

Analysis of Devonian Black Shales in Kentucky for Potential Carbon Dioxide Sequestration and Enhanced Natural Gas Production

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Abstract

Devonian gas shales underlie approximately two-thirds of Kentucky. In the shale, natural gas is adsorbed on clay and kerogen surfaces. This is analogous to methane storage in coal beds, where CO₂ is preferentially adsorbed, displacing methane. Black shales may similarly desorb methane in the presence of CO₂.

Drill cuttings from the Kentucky Geological Survey Well Sample and Core Library are being sampled to collect CO₂ adsorption isotherms. Sidewall core samples have been acquired to investigate CO₂ displacement of methane. An electron capture spectroscopy log has been acquired to investigate possible correlations between adsorption capacity and mineralogy.

Average random vitrinite reflectance (R_{random}) data range from 0.78 to 1.59 (upper oil to wet gas and condensate hydrocarbon maturity range). Total organic content determined from acid-washed samples ranges from 0.69 to 4.62 percent. CO₂ adsorption capacities at 400 psi range from a low of 19 scf/ton in less organic-rich zones to more than 86 scf/ton in the Lower Huron Member of the shale.

Initial estimates based on these data indicate a sequestration capacity of 5.3 billion tons of CO₂ in the Lower Huron Member of the Ohio Shale of eastern Kentucky and as much as 28 billion tons total in the deeper and thicker parts of the Devonian shales in Kentucky. Should the black shales of Kentucky prove to be a viable geologic sink for CO₂, their extensive occurrence in Paleozoic basins across North America would make them an attractive regional target for economic CO₂ storage and enhanced natural gas production.

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Disclaimer

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Introduction

Carbon dioxide (CO₂) is an efficient heat-trapping gas occurring in Earth's atmosphere. Over the past decades, there has been a growing concern that anthropogenic emissions of CO₂ are contributing to a systematic warming of Earth's climate; that is, global warming. The majority of anthropogenic emissions of CO₂ are from fossil fuel combustion. Electric power generation, transportation fuels, and industrial applications are highly dependent on coal, crude oil, and natural gas. It is estimated that the reliance on fossil fuel combustion will extend well into the 21st century (EIA, 2000). In Kentucky, 95 percent of the total electric generation capacity relies on fossil fuels (EIA, 2002, Table 4), with annual emissions of 87 million metric tonnes of CO₂ (EIA, 2002, Table 7).

CO₂ emissions can be decreased by increasing the efficiency of fossil fuel combustion processes, switching to alternate and renewable fuels (biomass, nuclear, solar, wind), and capturing and sequestering CO₂. Each of these methods will undoubtedly be used to achieve goals for addressing global warming and meet increasing energy demands. For sequestering CO₂, marine and terrestrial options are being researched, but geologic sequestration is the focus of this project. Geologic sequestration includes long-term carbon storage in old oil and gas fields, coals, saline aquifers, and unconventional reservoirs.

Usually considered to be the seal for conventional oil and gas reservoirs, gas shales warrant study as a possible sequestration option. This research tests the hypothesis that organic- and gas-rich black shales can adsorb significant amounts of CO₂. In carrying out the research, the Devonian black shales of Kentucky are being tested in the laboratory to determine their CO₂ sorption capacity using powdered drill cuttings. The ability of sorbed CO₂ to displace methane is being tested on sidewall cores in order to assess the potential for enhanced natural gas production from the shales.

Organic matter in the Devonian gas shales has large surface areas similar to that found in coal. Coal seams are currently being investigated as potential sequestering sites for CO₂, the most important greenhouse gas (IEA Coal Research, 1999). Naturally occurring organic matter (kerogen) is a microporous material that possesses a very high surface area and hence sorption capacity for gas. In the subsurface, coal commonly has economically significant amounts of sorbed methane (coalbed methane). Because organic matter has a greater sorption affinity for CO₂ than methane, injection of CO₂ with simultaneous production of methane may be viable (see Reznik and others, 1982; Bachu and Gunter, 1998). Currently a pilot CO₂ injection project is under way in Alberta, led by the Alberta Research Council and a consortium of petroleum companies. In the San Juan Basin, New Mexico, Amoco has carried out a pilot investigation of CO₂ injection, and Burlington Resources is currently evaluating the utility of CO₂ injection to enhance recovery of methane from coal. Results from these tests have shown that CO₂ injection and co-production of coalbed methane is technically and economically feasible. Since 1996, over 57 million m³ of CO₂ has been sequestered in Cretaceous coal of the San Juan Basin, New Mexico. The question is: can Devonian gas shales adsorb sufficient amounts of CO₂, making them significant targets for CO₂ sequestration?

Study Area

The study area is primarily confined to the major gas-producing area of the Ohio Shale in the Big Sandy Gas Field, eastern Kentucky (Figure 1, main concentration of producing localities). As key wells and available samples are identified, wells in deep (at least 1,000 feet) and thick (at least 50 feet) areas will be included. Two Illinois Basin wells have also been sampled. Battelle has contributed drill cuttings through the Devonian shale from their deep AEP CO₂ sequestration project well in Mason County, W. Va.

Regional Geology

Thinly bedded, fissile shales of Early Mississippian and Late Devonian age occur in the subsurface of nearly two-thirds of Kentucky. In general, the shales are thicker and deeper in eastern and western Kentucky (Figure 1) and are absent in the Bluegrass Region of central Kentucky and the Mississippi Embayment Region in the Jackson Purchase area of extreme western Kentucky. Along the axis of the Cincinnati Arch in central Kentucky, the thickness of the shale is usually 50 feet or less. The shale thickens eastward to more than 1,700 feet in Pike County. The shale is exposed in outcrop around the margin of the Jessamine Dome (along the perimeter of the Inner and Outer Bluegrass Regions of central Kentucky) and along the Cumberland River drainage in south-central Kentucky. A subcrop of the shale has been identified beneath the Cretaceous sediments of the Mississippi Embayment Region of western Kentucky. Figure 2 shows the elevation of the top of the Devonian shale in Kentucky and illustrates the progressive deepening of the shale east and west of the Cincinnati Arch area of central Kentucky.

Stratigraphy

Figure 3 shows the distribution of the Devonian shales in Kentucky, known variously as the New Albany (Illinois Basin), Chattanooga (central Kentucky, Cincinnati Arch area), and Ohio (Appalachian Basin) Shales. Reservoir integrity for CO₂ sequestration is a concern. Figure 4 provides a composite general geologic column illustrating more than 3,800 feet of Mississippian and Pennsylvanian lithologies, including carbonate, sand, shale, and coal that have proven an effective seal for existing shale gas resources. The assumption that sequestration will take place in the shale at depths of at least 1,000 feet recognizes the possible limitations of a fractured reservoir to act as an effective seal. Testing the integrity of this seal with respect to CO₂ is beyond the scope of this project and will be the subject of any subsequent CO₂ injection demonstration project.

The Ohio Shale is subdivided into seven recognizable units (Figure 5): Cleveland Shale, Three Lick Bed, Upper, Middle, and Lower Huron, Olentangy, and Rhinestreet. The Olentangy and Rhinestreet black shales correspond to the Java Formation of West Virginia, and thin and pinch out westward. Some authors consider that the Olentangy and Rhinestreet are members of the Devonian Ohio Shale. Although they are not everywhere present in the subsurface in the study area, the units are included in the analyses where samples are available.

Production

The first Devonian shale gas wells were drilled between 1863 and 1865 in Meade County, west-central Kentucky, and were used to fuel street lamps and provide heat in Louisville. Shale gas was discovered in eastern Kentucky circa 1892 in Floyd County (Hoeing, 1905). Overall, cumulative Devonian shale gas production in Kentucky probably exceeds 84.9 billion cubic meters (bm³); gas in place is estimated by various investigators to be between 26 trillion cubic meters (tm³) and 73 tm³ (Hamilton-Smith, 1993, p. 5). According to production data on file at the Kentucky Geological Survey, the giant Big Sandy Gas Field of Floyd, Knott, Letcher, Martin, and

Pike Counties produced 77 percent of the nearly 2.5 bm^3 of natural gas produced in Kentucky in 2002.

Reservoir parameters for the Big Sandy Gas Field were summarized in the "Atlas of Major Appalachian Gas Plays" (Boswell, 1996). The average completed interval exceeds 500 feet in thickness. Average porosity is 4.3 percent, with a maximum of 11 percent. Reservoir temperature averages 84°F, with an initial reservoir pressure of 800 psi or more. Current reservoir pressure averages 400 psi. Limited permeability data are available, but indicate less than 0.1 millidarcy of matrix permeability. Fracture permeability may exceed several hundred millidarcies.

Drilling and completions target organic-rich intervals with abundant natural fractures, mostly in the Lower Huron Member of the Ohio Shale (Figure 5) of eastern Kentucky. Nitrogen is typically used as the carrier fluid in hydraulic fracturing stimulations, which are intended to intersect with and enhance any natural fractures. Sand is generally employed as a proppant to maintain an open fracture system. The industry rule of thumb is that a shale well can be expected to produce 300 million cubic feet of natural gas (MMcf). Some wells often produce from 500 MMcf to more than 1 billion cubic feet. Devonian shale gas production tends to be long-term. This long-term production (with many wells exhibiting flat, or inclining production; see Figure 6) and high organic content suggest the shale contains a large component of adsorbed methane.

Methods

Drill Cuttings

Drill cuttings on file at the Kentucky Geological Survey Well Sample and Core Library and sidewall cores are the main source of material for analysis. Unwashed sets of recently acquired drill cuttings were used to minimize weathering of material and to maximize volume of material for analysis. Drill cuttings are commonly collected during drilling in 5- to 10-foot intervals and consist of a mix of chipped rock fragments and powder. 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 5). 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 were composited as a separate sample. Some wells have an insufficient volume of cuttings available to analyze the individual members of the Ohio Shale; in these cases the entire shale sequence was composited into a single sample. The rock chip and powder samples were divided into two splits: one for TOC, vitrinite reflectance, and X-ray diffraction analyses, and one for determination of CO_2 isotherms. Each split was then milled and sieved to the specifications of the respective analytical technique. Figure 7 shows the location of wells sampled to date in eastern Kentucky.

Total Organic Carbon

To investigate any relation between organic content and CO_2 sorption capacity, total organic carbon content (TOC) is being determined. For total organic carbon analyses, samples were first crushed to a maximum particle size of 200 microns (-60 mesh). Samples were run in duplicate. One split was run "as is." Another split was treated with 30 percent hydrochloric acid (HCl) for 12 to 24 hours to remove any carbonate minerals from the matrix, prior to analysis. Although carbonate minerals are typically a rare component of Devonian shales, they present a

possible bias in the calculation of TOC. Like organic material, carbonate minerals dissociate in the combustion chamber and form CO₂. The hydrochloric acid was removed by repeated washings with distilled water, followed by centrifugation. The samples were then placed in a drying oven (50°C).

Total organic carbon was measured on a LECO SC-144 DR dual range sulfur and carbon analyzer, which is a nondispersive, infrared, digitally controlled instrument designed to measure sulfur and carbon in a wide variety of organic and inorganic materials. The unit combusts samples in a pure oxygen environment at 1,350°C. Sulfur compounds are immediately oxidized and form sulfur dioxide (SO₂); carbon compounds are oxidized to CO₂. From the combustion system, sample gases pass through two tubes containing magnesium perchlorate (MgClO₄), which removes moisture, and then are routed to the infrared (IR) detection cells. A sulfur IR cell measures the amount of SO₂ present in the gas stream, and a carbon IR cell does the same for CO₂. All molecules, with the exception of bipolar species (e.g., N₂, H₂, O₂), absorb energy in the infrared region. As radiant energy is projected through the sample material an IR absorption spectrum is produced. Since no two molecules produce the same spectrum, the identity and quantity of a compound can be readily, and accurately, determined.

Vitrinite Reflectance

Vitrinite reflectance is used as a measure of the maturity of the organic matter in shale and that maturity may influence CO₂ sorption capacity. Mean random reflectance ($R_{0random}$) on dispersed vitrinite particles in the samples was determined on a Zeiss USMP incident light microscope calibrated using glass standards of known reflectance. Depending on the amount of vitrinite in the samples, 50 or 100 grains were measured at a magnification of 640x to determine mean reflectance. Mean random reflectance was used because it eliminates the need to rotate the stage to determine maximum and minimum reflectance values. As the vitrinite particles in the analyzed samples were quite small (usually less than 10 microns), stage rotation simply wasn't practical, because it often resulted in the reflectance measuring spot moving off the grain. Maximum vitrinite reflectance values (R_{0max}) can be estimated by multiplying the mean random measurements by 1.066 (Ting, 1978).

Adsorption Isotherms

The classic theory used to describe the type I isotherm for microporous materials with small external surface area is based on the Langmuir equation (1916). The type I isotherm displays a steep increase in adsorption at low relative pressures due to enhanced adsorption caused by the overlapping adsorption potentials between the walls of pores whose diameters are commensurate in size with the adsorbate molecule. The type I isotherm then flattens out into a plateau region at higher relative pressure, which is believed to be caused by the completion of a monolayer of adsorbed gas. The micropore volume is thought to then be filled by only a few molecular layers of adsorbate, and further uptake is limited by the dimensions of the micropores.

The Langmuir model assumes that a state of dynamic equilibrium is established between the adsorbate vapor and the adsorbent surface and that adsorption is restricted to a single monolayer. The adsorbent surface is thought to be composed of a regular array of energetically homogeneous adsorption sites upon which an adsorbed monolayer is assumed to form. The rate of condensation is assumed to be equal to the rate of evaporation from the adsorbed monolayer at a given relative pressure and constant temperature. The Langmuir equation was developed with these assumptions and takes the following form:

$$\frac{P}{V} = \frac{1}{BV_m} + \frac{P}{V_m}$$

where P is the equilibrium pressure, V is the volume of gas adsorbed at equilibrium, V_m is the volume of adsorbate occupying the monolayer, and B is an empirical constant. A plot of P/V vs. relative pressure should yield a straight line whose slope will yield V_m , from which the surface area may be obtained.

The Langmuir isotherm can be written:

$$V(P) = \frac{V_L P}{P_L + P}$$

- P = gas pressure
- $V(P)$ = predicted amount of gas adsorbed at P
- V_L = Langmuir volume parameter
- P_L = Langmuir pressure parameter

The difference between the measured amount of gas adsorbed ($V(P)$) and that predicted using the Langmuir equation ($V_i(P)$) is a measure of error and is given as:

$$Err(P) = V_i(P) - V(P)$$

This error may be positive or negative. The square of the error is always positive and is a measure of how well the calculated isotherm matches the data. This error can be calculated for each point and summed giving a measure of the overall error:

$$SSE = \sum_{i=1}^N Err_i^2$$

- N = number of measured points

The goodness of fit of the isotherm is expressed by calculating the correlation coefficient between the measured points and the calculated points. The results generally yield correlations that are better than $r^2 = 0.99$, and standard errors of Langmuir volumes of ± 2 percent. The reported CO_2 sorption capacity and corresponding pressure (P) are calculated coefficients of the Langmuir model and are used to determine the sorption capacity at reservoir-appropriate pressures (Table 2).

Adsorption analyses were performed using a high-pressure volumetric adsorption technique similar to that described by Mavor and others (1990). Isotherms were measured on a custom-made apparatus modeled after a similar module designed and built at CSIRO in Lucas Heights, Australia. The apparatus is based on Boyle's Law. In simple terms, a known volume of gas within a reference cell is used to dose a sample cell that contains the sample. The amount of gas adsorbed in the sample cell is then determined, based on a change in pressure in the sample cell using the Real Gas Law. Following dosing of the sample cell, the pressure drops until equilibrium is reached (i.e., no more gas can be adsorbed by a sample at a particular pressure). When equilibrium is reached, the sample is dosed at a higher pressure. Typically, 11 separate pressure points are selected and measured so that a Langmuir regression curve can

be accurately generated. The pressures in the reference and sample cells are measured using pressure transducers that are interfaced to a computer equipped with special boards and software. The computer monitors the transducers and determines when equilibrium is reached; it also controls valves and switches for dosing and purging the cells.

Sidewall Cores and Elemental Capture Spectroscopy Logging

Laboratory investigation of methane displacement in the presence of CO₂ is being performed on whole rock core samples. In cooperation with Columbia Natural Resources, access to a well in Knott County, eastern Kentucky, was obtained for logging and collection of sidewall cores. Schlumberger Oilfield Services provided electron capture spectroscopy logging for mineral identification and cut the sidewall cores. Electron capture spectroscopy is an advanced tool used for lithology and mineral determination that uses the same technology employed by NASA on the Mars Rover missions. The sidewall core plugs are being saturated with methane. To test the potential for enhanced natural gas production, the cores are being subjected to simulated injection of CO₂, and the amount of methane displaced during injection is being measured. Laboratory setup and analyses are similar to the standard procedure for obtaining adsorption isotherms.

Sequestration Capacity of the Shale

ArcView GIS software was used to develop a method to compile an estimate of the sequestration capacity of the shale. The method uses a cell-based approach that enables combining shale thickness and depth information in the form of continuous grids with shale density and spatially variable CO₂ adsorption capacity data. Preliminary estimates were compiled using a uniform, minimum CO₂ adsorption capacity and include data projected into the Illinois Basin portion of western Kentucky.

Results to Date

Twenty-six samples have been collected from seven wells, including three cuttings samples and 10 sidewall cores from the Columbia Natural Resources No. 24752 Elkhorn Coal Corporation well in Knott County (Figure 8). Data for completed analyses are presented in Table 1.

Table 1. Gas storage capacity, total carbon (TC), total organic carbon (TOC), and vitrinite reflectance data for completed samples.

Sample	Formation	Reported		TC as rec'd	TOC (acid*)	R _{0random}
		CO ₂ scf/ton	CO ₂ psia			
107928-1	Upper Ohio	37.5	681.1	1.67	0.69	1.55
107928-2	Lower Huron	67.6	243.7	3.94	2.95	1.48
107928-3	Lower Ohio	34.6	253.1	3.55	1.60	1.59
121774-1	Ohio Shale	126.5	989.8	6.15	3.66	1.10
124789-1	Upper Ohio	740.8	6419.1	4.41	3.26	0.78
124789-2	Lower Huron	2077.6	14283.5	5.69	4.62	0.81
124789-3	Lower Ohio	116.2	957.9	3.27	1.78	0.83
123486-1	Upper Ohio	228.9	2230.4	3.64	2.44	0.78
123486-2	Lower Ohio	309.3	2106.0	5.00	4.13	0.82
121162-1	Ohio Shale	164.2	1561.3	2.51	2.37	0.85
121464-1	Upper Ohio	52.6	708.9	1.33	1.18	1.52
121464-2	Lower Huron	248.7	751.2	4.21	3.60	1.52
121464-3	Lower Ohio	108	819	2.81	2.31	1.51

* Samples washed in HCl to remove carbonate (inorganic carbon)

Scf/ton = standard cubic feet per ton

psia = pressure, pounds per square inch absolute

Adsorption isotherms for these samples are presented in Figure 9. The Langmuir volume and pressure data reported in Table 1 must be compared on a uniform pressure basis by formation. These summary data are shown in Table 2, and Figure 10 presents calculated adsorption capacities at three pressure values expected to be typical of the range of observed Devonian shale gas reservoir conditions.

Table 2. Summary of CO₂ adsorption capacity in standard cubic feet per ton at selected pressures.

Sample	FM	PSIA		
		300	400	500
121162-1	Ohio Shale	26.5	33.5	39.8
121774-1	Ohio Shale	29.4	36.4	42.5
Average	Ohio Shale Undifferentiated	27.9	34.9	41.1
107928-1	Upper Ohio	11.5	13.9	15.9
121464-1	Upper Ohio	15.6	19	21.8
124789-1	Upper Ohio	33.1	43.5	53.5
Average	Upper Ohio Shale	20.1	25.4	30.4
107928-2	Lower Huron	37.3	42	45.4
121464-2	Lower Huron	71	86.4	99.4
124789-2	Lower Huron	42.7	56.6	70.3
Average	Lower Huron	50.3	61.7	71.7
107928-3	Lower Ohio	18.8	21.2	23
121464-3	Lower Ohio	29	35.4	40.9
124789-3	Lower Ohio	27.7	34.2	39.9
Average	Lower Ohio Shale	25.1	30.3	34.6
Average	Overall	31.1	38.4	44.8

The ECS log and sidewall core plugs have been obtained. A portion of the ECS log through the Lower Huron section of the Columbia Natural Resources No. 24752 Elk Horn Coal well in Knott County, eastern Kentucky, is shown in Figure 11. The variability of clay and quartz content is shown with a gamma-ray trace for correlation in the left track. The traces in the right track show relative abundance of selected elements at various scales; for example, the iron (Fe) and sulfur (S) tracks show variations in pyrite content of the shale. Gadolinium (Gd) is a radioactive trace element that has been correlated with clay content and is a proxy used in the calculation of the abundance of clay minerals shown on the left.

Preliminary Interpretation

Initial estimates of CO₂ sequestration capacity have been calculated using selected data. An initial estimate of the sequestration volume of the Lower Huron was compiled using areal distribution and thickness data from Dillman and Eddensohn (1980). Initial calculations indicate that 91 x 10¹² cubic feet (2.6 x 10¹² cubic meters) of CO₂ could be sequestered in the Lower Huron using a Langmuir volume of 67.6 scf/ton (2.1 m³/tonne; raw data from sample 107928-2, Table 1) and an average thickness of 150 feet over the area of Boyd, Breathitt, Floyd, Johnson, Knott, Lawrence, Leslie, Magoffin, Martin, Perry, and Pike Counties combined. Assuming 30 percent of this theoretical saturation, approximately 1.6 billion tons (1.5 billion metric tonnes) of CO₂ could be sequestered. Using a 1-kilometer grid, a depth to top of shale of 1,000 feet or greater, a shale thickness of 50 feet or more, and a constant adsorption capacity equal to a thickness-weighted average of 40 scf/ft³ (1.2 m³/tonne; raw data from samples 107928-1, 107928-2, and 107928-3, Table 1), estimated initial CO₂ sequestration capacity of the Devonian shale in Kentucky is 27.7 billion tons (25.1 billion metric tonnes) (Figure 12).

Future Work

On this project, sampling and collection TOC, $R_{0random}$, and adsorption data are continuing. X-ray diffraction analyses are being completed for the current round of samples. Sidewall core plugs have been submitted for adsorption and methane displacement analyses. Mineral and compositional data from X-ray and logging will be correlated to CO_2 adsorption capacity.

A vital next step will be to test CO_2 adsorption and the potential of enhanced natural gas production with a demonstration project. Negotiations to identify potential industry partners and CO_2 sources are under way.

Preliminary Conclusions

Preliminary data indicate that black, organic-rich gas shales can serve as targets for sequestration of significant volumes of anthropogenic CO_2 . At Kentucky's current rate of power plant emissions, the organic-rich, black shale in the state could sequester more than 300 years' worth of that carbon. Enhanced production of natural gas displaced by the injected CO_2 would contribute to a long-term increase in the supply of what is considered a "greener" fuel.

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Figures

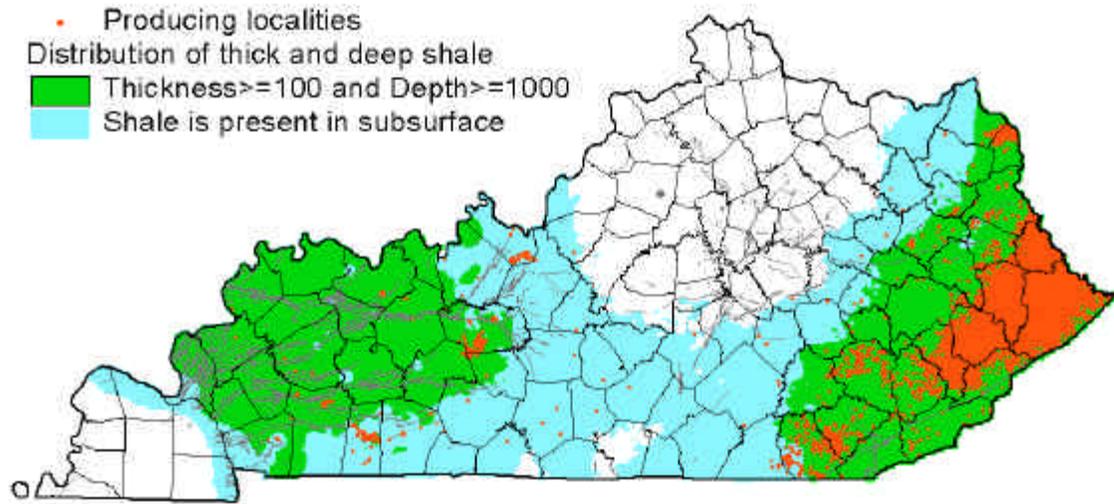


Figure 1. Distribution of the Devonian shale in Kentucky, showing the occurrence of deeper and thicker shale with possibly greater potential for geologic sequestration of CO₂.

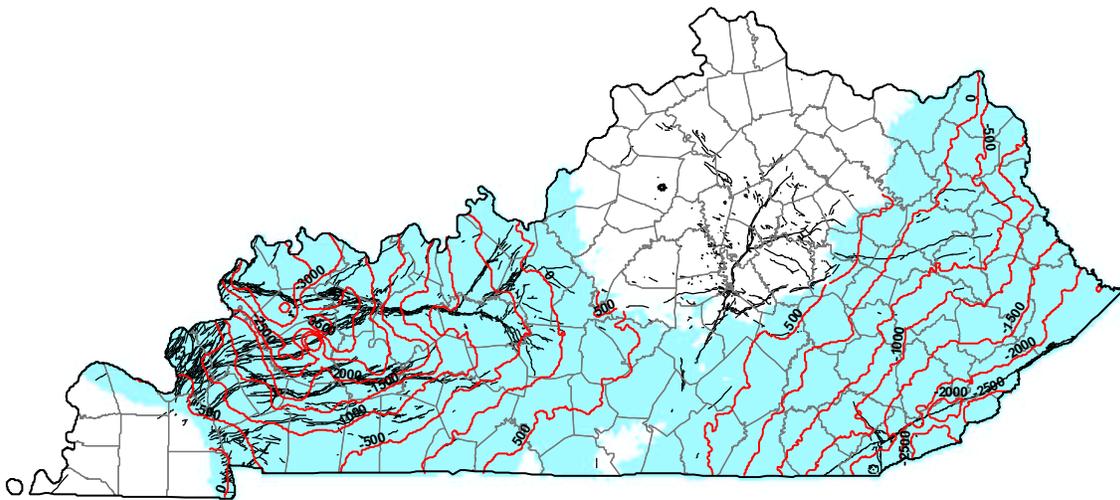


Figure 2. General structure of the Devonian shale, showing presence of shale in the subsurface (shading).

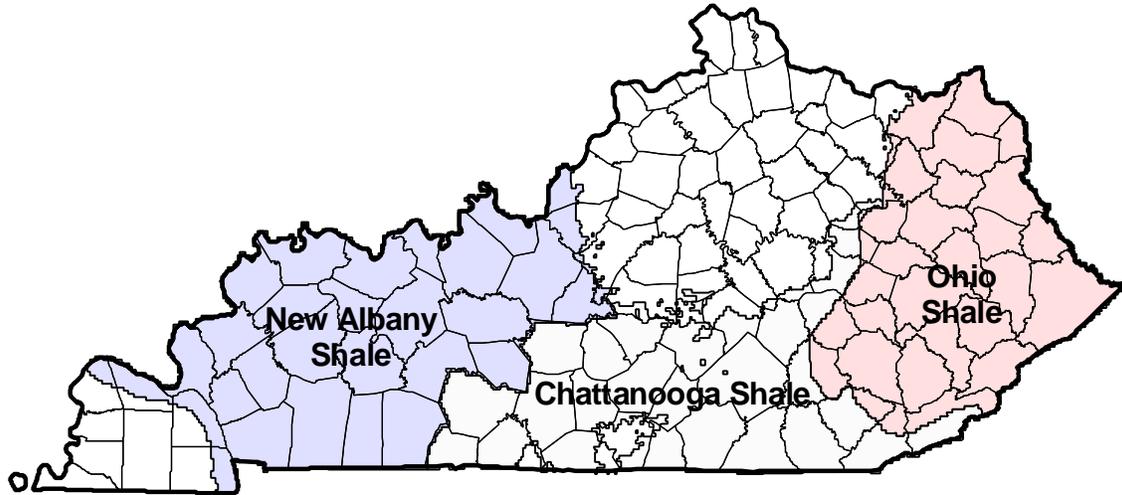


Figure 3. Distribution and nomenclature of Devonian shales of Kentucky (Hamilton-Smith, 1993, p. 3).

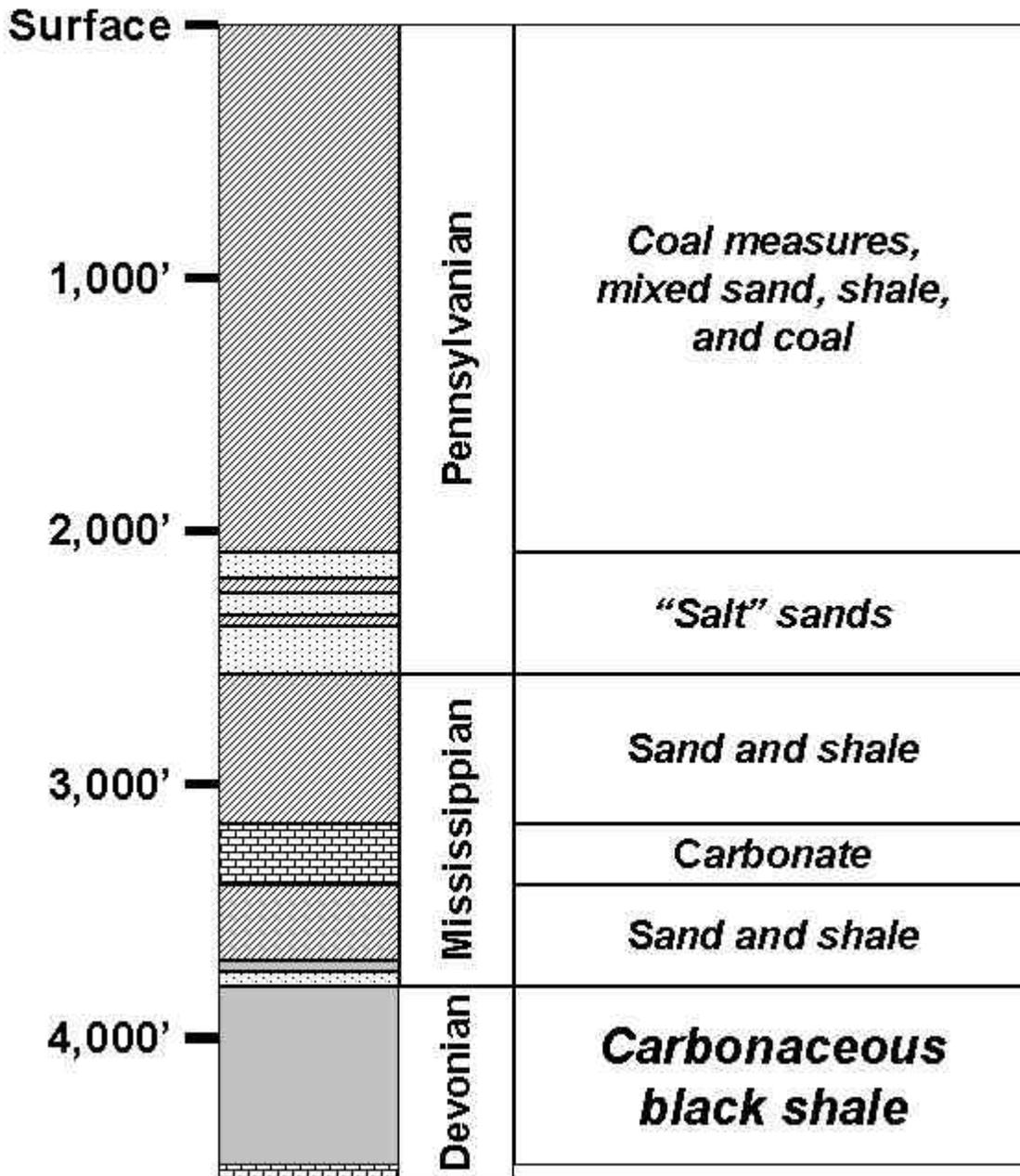


Figure 4. General geologic column showing approximately 3,800 feet of overlying Mississippian and Pennsylvanian lithologies adequate for ensuring reservoir integrity in the Devonian shale. Note: Devonian shale is underlain by Devonian carbonates.

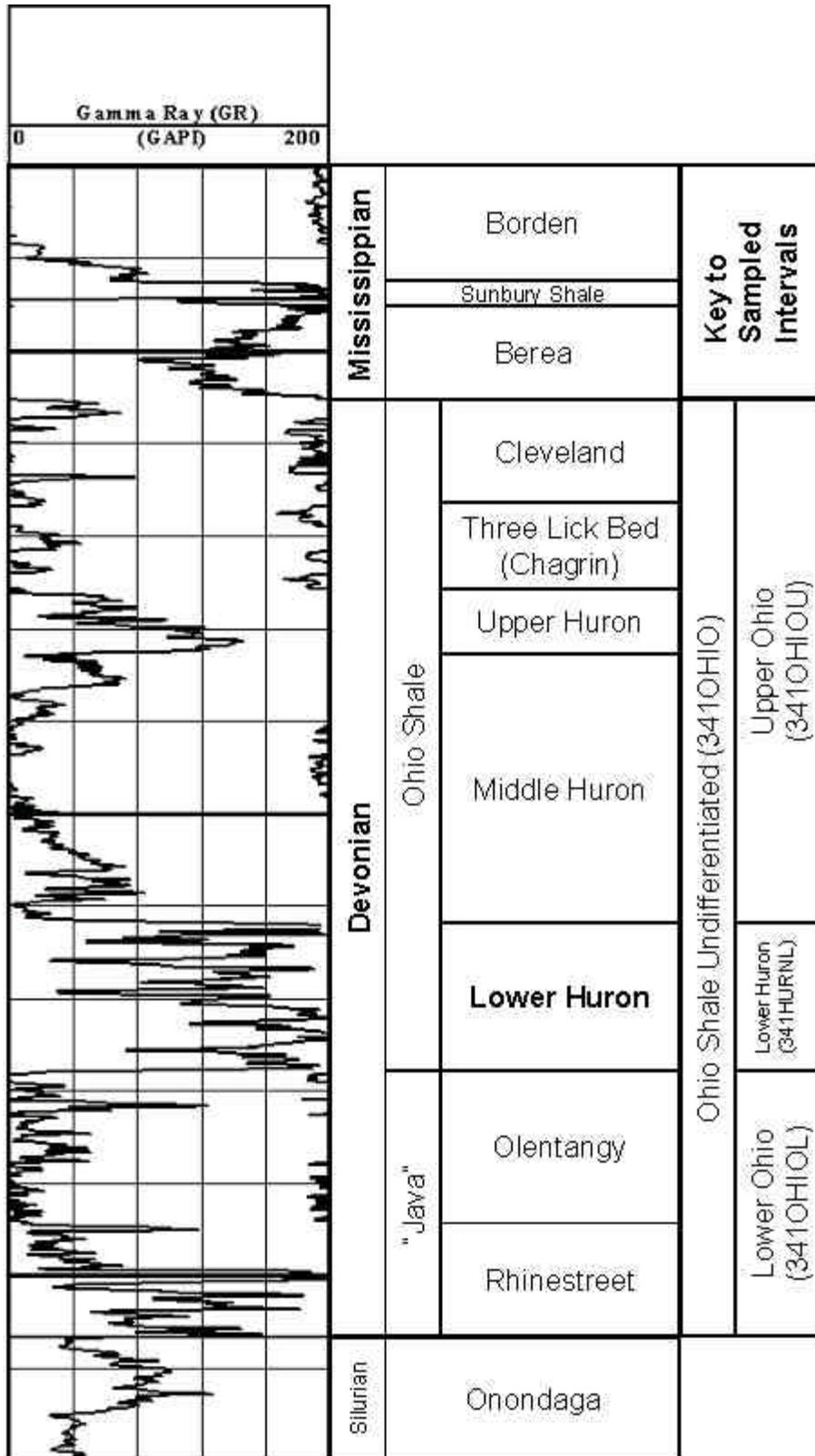


Figure 5. Nomenclature of Mississippian and Devonian shales of eastern Kentucky and key to names and codes used for intervals sampled.

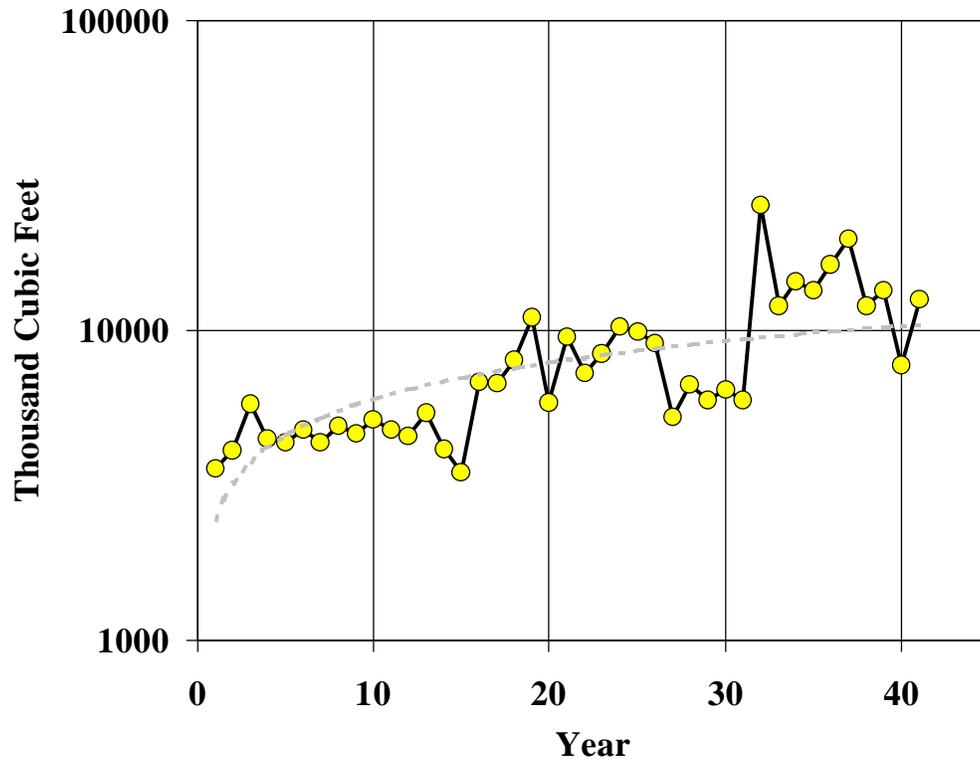


Figure 6. Eastern Kentucky Devonian shale natural-gas production (proprietary data), showing long-term increase. Dotted line is exponential best fit of observed rate-time data.

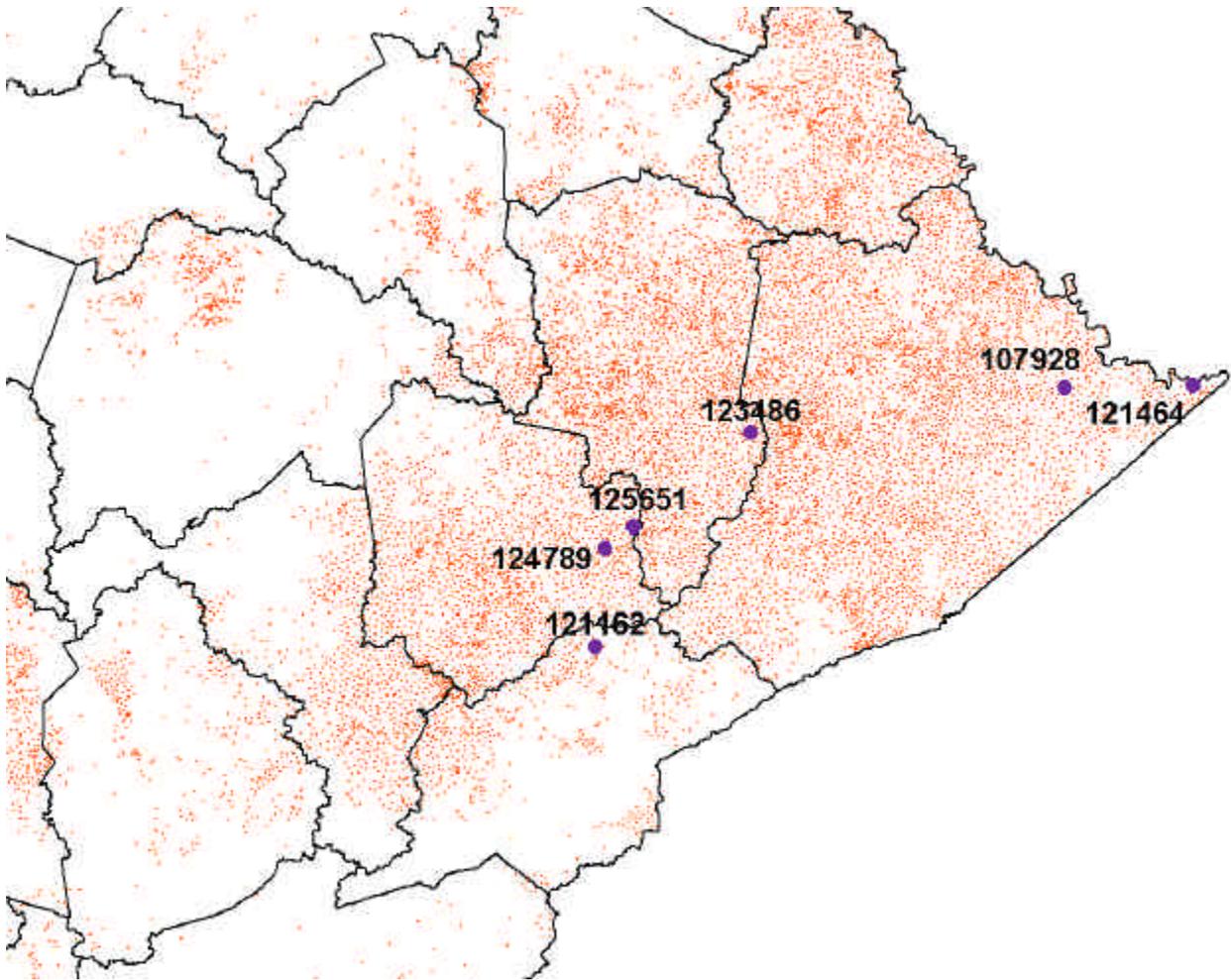


Figure 7. Location of wells in eastern Kentucky sampled to date. Includes the CNR 24752 Elk Horn Coal well (125651) with ECS log, sidewall cores, and drill cuttings. Small dots are existing gas wells in region.

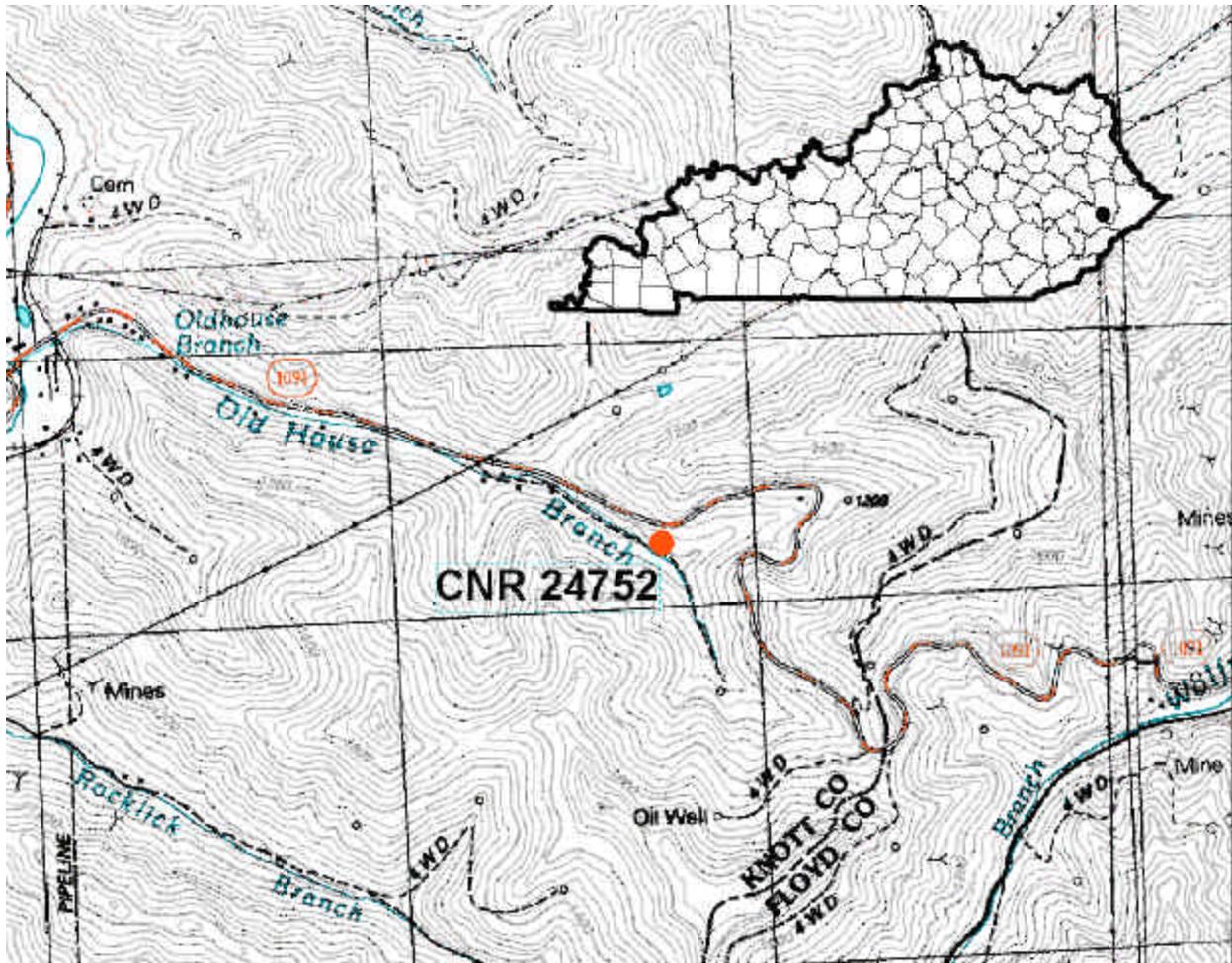
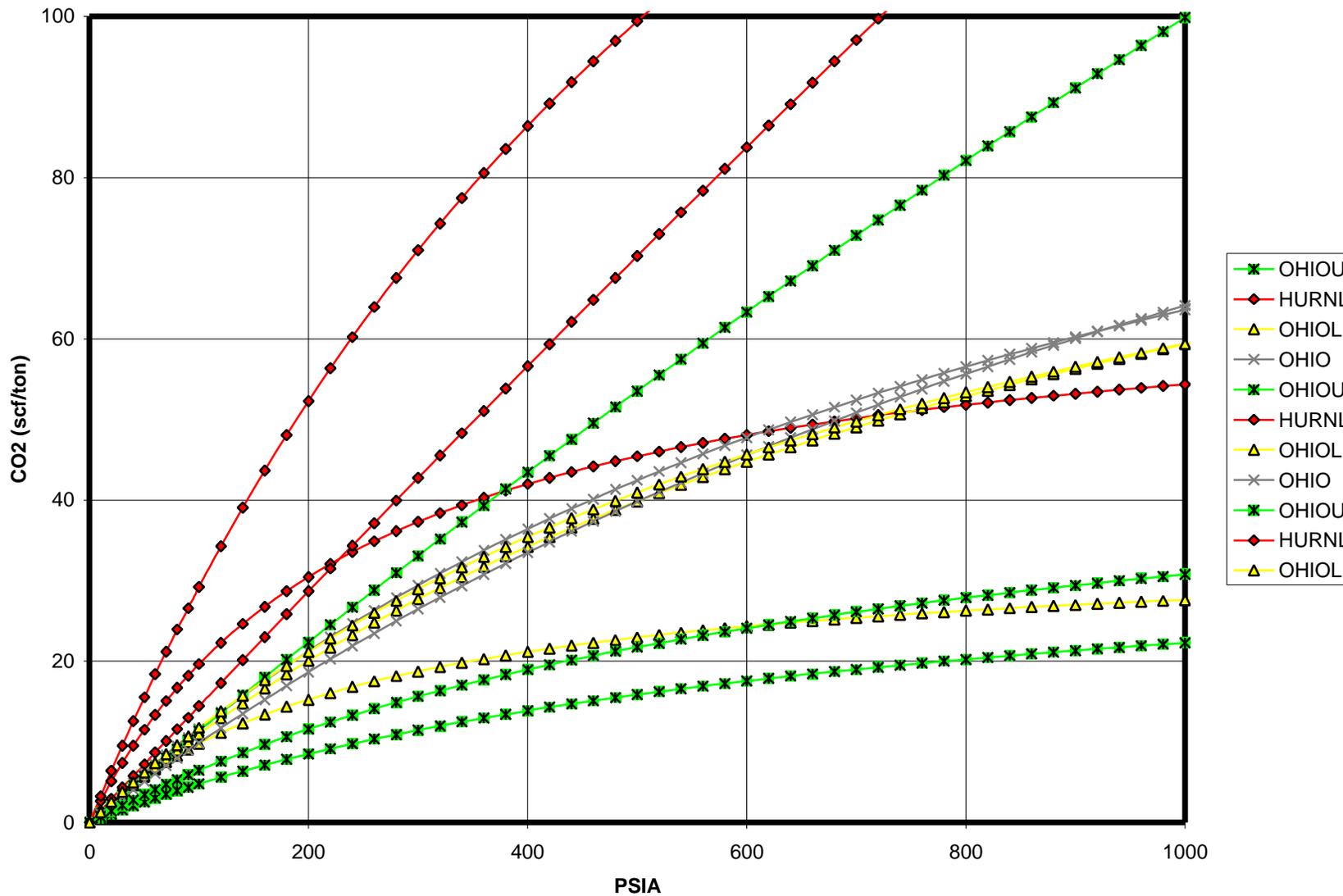


Figure 8. Location of the Columbia Natural Resources 24752 Elk Horn Coal Company well, permit 94539, Knott County, Ky., Carter coordinate 11-K-81, latitude 37.37019° N, longitude 82.76441° W (NAD 1983).

Figure 9. Summary of adsorption isotherms by formation.



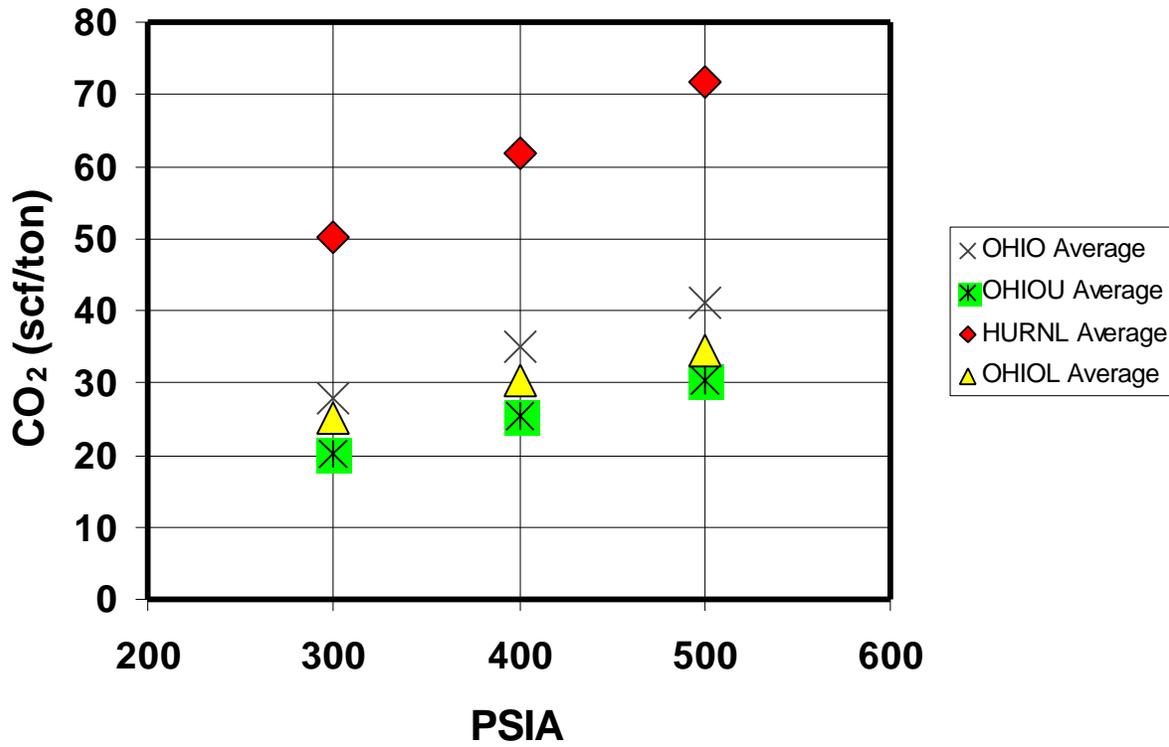


Figure 10. Average calculated adsorption capacities by formation at selected pressures.

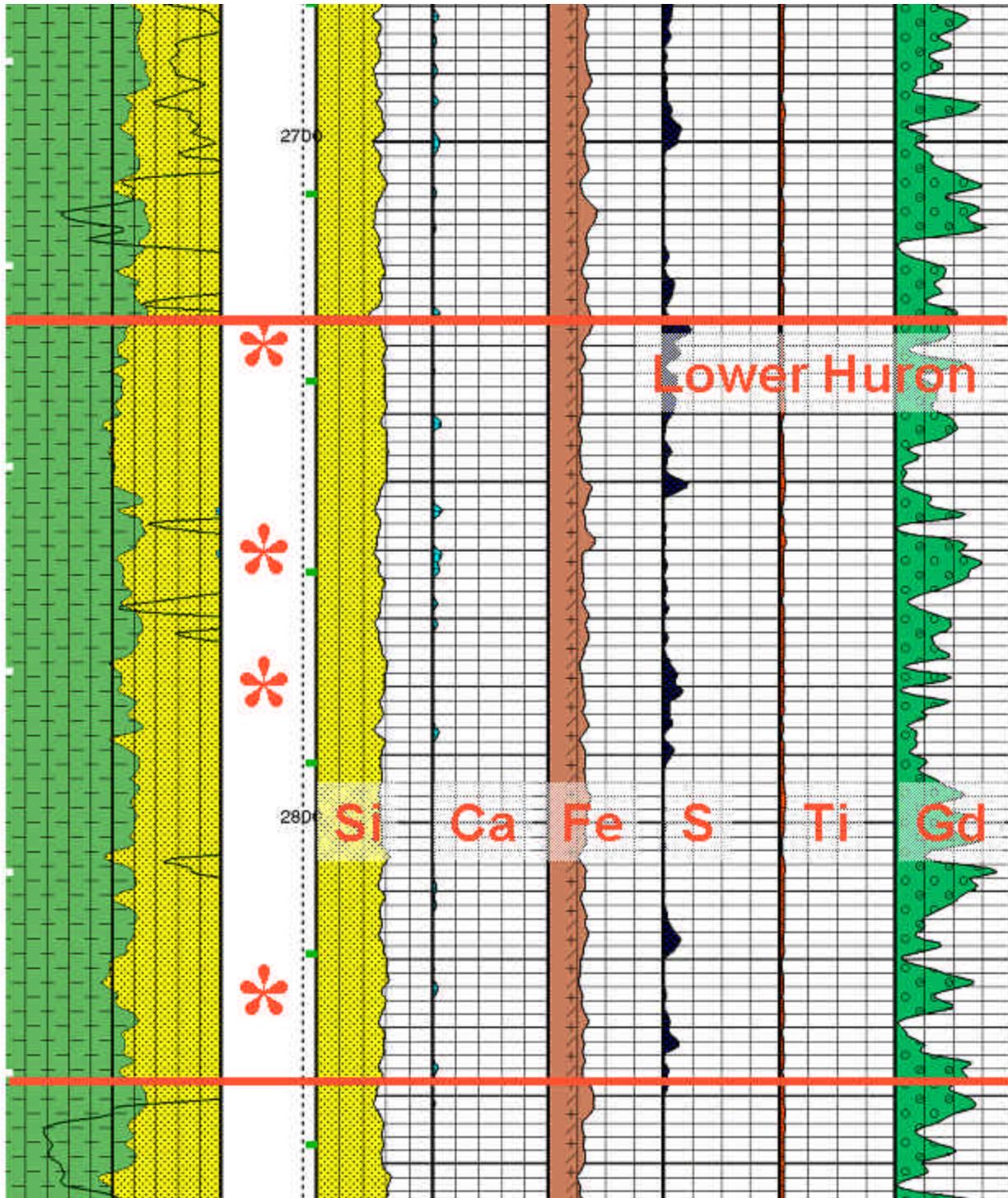


Figure 11. Section of electron capture spectroscopy log through the Lower Huron section of the Columbia Natural Resources No. 24752 Elk Horn Coal well, Knott County, Ky., showing relative abundance of species related to mineral and lithologic identification. Asterisks denote depths where sidewall cores were recovered.

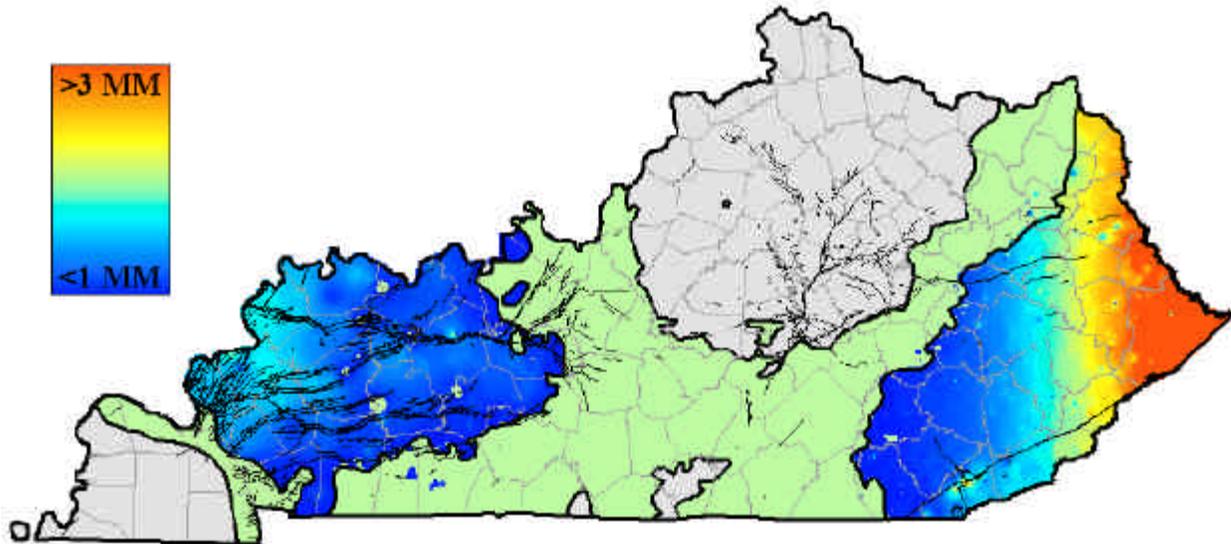


Figure 12. Preliminary estimated CO₂ storage capacity per square kilometer (in million tons) in the areas of deeper ($\geq 1,000$ feet) and thicker (≥ 50 feet) Devonian shale.