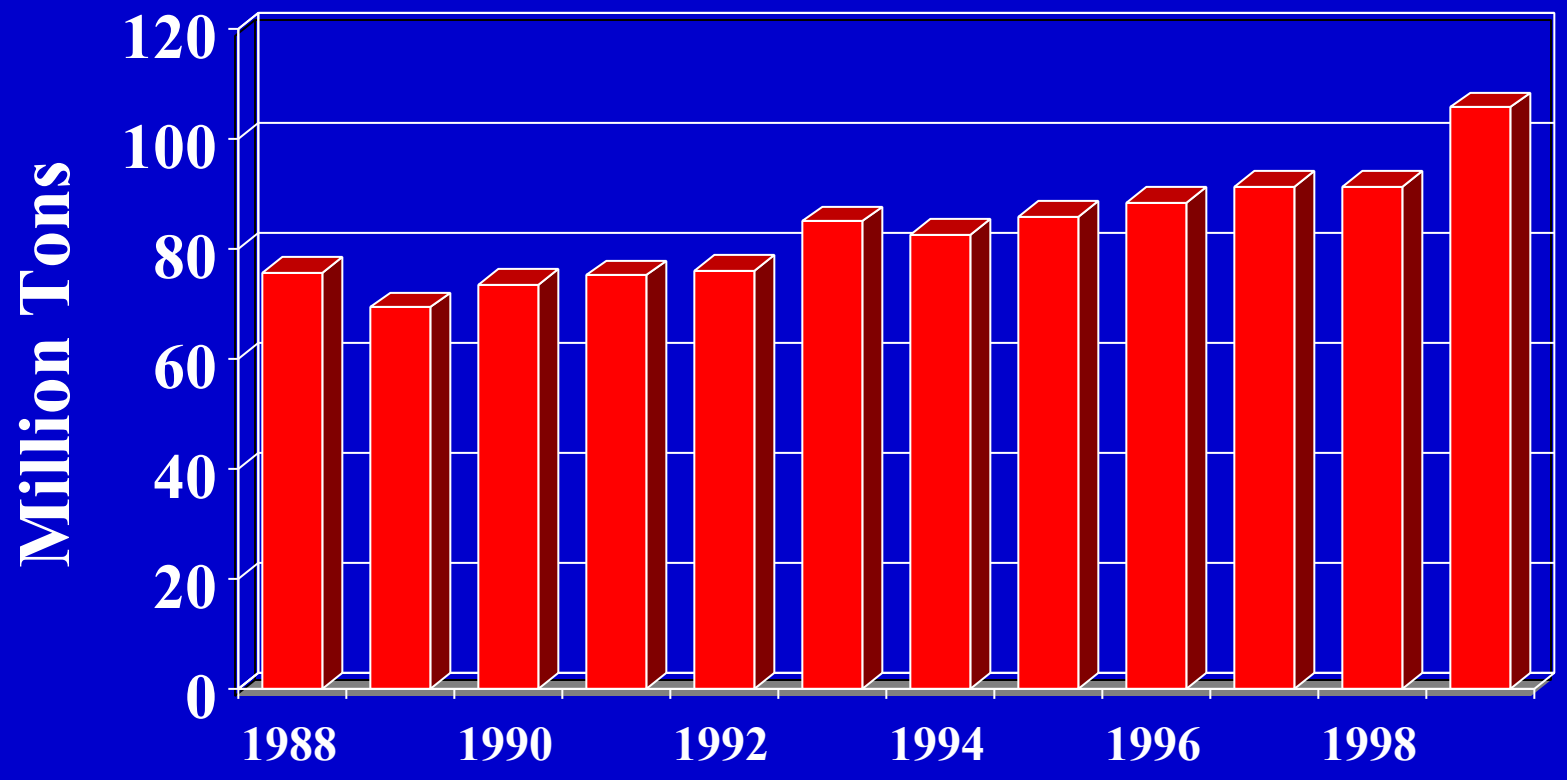
Analysis of the Devonian Shale in Kentucky for Potential CO_2 Sequestration and Enhanced Natural Gas Production

U.S. DOE/NETL DE-FC26-02NT41442

Brandon C. Nuttall, James A. Drahovzal, Cortland F. Eble, R. Marc Bustin

Kentucky Geological Survey
UNIVERSITY OF KENTUCKY

Kentucky CO_2 Emissions



Compiled from www.eia.doe.gov

Mitigate Atmospheric CO_2

- Reduce emissions
- Seqestration (disposal)

CO_2 Sequestration Strategies

- **Marine**

- ✓ Droplet plume
- ✓ Towed pipe
- ✓ Dry ice
- ✓ CO_2 lake (depths below 3,000 meters)

CO_2 Sequestration Strategies

- Marine
- Terrestrial

✓Soils

✓Biosphere

CO_2 Sequestration Strategies

- Marine
- Terrestrial
- Geologic

✓ Oil and gas fields

✓ Saline aquifers

✓ Unconventional reservoirs

✓ Coal

✓ Organic-rich black shale?

KGS

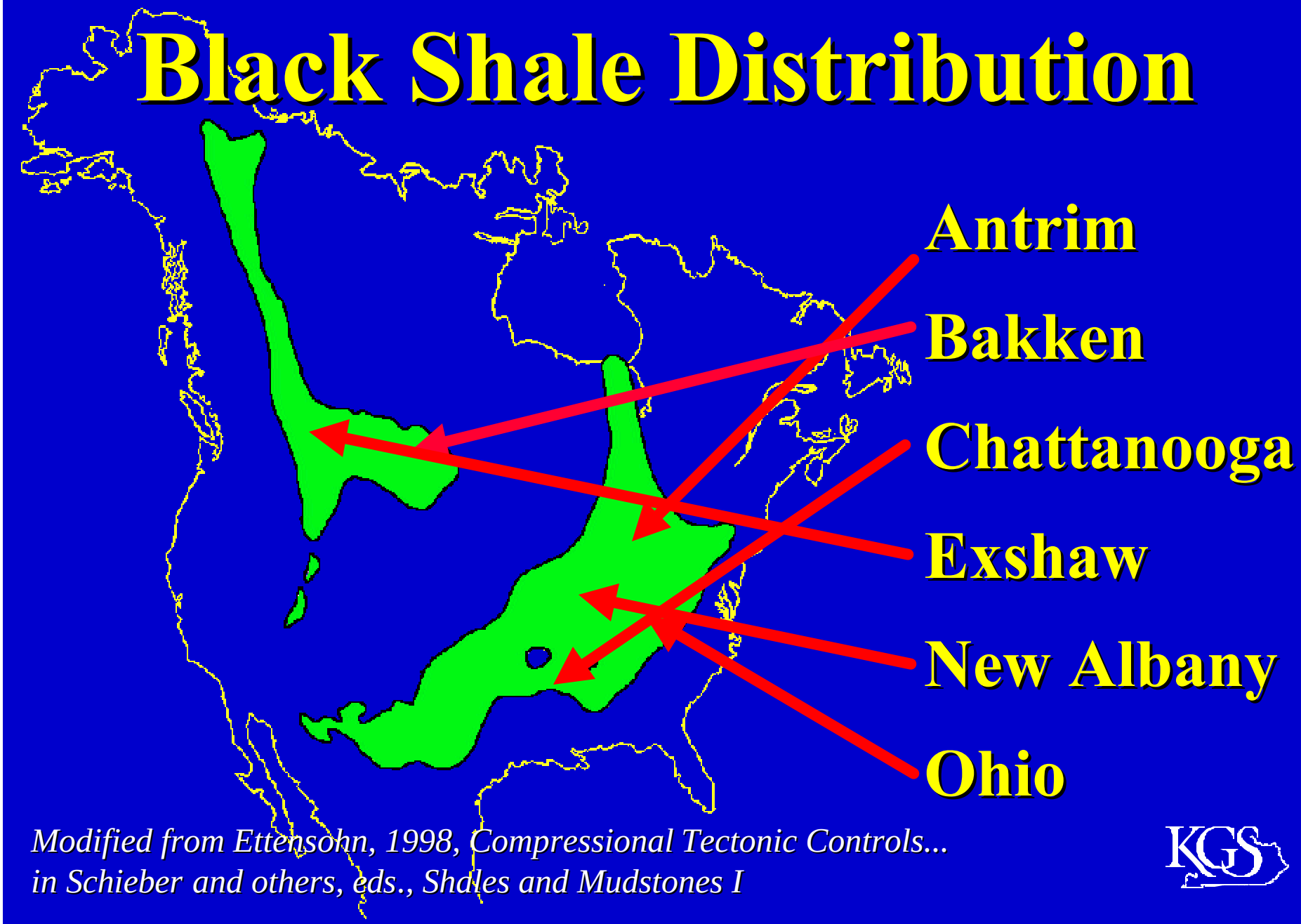
Basic Goals

- CO_2 sorption capacity
- CH_4 displacement potential

Why Black Shales?

- Distribution and potential storage volume
- Known producer
  - Gas adsorbed on kerogen and clay
- Analogous to CBM?

Black Shale Distribution

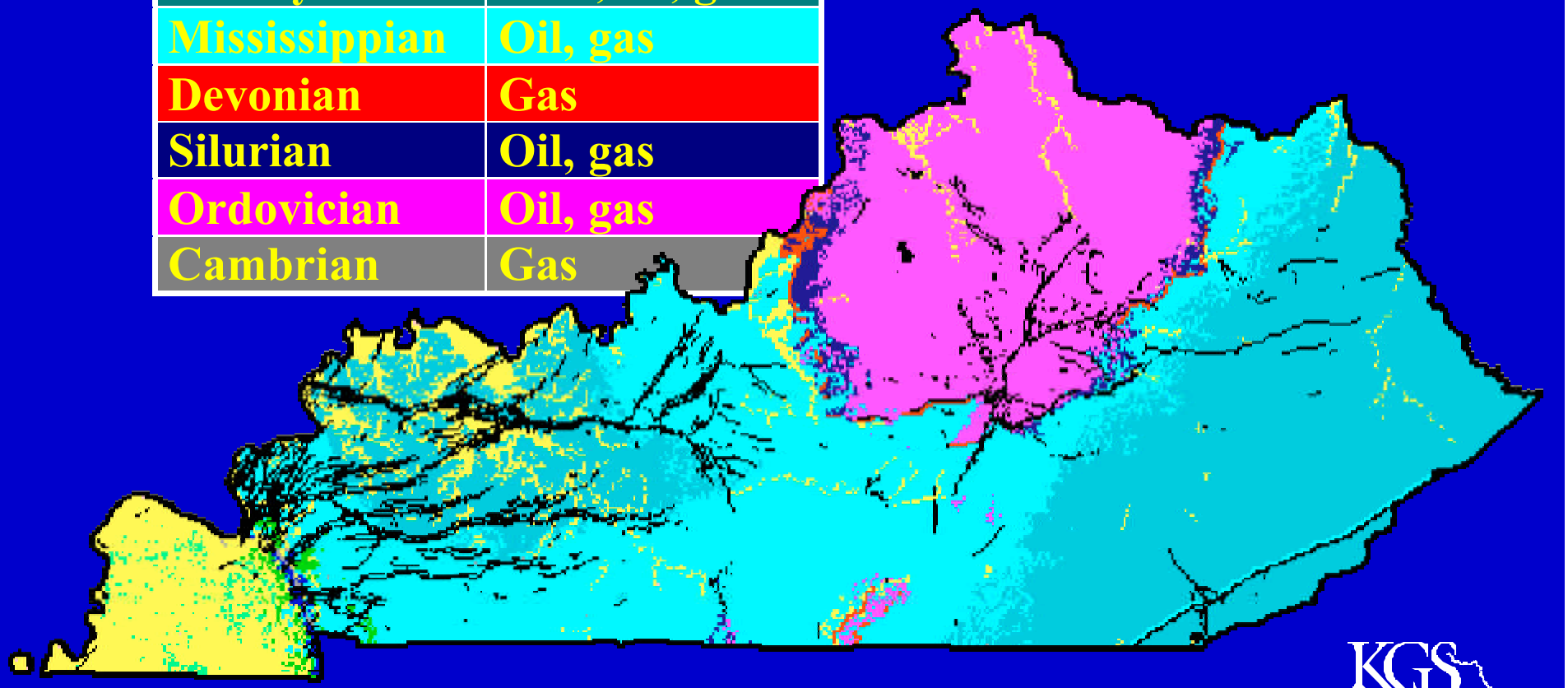


Modified from Ettensohn, 1998, Compressional Tectonic Controls... in Schieber and others, eds., Shales and Mudstones I

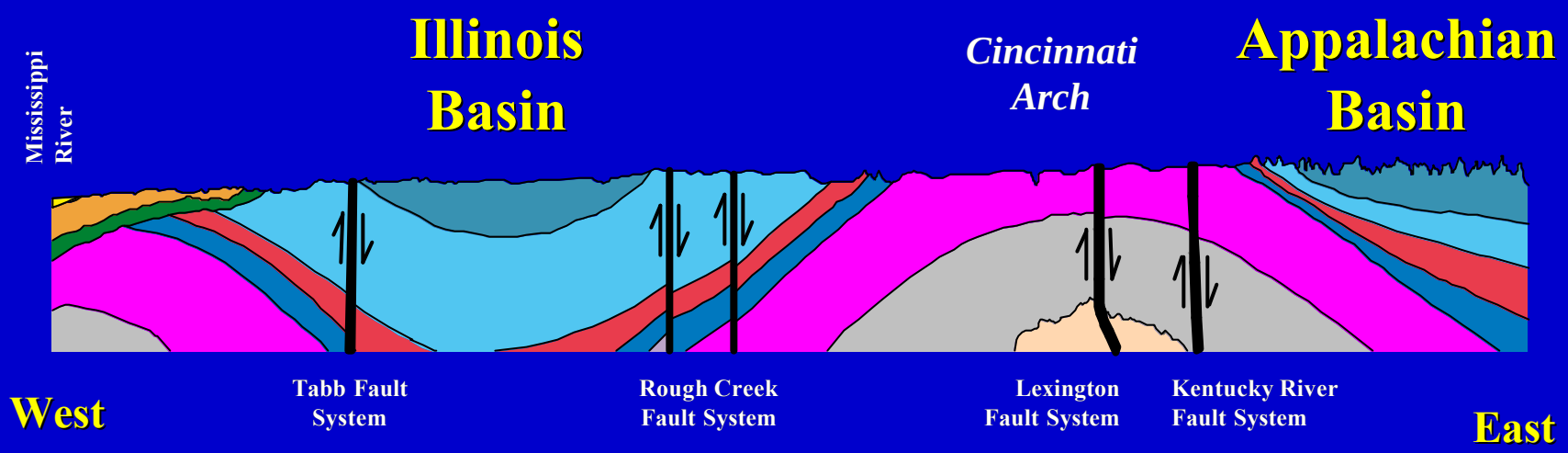
KGS

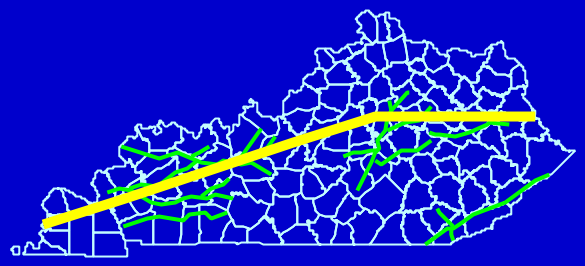
Geology of Kentucky

System	Resource
Pennsylvanian	Coal, oil, gas
Mississippian	Oil, gas
Devonian	Gas
Silurian	Oil, gas
Ordovician	Oil, gas
Cambrian	Gas



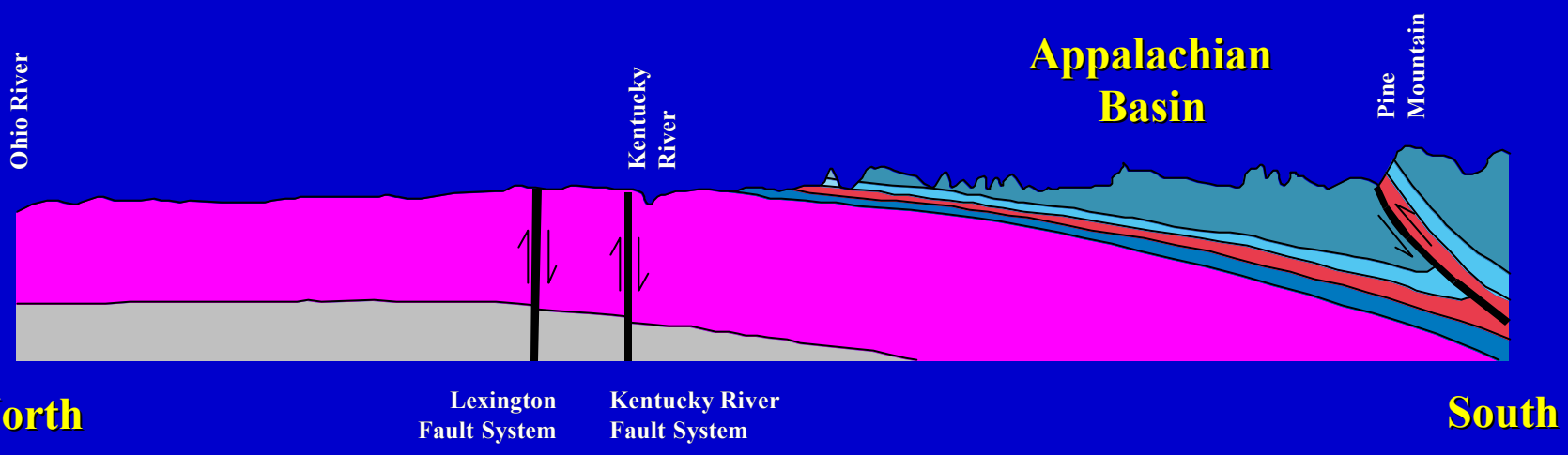
W–E Cross Section

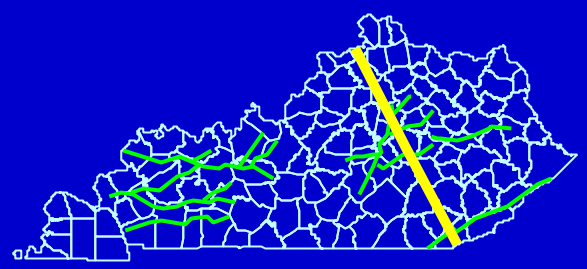




Two major coal basins separated by an arch.

N–S Cross Section

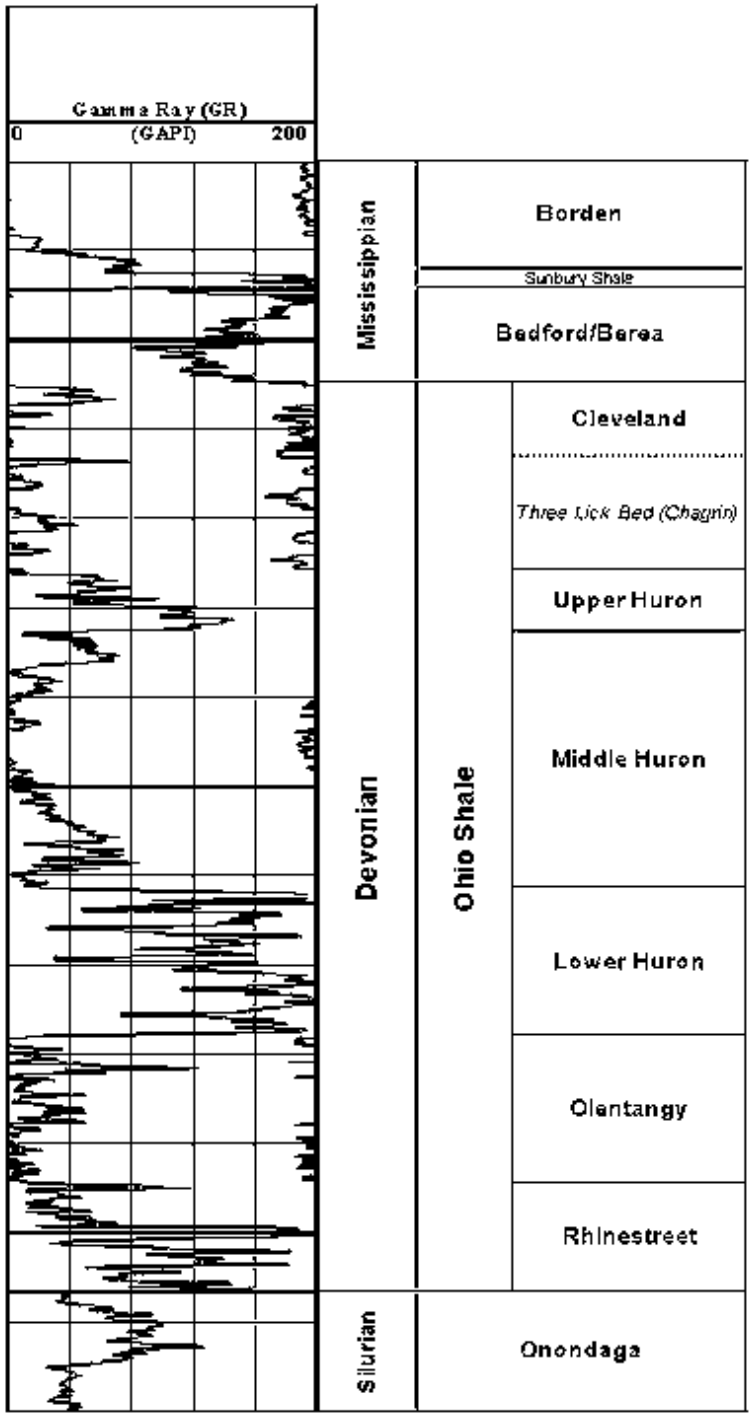




Basin subdivided by fault at Pine Mountain.

Shale Nomenclature

Hamilton-Smith, 1993, Gas Exploration in the Devonian Shales of Kentucky: KGS, Ser 10, Bul. 4.

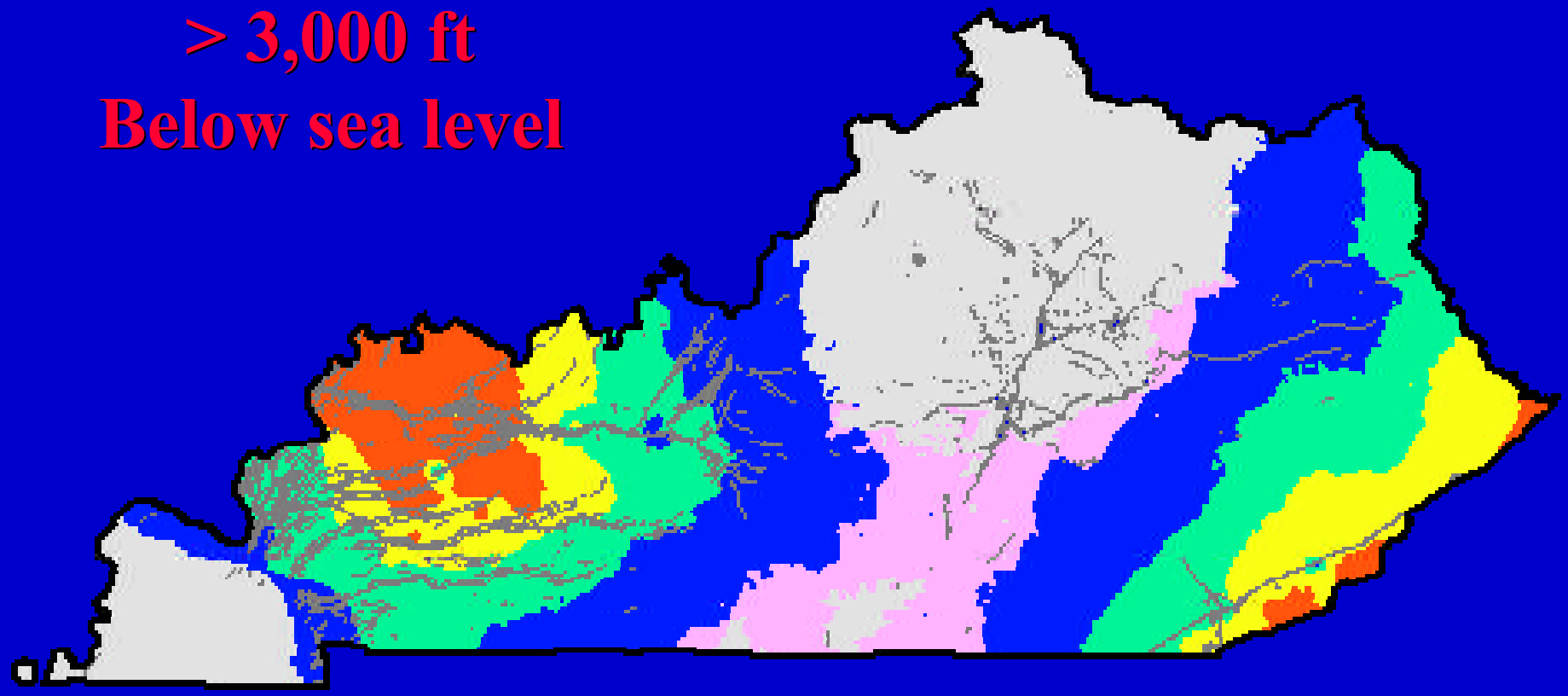


Devonian Shale Type Log, Eastern Kentucky

Lower Huron is thought to have the most sequestration potential.

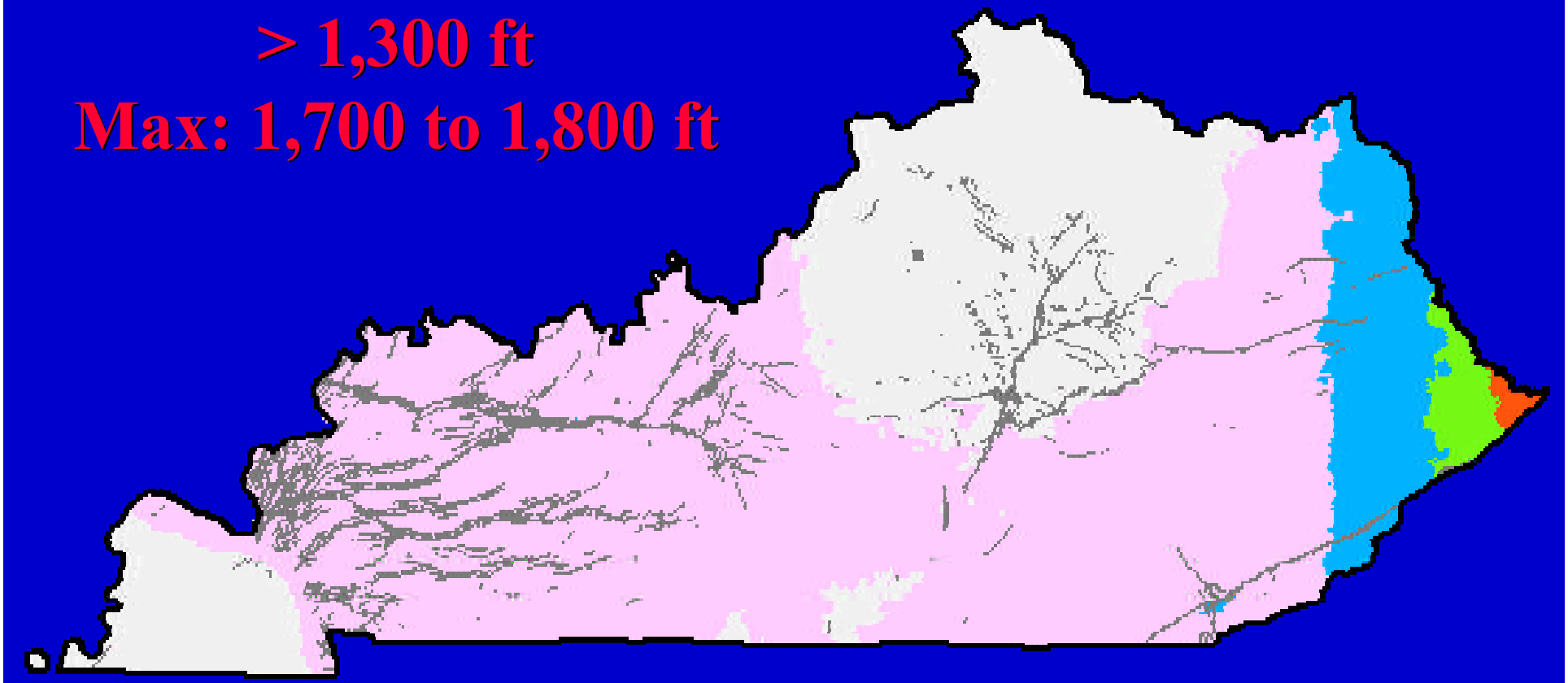
Structure on Top of Shale

> 3,000 ft
Below sea level



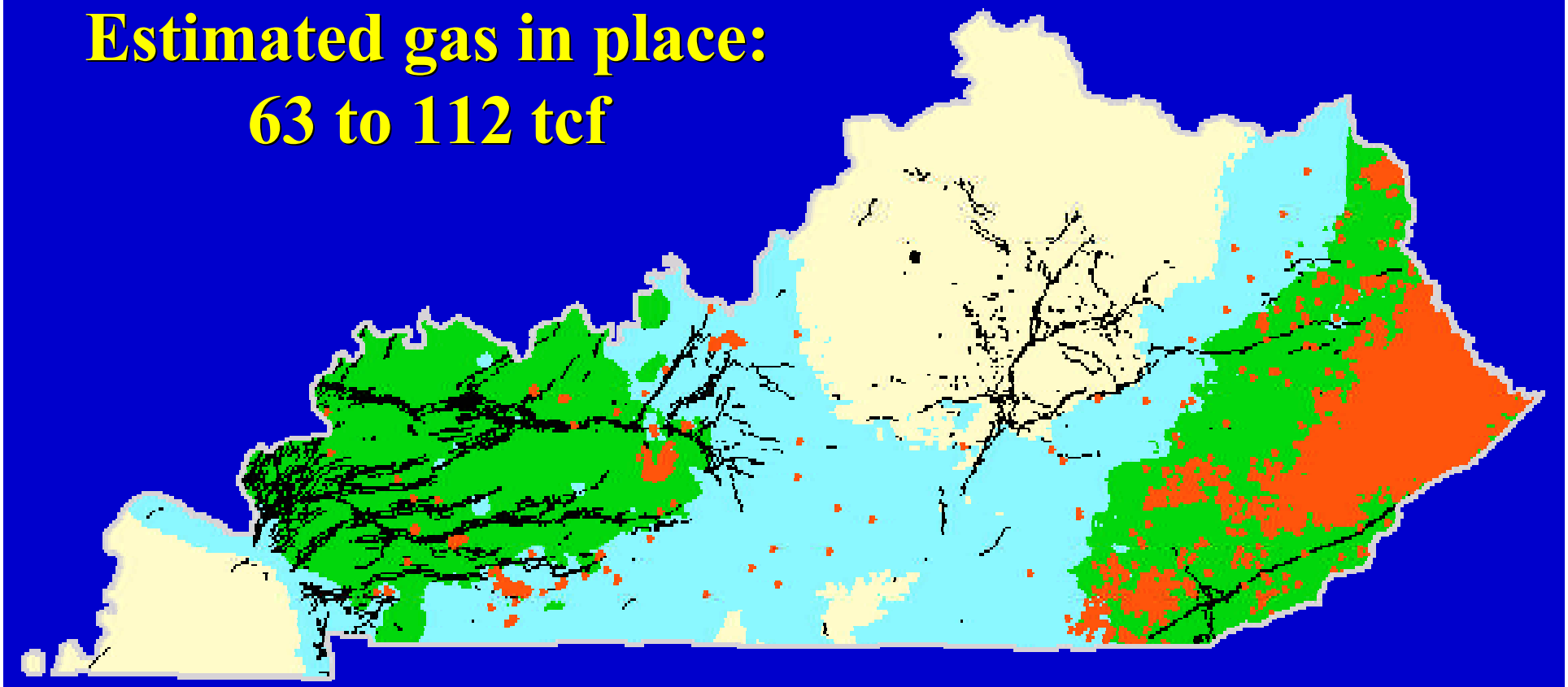
Shale Isopach

> 1,300 ft
Max: 1,700 to 1,800 ft



Devonian Shale in Kentucky

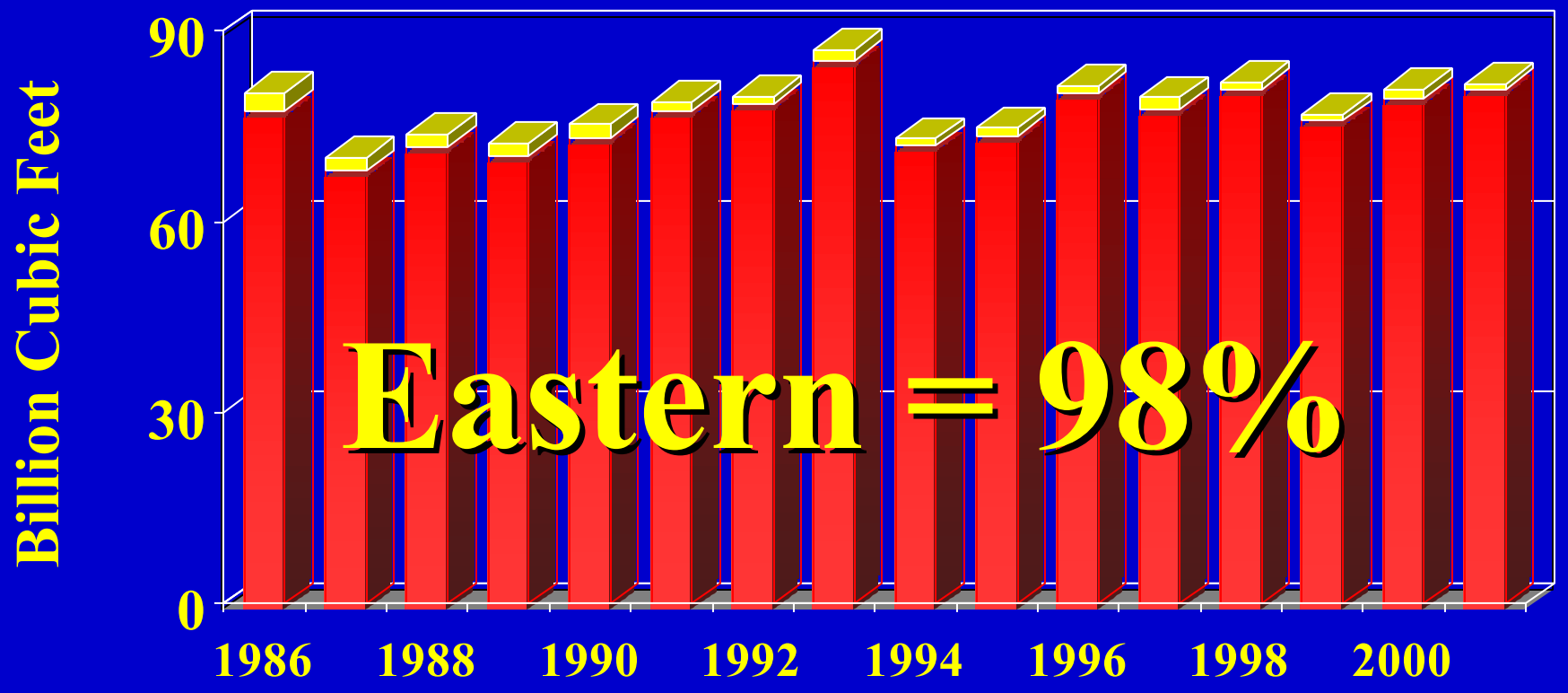
Estimated gas in place:
63 to 112 tcf



Gas-producing fields **>1,000 ft deep & >100 ft thick**

KGS

Gas Production

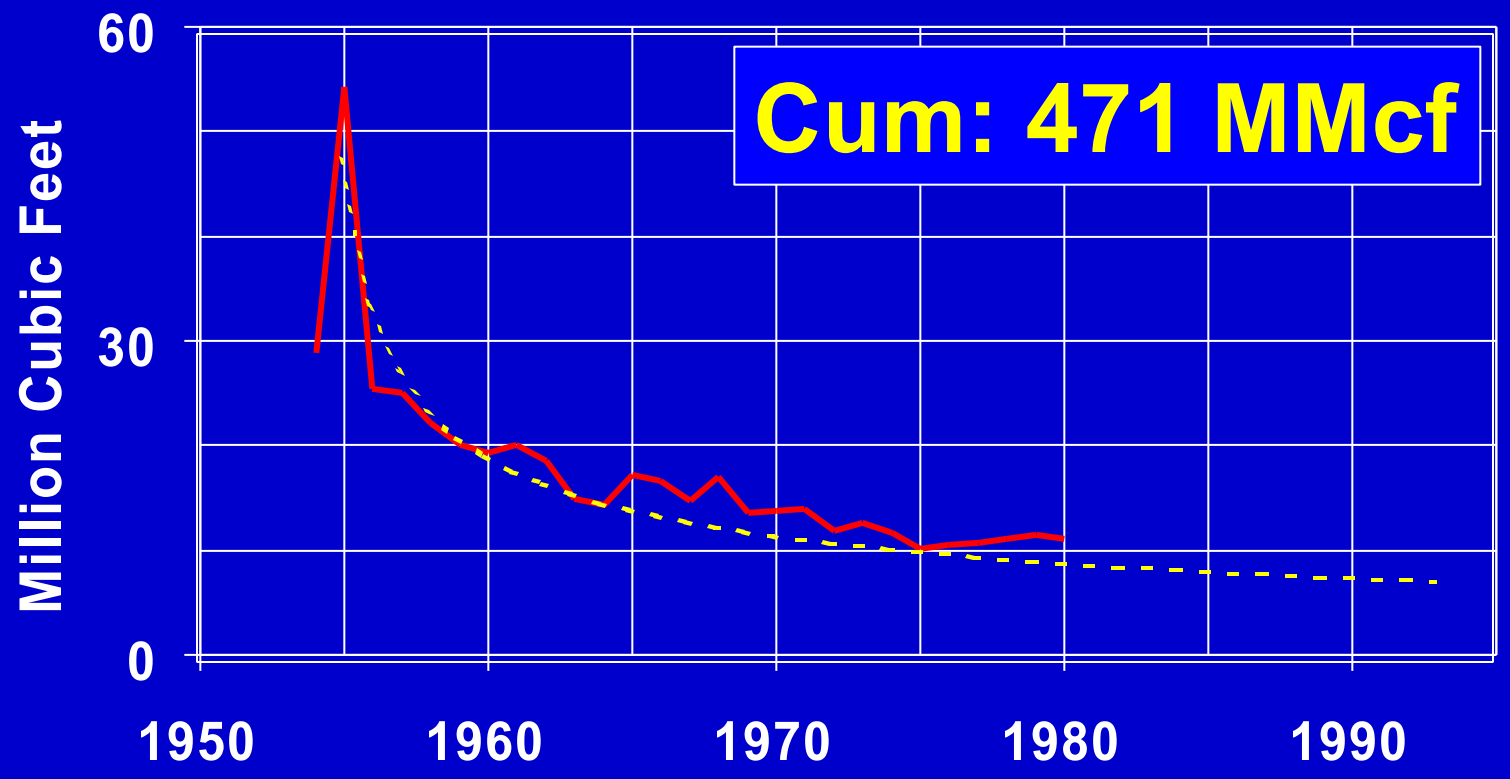


Organic Content

- Mixture type I and type II
- 7 weight-% average
- Range < 0.5 to > 23 weight-%

Ettensohn, 1998, Compressional Tectonic Controls...
in Schieber and others, eds., Shales and Mudstones I

Classic Production Decline



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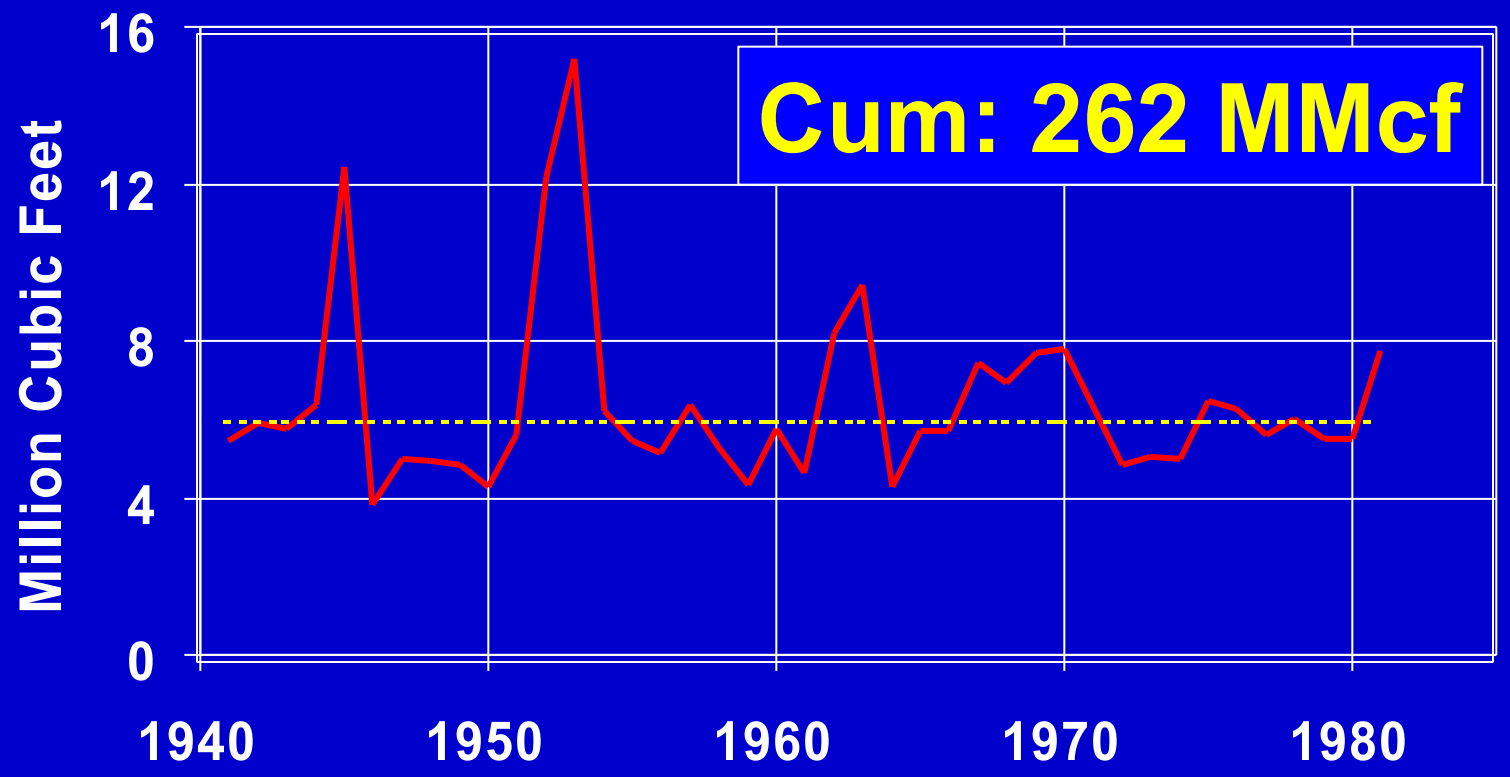
Eastern Kentucky Devonian Shale Gas Production

KGS

Flat Production



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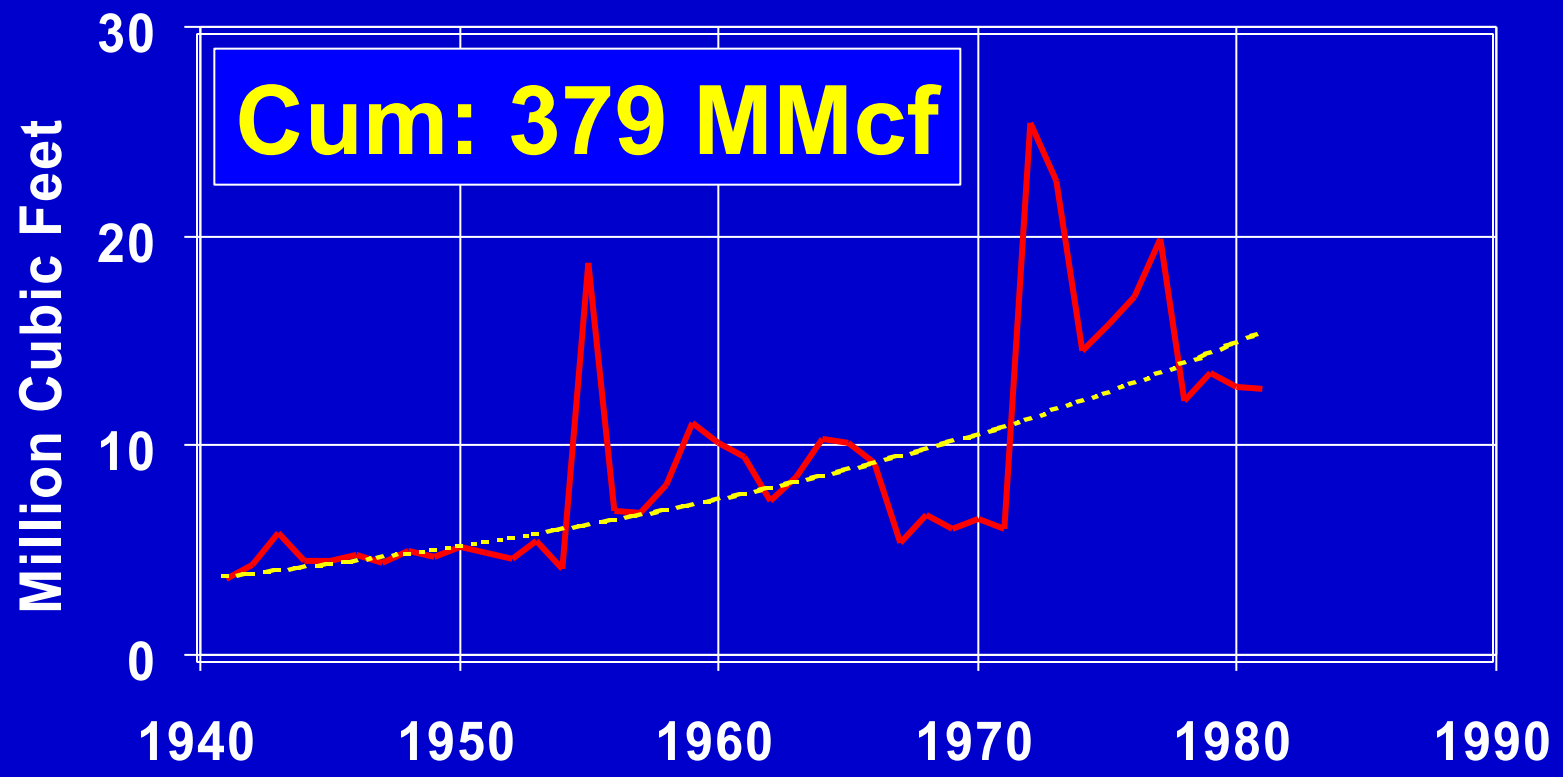
Eastern Kentucky Devonian Shale Gas Production

KGS

Production Incline Suggests Adsorbed Gas

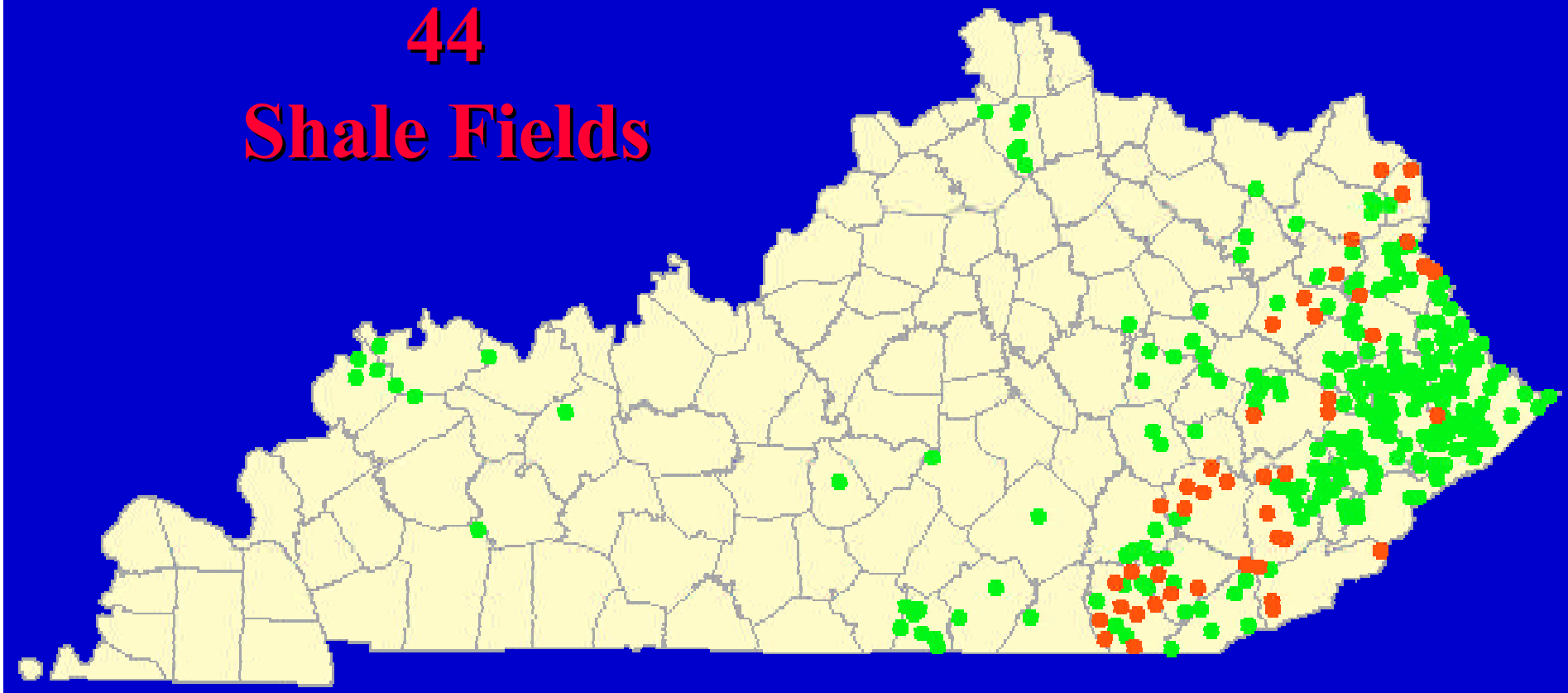


Eastern Kentucky Devonian Shale Gas Production

Gas Atlas and TORIS

44

Shale Fields



Locations approximated using centroids

Estimate Storage Capacity

$$43560\,A\,t\,f\left(1 \quad S_w\right)\frac{520}{460+T_r}\frac{P_r}{14.73}Z_r^{\;1}$$

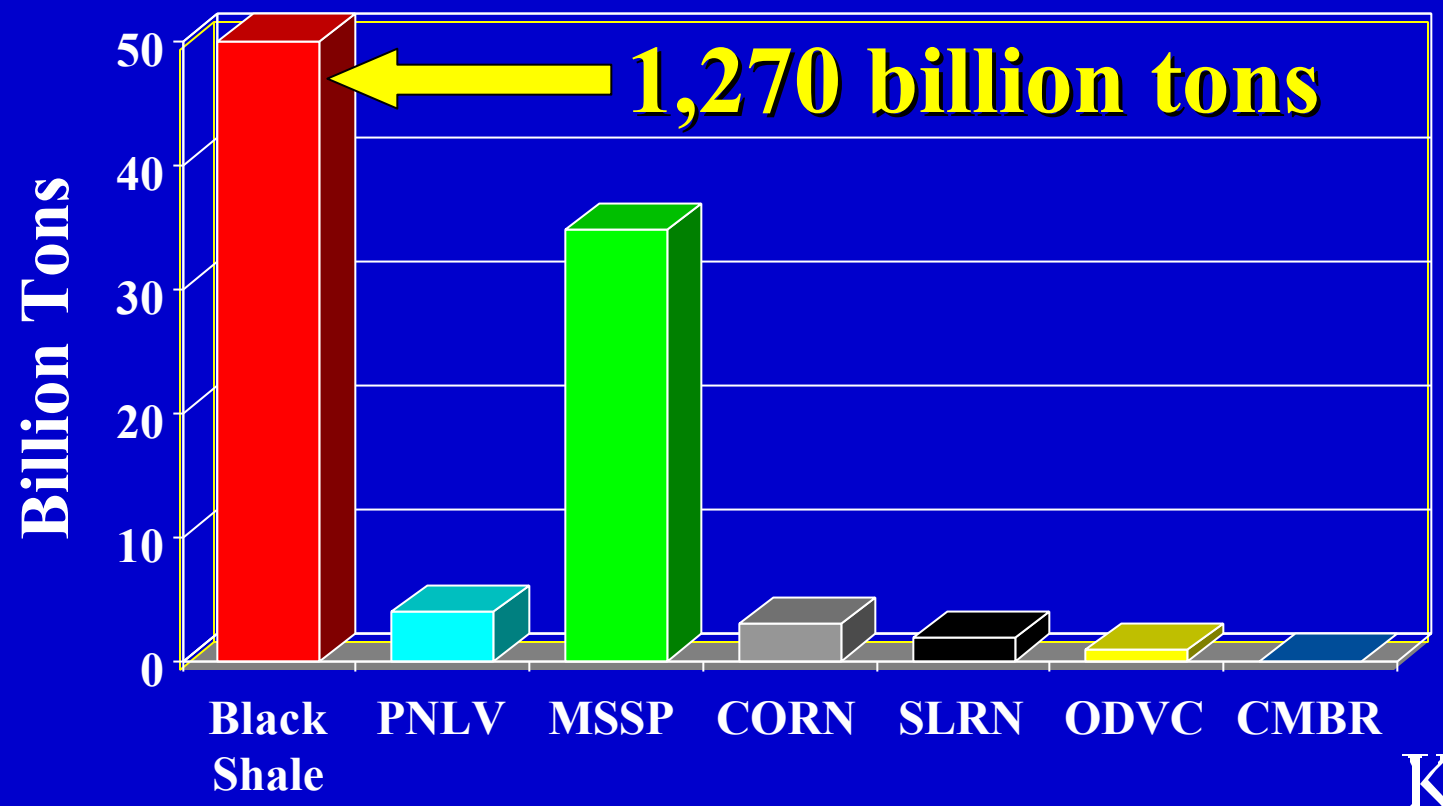
- Acres
- Thickness
- Porosity
- Water saturation
- Temperature
- Pressure
- Compressibility

Assumptions for Missing Data

- Area = wells * spacing
- Thick = completion, else 10 ft
- Porosity = 4.5% (shale) else 11%
- Sw = 1.5% (shale) else 30%
- Temp = 61 + 0.007 * depth
- Press = 300 (median, shale) else 0.4 * depth

Preliminary CO_2 Capacity

±12,000 times the 1999 Kentucky emissions

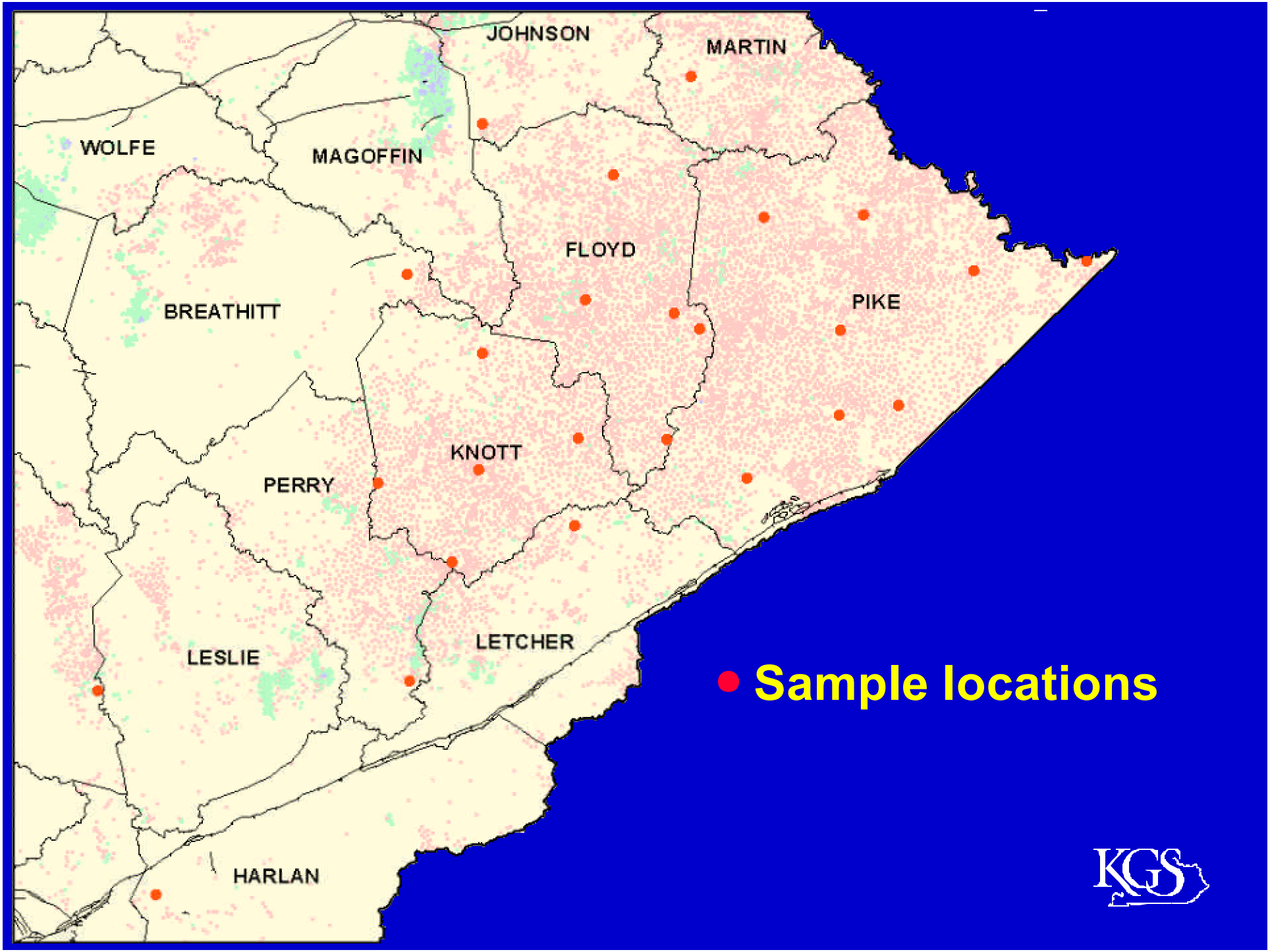


Work Plan: Year 1

- KGS Well Sample Library
  - Identify drill cuttings
  - Petrology
  - Sorption isotherms
  - Identify optimum shale facies

Sampling Criteria

- Minimize sample alterations
  - Recent wells
  - Unwashed samples
- Geophysical logs available
- Distributed over shale gas producing area


JOHNSON
MARTIN
WOLFE
MAGOFFIN
FLOYD
PIKE
BREATHITT
KNOTT
PERRY
LETCHER
LESLIE
HARLAN
Sample locations
KGS

Samples As Received

Operators must submit samples if requested by the Survey.

Unwashed Samples

Sample sets are identified, boxed, and shelved.

Sorting cuttings

Drill cuttings are sorted by depth and placed into polyethylene bags.

Sampling Drill Cuttings

Drill cuttings are sampled and the composite samples are submitted for analysis.

Petrographic Analysis

Cuttings are processed into standard pellets for analysis.

Work Plan: Year 2

- Cooperative access to new well
  - Sidewall core
  - ECS logging suite
  - Petrology
  - CO_2 sorption/CH_4 displacement

Work Plan: Year 3

- Reporting and technology transfer
  - Finish long-term sorption analyses
  - Implement Web data interface
  - Final report

Conclusion

The organic-rich Mississippian–Devonian shales of Kentucky have the potential to sequester large volumes of CO_2.

(If the idea works.)

ANALYSIS OF DEVONIAN BLACK SHALES IN KENTUCKY FOR POTENTIAL CARBON DIOXIDE SEQUESTRATION AND ENHANCED NATURAL GAS PRODUCTION

QUARTERLY REPORT
January 1, 2003 to March 31, 2003

Brandon C. Nuttall

Report Issued: April 28, 2003

DE-FC26-02NT41442

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Abstract

Proposed carbon management technologies include geologic sequestration of CO_2. A possible, but untested, strategy is to inject CO_2 into organic-rich shales of Devonian age. Devonian black shales underlie approximately two-thirds of Kentucky and are generally thicker and deeper in the Illinois and Appalachian Basin portions of Kentucky. The Devonian black shales serve as both the source and trap for large quantities of natural gas; total gas in place for the shales in Kentucky is estimated to be between 63 and 112 trillion cubic feet. Most of this natural gas is adsorbed on clay and kerogen surfaces, analogous to the way methane is stored in coal beds. In coals, it has been demonstrated that CO_2 is preferentially adsorbed, displacing methane at a ratio of two to one. Black shales may similarly desorb methane in the presence of CO_2. If black shales similarly desorb methane in the presence of CO_2, the shales may be an excellent sink for CO_2 with the added benefit of serving to enhance natural gas production.

The concept that black, organic-rich Devonian shales could serve as a significant geologic sink for CO_2 is the subject this research. To accomplish this investigation, drill cuttings and cores will be selected from the Kentucky Geological Survey Well Sample and Core Library. CO_2 adsorption analyses will be performed in order to determine the gas-storage potential of the shale and to identify shale facies with the most sequestration potential. In addition, new drill cuttings and sidewall core samples will be acquired to investigate specific black-shale facies, their uptake of CO_2, and the resultant displacement of methane. Advanced logging techniques (elemental capture spectroscopy) will be used to investigate possible correlations between adsorption capacity and geophysical log measurements.

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Executive Summary

Increased emissions of CO_2, especially from the combustion of fossil fuels, are being linked to global climate change and are of considerable global concern. These concerns are driving initiatives to develop carbon management technologies, including geologic sequestration of CO_2. One option for sequestration may be Devonian black shales, organic-rich rocks that serve as both the source and trap for natural gas. Most of the natural gas is adsorbed on clay and kerogen surfaces, very similar to the way methane is stored within coal beds. It has been demonstrated in gassy coals that, on average, CO_2 is preferentially adsorbed, displacing methane at a ratio of two for one. Black shales may similarly desorb methane in the presence of adsorbing CO_2. If this is the case, black shales may be an excellent sink for CO_2 and have the added benefit of serving to enhance natural-gas production. A bibliography of Devonian shale has been compiled to identify previous work and provide supporting data for continued research.

Because of the volume of material lost during washing the sampling protocol has been modified to collect cuttings before washing. Unwashed candidate samples have been selected and are being prepared for total organic carbon (TOC), vitrinite reflectance ($R_{0\ random}$), and petrographic and CO_2 adsorption analyses to determine the gas-storage potential of the shale and to identify shale facies with the most sequestration potential.

Introduction

Since the discovery of natural gas production from the Devonian shales of Kentucky between 1858 and 1865, these carbonaceous shales have constituted an important energy resource in Kentucky. Thick and deep sequences of shale exist in both the Illinois and Appalachian Basins (Figure 1). Greenhouse gases, CO_2 emissions in particular, are being linked to global climate change. If regulations are adopted that require limiting CO_2 emissions, disposal strategies must be identified. Using CO_2 flooding of coals as a model, the large component of adsorbed natural gas in organic-rich shales suggest that black shale might be an attractive sequestration target.

The project is concentrating on the Devonian Ohio shale of eastern Kentucky (Figure 2). This area is both the most active area (number of wells drilled over the past 5 years) and the most prolific natural gas producing area in the state accounting for 98 percent of Kentucky's gas production. The Kentucky Geological Survey maintains an extensive collection of cuttings recovered during oil and gas well drilling in the Well Sample and Core Library.

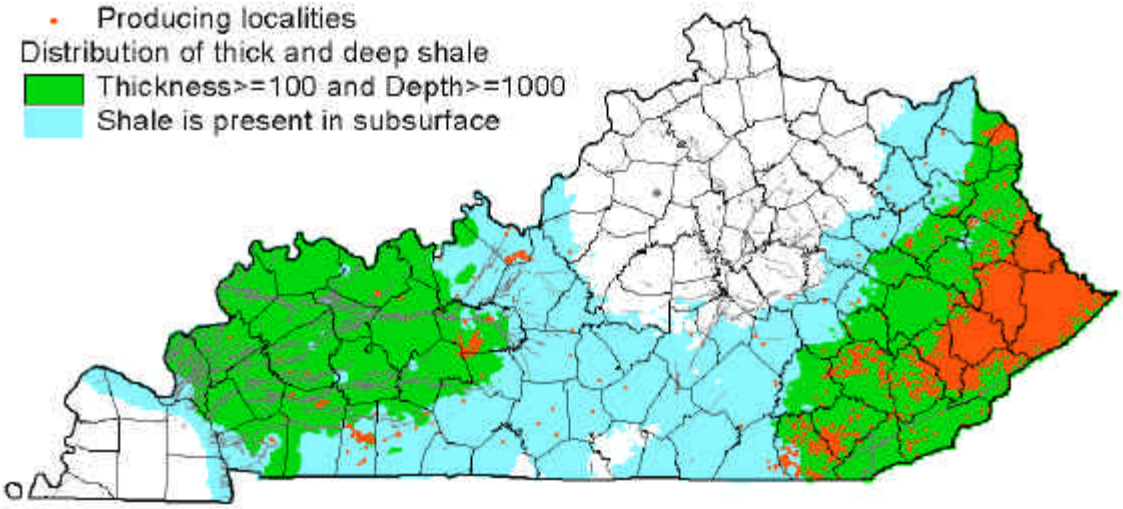


Figure 1. Map of the distribution of the Devonian shale in Kentucky, showing the occurrence of deeper and thicker shale with possibly greater potential for geologic sequestration of CO_2.

Figure 2. Map showing distribution and nomenclature of Devonian shales of Kentucky (Hamilton-Smith, 1993, p. 3)

Experimental

1) The sampling protocol has been modified to eliminate washing and air-drying of drill cuttings. Washing the samples resulted in the loss of too much material. In one case, a substitute for a selected well had to be chosen because insufficient material was available for sampling after washing. Eliminating air drying of the samples saves about one week per each well sampled.
2) Unwashed sets of recently acquired drill cuttings have been identified. These samples are being sorted and processed to place them in permanent storage bags and boxes.
3) The well sample data spreadsheet has been matched to the main oil and gas well record database in order to compile a GIS coverage of these data (**Figure 4**). The GIS was used to select wells that best represent a uniform coverage of the study area and provide information useful for targeting the area to be sampled by sidewall coring in year 2.

Results and Discussion

Distribution and stratigraphy of the Devonian shale in eastern Kentucky suggest dividing well cuttings into up to three samples for adsorption analysis. The upper part of the shale from the Cleveland Member to the Middle Huron is generally less organic-rich as indicated by the gamma-ray response on standard geophysical well logs (Figure 3). Drill cuttings of this sequence generally have a lighter gray color and more recognizable quartz material than the darker gray to black samples with sparse pyrite that are characteristic of the Lower Huron Member. In some areas of the Big Sandy Gas Field, the Olentangy and Rhinestreet members of the Ohio shale are present but have a somewhat lesser organic content. Where present, these shales will be composited as a separate sample.

A database of candidate Devonian shale wells for sampling was compiled. Kentucky statutes [KRS 353.660(2)] provide the Survey with the right to request well samples. In anticipation of this project, samples were requested for proposed Devonian shale penetrations in eastern Kentucky. Paper records of well samples received were requested from staff of the well cuttings and cores repository and entered into an Excel spreadsheet. A total of 595 candidate wells have been identified (**Figure 4**). Geophysical logs

from these wells are being scanned to assist in stratigraphic interpretation. A GIS will be used to select wells that best represent a uniform coverage of the study area and provide information useful for targeting the area to be sampled by sidewall coring in year 2.

While processing unwashed and cataloged drill cuttings at the Well Sample and Core Library, several pallets of recently received, unwashed, but uncataloged, cuttings were located. These drill cuttings have been identified and incorporated into the GIS for sampling.

The final distribution of wells selected for sampling is illustrated in Figure 5. A list of these wells is provided in Table 1.

Table 1. Wells to sample for the Devonian Shale CO_2 Sequestration project.

PERMIT	OPERATOR	WELL	FARM_NAME	COUNTY	SEC	LTR	NUM	TOTAL_	TDFM
84653	ASHLAND EXPLORATION, INC	60	FORD MOTOR COMPANY	Pike	19	M	88	6130	361SQTC
90973	BRADLEY, CHARLES R DBA BASIN ENE	1	NORDMAN, EARLENE	Magoffin	1	O	79	2390	357CBOC
91129	KINZER, J W	1003	PIKE LETCHER LAND CO	Letcher	4	I	81	3814	341OHIO
91151	EQUITABLE PRODUCTION COMPANY	KF-4448	EQUITABLE PRODUCTION CO	Floyd	25	K	83	3964	341OLNG
91182	EQUITABLE PRODUCTION COMPANY	KL4390	HOPKINS, JC & VALENTINE	Floyd	4	N	82	2358	341OLNG
91355	KINZER, J W	1052	KINZER, J W	Pike	20	M	90	5199	347HDBG
91796	PENN-VIRGINIA OIL & GAS CORP	11	KENTENIA	Harlan	7	D	73	4327	361ODVCU
92640	EQUITABLE PRODUCTION COMPANY	KL4-504695	LOWE, A HEIRS	Pike	20	N	84	3639	341OLNG
92647	ENERGY ASSOCIATES, INC	1	ASHER, IDA ET AL	Clay	8	G	72	2755	357CLNT
92715	COLUMBIA NATURAL RES, INC	24526	BUSH, JOHN ET AL	Floyd	9	L	83	3268	341OHIO
93241	EQUITABLE PRODUCTION COMPANY	505045	EVANS, E J	Knott	12	L	79	2770	341HURNL
93411	EQUITABLE PRODUCTION COMPANY	505040	EQUITABLE PRODUCTION COMPANY	Breathitt	7	M	78	2760	341OLNG
93453	EQUITABLE PRODUCTION COMPANY	504725	EQUITABLE PRODUCTION CO	Knott	11	I	78	3550	341OLNG
93520	EQUITABLE PRODUCTION COMPANY	504984	EQUITABLE PRODUCTION CO	Knott	9	J	77	3682	341OLNG
93560	EQUITABLE PRODUCTION COMPANY	504384	THE ELK HORN COAL CORP	Floyd	22	M	81	2510	341OLNG
93762	C D & G ENT - JOHNSON, GARY C	1	MCGINNIS, BASIL ET AL	Martin	19	P	83	2879	341OHIO
93844	BRADLEY, CHARLES R DBA BASIN ENE	1	RIDDLE, TROY	Perry	6	G	78	3905	341OHIO
94045	COLUMBIA NATURAL RES, INC	24875	KENTUCKY BERWIND LAND CO	Pike	14	K	87	4975	341OHIO
94086	INTERSTATE NATURAL GAS CO	4	DAVIS, IDA	Knott	24	K	81	3190	341OHIO
94088	EQUITABLE PRODUCTION COMPANY	505313	EQUITABLE PRODUCTION CO	Pike	16	K	86	4182	341OLNG
94107	EQUITABLE PRODUCTION COMPANY	505333	EQUITABLE PRODUCTION CO	Pike	14	L	86	4360	341OLNG
94174	COLUMBIA NATURAL RES, INC	23798	HAYS, LUTITIA ET AL	Knott	8	J	79	3256	341OHIO
94175	EQUITABLE PRODUCTION COMPANY	504790	TIERNEY, LAWRENCE E	Pike	19	N	86	4150	341OLNG
94210	EQUITABLE PRODUCTION COMPANY	565386	EQUITABLE PRODUCTION CO	Pike	13	J	84	4620	341OLNG
94229	COLUMBIA NATURAL RES, INC	24945	THE ELK HORN COAL CORP / HUNT	Floyd	4	L	83	3126	341OHIO

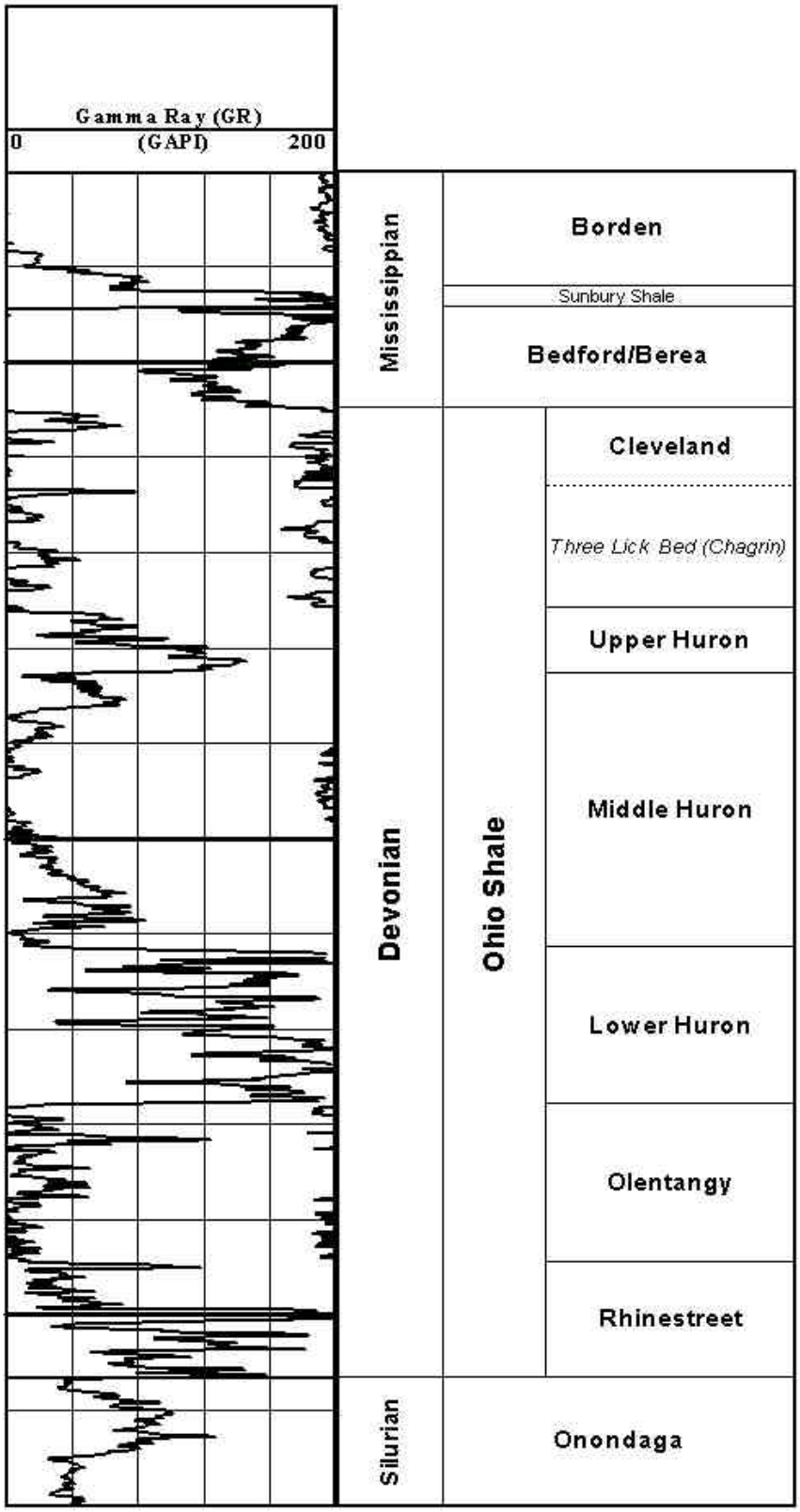


Figure 3. Chart showing nomenclature of Mississippian and Devonian shales of eastern Kentucky.

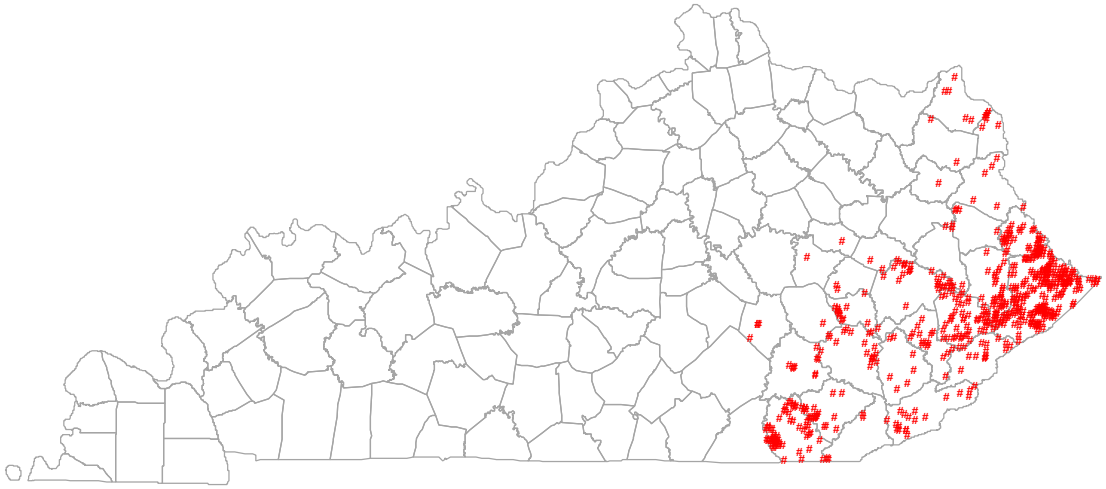


Figure 4. Initial distribution of Devonian shale drill cuttings sample sets.

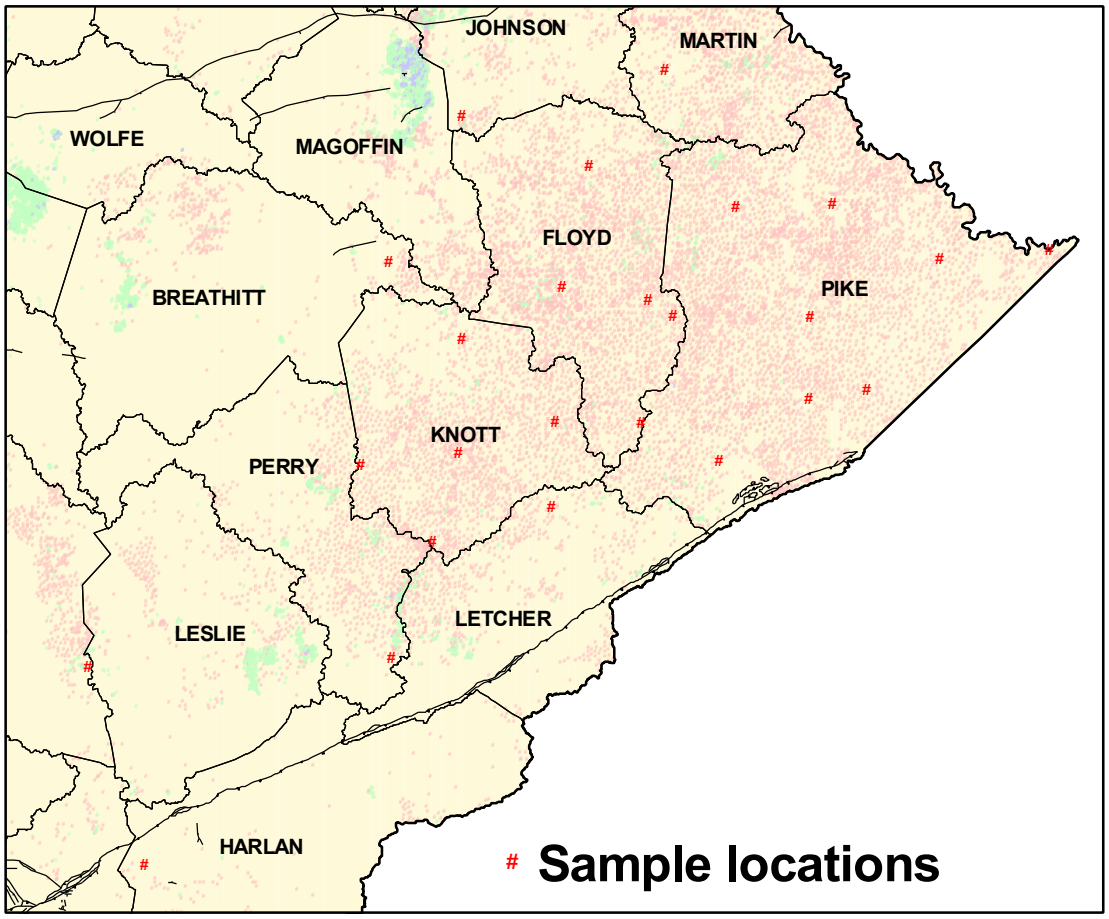


Figure 5. Eastern Kentucky Devonian Shale CO2 Sequestration sample locations.

The Kentucky Well Sample and Core Library is a facility housing a legacy data set of subsurface information for the Commonwealth. Drill cuttings are received at the warehouse, cataloged, and shelved while awaiting processing. Sample bags are identified by well and depth information and roughly sorted. The contents of each bag are emptied into a 160 mesh copper sieve with a serial identifier. For each sample bag, a sample label is prepared with the sieve number, footage, and catalogue number. This label is mounted on a plastic insert that will become a permanent part of the sample collection. Once loaded into the sieves, the samples are placed on a tray and run through a conveyor driven sample washer. For this project, the drying oven is turned off and all samples are air-dried. After drying, the plastic identifying tags are matched to the sieves. The tag and cuttings are stored together in a self-sealing polyethylene bag. The identified bags are then sorted by depth and loaded into corrugated boxes for storage in the library.

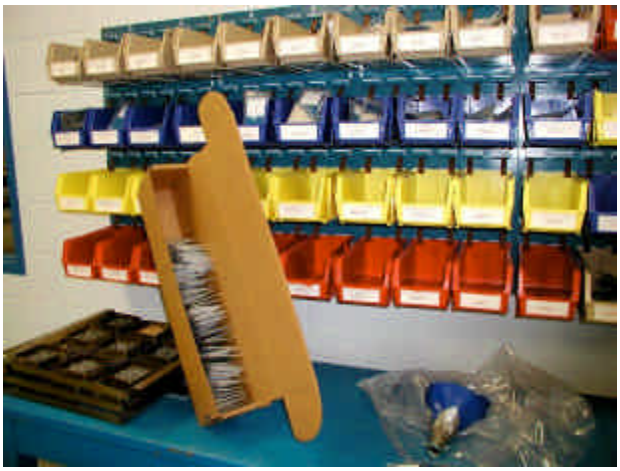
For this project, the intervals to be samples are identified from the drillers' logs and geophysical logs on file (see **Figure 4** for a type log). Equal amounts of cuttings from each interval are incorporated into the composite sample for adsorption and petrographic analysis. If there are multiple sample bags for the same interval, only one bag is sampled. The composite samples are mixed and split into fractions as required for each procedure.

Unwashed drill cuttings that have been checked in and cataloged

Pallet of unwashed drill cuttings as received (not cataloged)

Drill cuttings readied for sorting and processing.

Sorting samples in preparation for loading into polyethelyene sample bags.



Sorted drill cuttings are packed into individual bags

Leah Barth collecting composite sample for CO_2 adsorption and petrographic analyses

Splitting composite sample for petrographic and adsorption analyses

Cortland Eble examining samples for petrographic analysis

Conclusion

Collecting drill cuttings for composite sampling is proceeding. Uncatalogued sample sets are being identified for incorporation into the project. The sampling procedures have been revised to eliminate washing in order to increase the amount of available material in the drill cuttings. Geophysical logs are being correlated to direct sampling efforts. Sample sets are being delivered to partners for analysis.

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