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Water Management Strategies for Improved Coalbed Methane Production in the Black Warrior Basin

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ABSTRACT

The modern coalbed methane industry was born in the Black Warrior Basin of Alabama and has to date produced more than 2.6 trillion cubic feet of gas and 1.6 billion barrels of water. The coalbed gas industry in this area is dependent on instream disposal of co-produced water, which ranges from nearly potable sodium-bicarbonate water to hypersaline sodium-chloride water. This study employed diverse analytical methods to characterize water chemistry in light of the regional geologic framework and to evaluate the full range of water management options for the Black Warrior coalbed methane industry.

Results reveal strong interrelationships among regional geology, water chemistry, and gas chemistry. Coalbed methane is produced from multiple coal seams in Pennsylvanian-age strata of the Pottsville Coal Interval, in which water chemistry is influenced by a structurally controlled meteoric recharge area along the southeastern margin of the basin. The most important constituents of concern in the produced water include chlorides, ammonia compounds, and organic substances. Regional mapping and statistical analysis indicate that the concentrations of most ionic compounds, metallic substances, and nonmetallic substances correlate with total dissolved solids and chlorides.

Gas is effectively produced at pipeline quality, and the only significant impurity is N_2. Geochemical analysis indicates that the gas is of mixed thermogenic-biogenic origin. Stable isotopic analysis of produced gas and calcite vein fills indicates that widespread late-stage microbial methanogenesis occurred primarily along a CO_2 reduction metabolic pathway. Organic compounds in the produced water appear to have helped sustain microbial communities. Ammonia and ammonium levels increase with total dissolved solids content and appear to have played a role in late-stage microbial methanogenesis and the generation of N_2.

Gas production tends to decline exponentially, whereas water production tends to decline hyperbolically. Hyperbolic decline indicates that water volume is of greatest concern early in the life of a coalbed methane project. Regional mapping indicates that gas production is controlled primarily by the ability to depressurize permeable coal seams that are natively within the steep part of the adsorption isotherm. Water production is greatest within the freshwater intrusion and below thick Cretaceous cover strata and is least in areas of underpressure.

Water management strategies include instream disposal, which can be applied effectively in most parts of the basin. Deep disposal may be applicable locally, particularly where high salinity limits the ability to dispose into streams. Artificial wetlands show promise for the management of saline water, especially where the reservoir yield is limited. Beneficial use options include municipal water supply, agricultural use, and industrial use. The water may be of use to an inland shrimp farming industry, which is active around the southwestern coalbed methane fields. The best opportunities for beneficial use are reuse of water by the coalbed methane industry for drilling and hydraulic fracturing. This research has further highlighted opportunities for additional research on treatment efficiency, the origin of nitrogen compounds, organic geochemistry, biogenic gas generation, flow modeling, and computer simulation. Results of this study are being disseminated through a vigorous technology transfer program that includes web resources, numerous presentations to stakeholders, and a variety of technical publications.

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EXECUTIVE SUMMARY

The Black Warrior Basin of Alabama is the cradle of the modern coalbed methane industry and has produced more than 2.6 trillion cubic feet of gas and 1.6 billion barrels of water since 1980. The coalbed gas industry in this area is dependent on instream disposal of co-produced water, which ranges from nearly potable sodium-bicarbonate water to hypersaline sodium-chloride water. This report summarizes a four-year effort that was directed at characterizing the geology and geochemistry of the produced fluids and evaluating water management strategies in the basin. Options for produced water management include instream disposal, underground injection, and beneficial use for water supply, agriculture, and industry.

This study employed diverse analytical methods. A range of subsurface and surface methods that utilized geophysical well logs and geological databases were employed to refine the stratigraphic, structural, and hydrodynamic framework of the basin. Wellhead water samples from 206 coalbed methane wells were analyzed for a broad range of geochemical parameters, including physical and aggregate properties, major ionic compounds, metallic and nonmetallic substances, organic compounds, and nitrogen compounds. Wellhead gas samples were taken from 103 sites and analyzed for bulk composition and stable isotopes, specifically carbon and deuterium. Petrologic techniques were applied to determine the framework composition of sandstone and shale and to analyze carbon and oxygen isotopes in calcite veins. Production data were compiled to evaluate the decline characteristics of coalbed methane wells. Cumulative, peak, and annual production data were analyzed statistically and mapped. A geographic information system was developed that assembles the broad range of data collected during this project. This system was used to evaluate historical and current water management practice and

to inform the identification of new practices that may be of value to the coalbed methane industry.

Integrated geological and geochemical analysis of produced water and gas reveals strong interrelationships among regional geology, water chemistry, and gas chemistry. Coalbed methane is produced from multiple coal seams in Pennsylvanian-age strata of the Pottsville Coal Interval, which constitutes a thick succession of shale, sandstone, and coal. Water chemistry in the Pottsville Coal Interval is influenced by a structurally controlled meteoric recharge area along the southeastern margin of the basin, and the most promising opportunities for beneficial use are near the recharge zone. Salinity increases with distance from the recharge zone, and the inability to pump wells to capacity where salinity is highest helps determine the economic viability of gas production. The most important constituents of concern in the produced water include chlorides, ammonia compounds, and organic substances. Regional mapping and statistical analysis indicate that the concentrations of most ionic compounds, metallic substances, and nonmetallic substances correlate with total dissolved solids and chlorides.

Bulk chemistry of the produced gas is nearly invariant, whereas the stable isotopic composition of the gas varies regionally. The produced gas is enriched in ^{13}C in medium-volatile and low-volatile bituminous coal, suggesting a significant thermogenic component of gas generation. However, regional unroofing and cooling indicates that the coal would have been greatly undersaturated with CH_4 without additional gas generated by late-stage microbial methanogenesis. The gas becomes depleted in ^{13}C as coal rank decreases to high volatile B bituminous away from the recharge area. Stable isotopic analysis of produced gas and calcite cement indicates that widespread late-stage microbial methanogenesis occurred primarily along a CO_2 reduction metabolic pathway.

Significant concentrations of organic compounds in the produced water appear to have helped sustain microbial communities. Ammonia and ammonium levels increase with total dissolved solids content and appear to have played a role in late-stage microbial methanogenesis and the generation of N_2. Indeed, a range of reactions involving organic matter, minerals, and formation water, may have contributed some N_2, which is the only significant nonhydrocarbon impurity in the produced gas. Biotic degradation of organic compounds may have been augmented by deionization of NH_4^+ thus providing multiple sources of H_2 for microbial CO_2 reduction.

Petrologic analysis indicates that sandstone in the Pottsville Coal Interval is principally litharenite with minimal porosity and permeability. Flow of water occurs mainly in natural fractures, and closely spaced cleats give the coal seams the ability to support commercial flow rates. Fractures are commonly filled with calcite, and carbon and oxygen isotopes are valuable recorders of ancient thermal and geochemical conditions. Carbon isotopic data confirm that microbial methanogenesis was an important process in the Pottsville Coal Interval. Oxygen isotopes, moreover, suggest that mineralization and microbial methanogenesis occurred at or near modern burial depth.

Analysis of production data indicates that gas production tends to decline exponentially, whereas water production tends to decline hyperbolically. Hyperbolic decline of water production indicates that managing water volume is of primary concern early in the life of a coalbed methane project and that wells tend to produce at steady rate later in the life cycle. Peak production correlates strongly with cumulative production and is thus a valuable early indicator of long-term well performance. Regional mapping indicates that gas production is controlled primarily by the ability to depressurize permeable coal seams that are natively within the steep

part of the adsorption isotherm. Water production is greatest in areas with near normal hydrostatic reservoir pressure within the freshwater intrusion and below thick Cretaceous cover strata. By comparison, water production is least in areas of induced underpressure associated with coal mining and in areas of natural underpressure basinward of the freshwater intrusion.

Water management strategies include instream disposal, which can be applied effectively in most parts of the basin. Deep disposal may be applicable locally, particularly where high salinity limits the ability to dispose into streams. Artificial wetlands show promise for the management of saline water, especially where the reservoir yield is limited. Beneficial use options include municipal water supply, agricultural use, and industrial use. The water may be of use to an inland shrimp farming industry, which is active around the southwestern coalbed methane fields. The best opportunities for beneficial use are reuse of water by the coalbed methane industry for drilling and hydraulic fracturing. This research has further highlighted opportunities for additional research on treatment efficiency, the origin of nitrogen compounds, organic geochemistry, biogenic gas generation, flow modeling, and computer simulation. Results of this study are being disseminated through a vigorous technology transfer program that includes web resources, numerous presentations to stakeholders, and a variety of technical publications.

INTRODUCTION

Natural gas is stored in coal primarily in an adsorbed state, and so the coal must be depressurized so the gas can be released from the coal matrix and produced (e.g., McKee and others, 1988; Seidle, 2011). Depressurization is accomplished principally by dewatering, and so large volumes of formation water are commonly co-produced with the natural gas. Importantly, the quantity and composition of this water varies greatly (e.g., Pashin and others, 1991; Ayers and Kaiser, 1994; Reddy, 2010). Therefore, management of produced water is one of the most critical issues facing the coalbed methane (CBM) industry, because the water must be processed and disposed in an environmentally responsible manner (e.g., Pashin and others, 1991; Ayers and Kaiser, 1994; van Voast, 2003; Pashin, 2007). The quantity and quality of formation water in coal, moreover, are intimately related to the architectural framework and geologic history of the host sedimentary basin. Thus, basin hydrology and geochemistry are fundamental considerations in the design and implementation of reservoir development protocols (e.g., Pashin and others, 1991; Pashin, 2007, 2008; Ayers and Kaiser, 1994; Scott, 2002).

The Black Warrior basin of Alabama (fig. 1) is a mature province within the rapidly expanding Birmingham-Tuscaloosa economic corridor, where CBM producers face a range of water management issues. In the Black Warrior CBM fields, freshwater has been disposed safely in streams for decades. Even so, this practice is a subject of increasing scrutiny by environmental groups and government agencies. Additionally, some of the produced water may have beneficial agricultural and industrial uses. In the southwestern fields, where significant potential exists for expansion of the CBM industry in Alabama, saline formation water limits the ability of producers to pump wells to depressurize coal, which in turn leads to underperforming gas production (Pashin, 2010a).

To assist the CBM industry in addressing these issues, the Geological Survey of Alabama (GSA) has completed a three-year study that was sponsored by the National Energy Technology Laboratory of the U.S. Department of Energy and was designed to develop a conceptual framework for the management of produced water from coal. This study employed an integrated, life-cycle approach drawing on a spectrum of geologic disciplines (fig. 2). The study used a spectrum of geologic, hydrologic, geochemical, petrologic, and GIS techniques to characterize

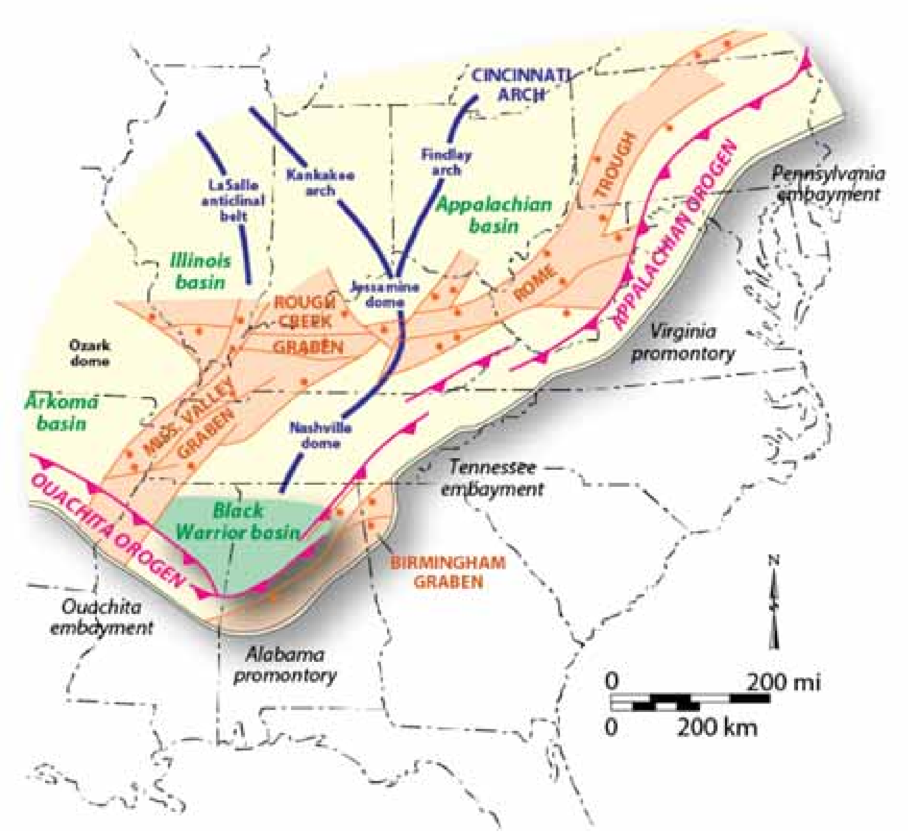


Figure 1.—Regional geologic setting of the Black Warrior Basin
(modified from Thomas, 1988).

the reservoir geology and basin hydrology of the Black Warrior basin and was designed to develop new water management strategies that ensure environmental protection, foster beneficial use of produced waters, and improve reservoir performance. This study included an intensive fluid sampling program that could not have been performed without the cooperation of the many CBM operators in the basin. The Black Warrior basin has a long and rich history of CBM development. The wealth of data and the geological diversity of the basin provides an unparalleled opportunity to evaluate water management strategies across a spectrum of reservoir conditions. Accordingly, this study will help natural gas producers develop basic geologic,

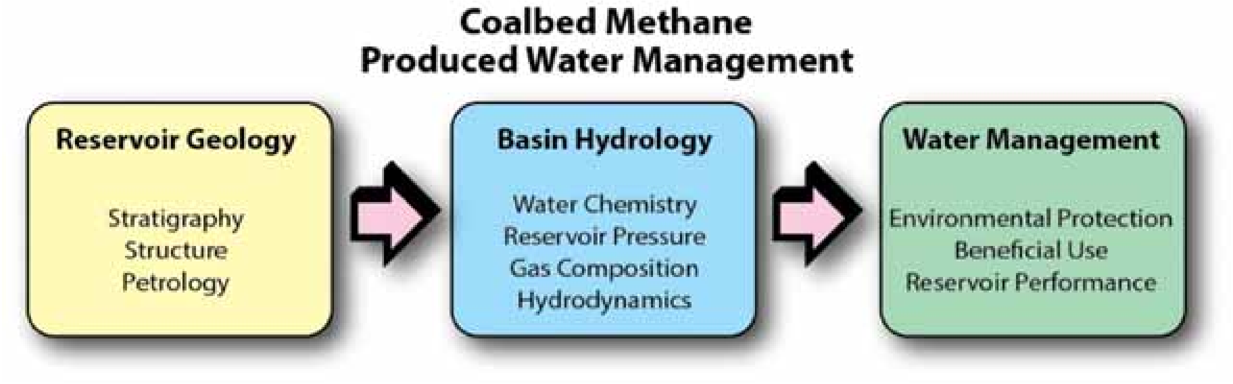


Figure 2.—Conceptual model of geology, hydrology and water management in coalbed methane reservoirs.

hydrologic, and water management concepts that can be applied to CBM plays throughout the world.

Natural Gas Resources and Production History

The Black Warrior basin is a cradle of the modern CBM industry that has provided a wealth of experience and has guided CBM development around the globe (e.g., Hewitt, 1984; McFall and others, 1986; O’Neil and others, 1989, 1993; Pashin, 1998, 2007). Degasification experiments focusing on mine safety began in the mid 1970s, and commercial production began in 1980 (Elder and Deul, 1974; Pashin and Hinkle, 1997). Nearly 2.6 trillion cubic feet (Tcf) of coalbed gas has been produced from the basin, which ranks third globally in cumulative CBM production. Currently, 5,747 wells are active in 12 CBM fields (fig. 3). Annual gas production was between 100 and 121 billion cubic feet (Bcf) from 1992 through 2011 (fig. 4), thus CBM has been an extremely stable natural gas supply for the Birmingham-Tuscaloosa corridor. Although the basin is considered mature and is currently challenged by low natural gas prices, operations remain active and will continue to do so for the foreseeable future.

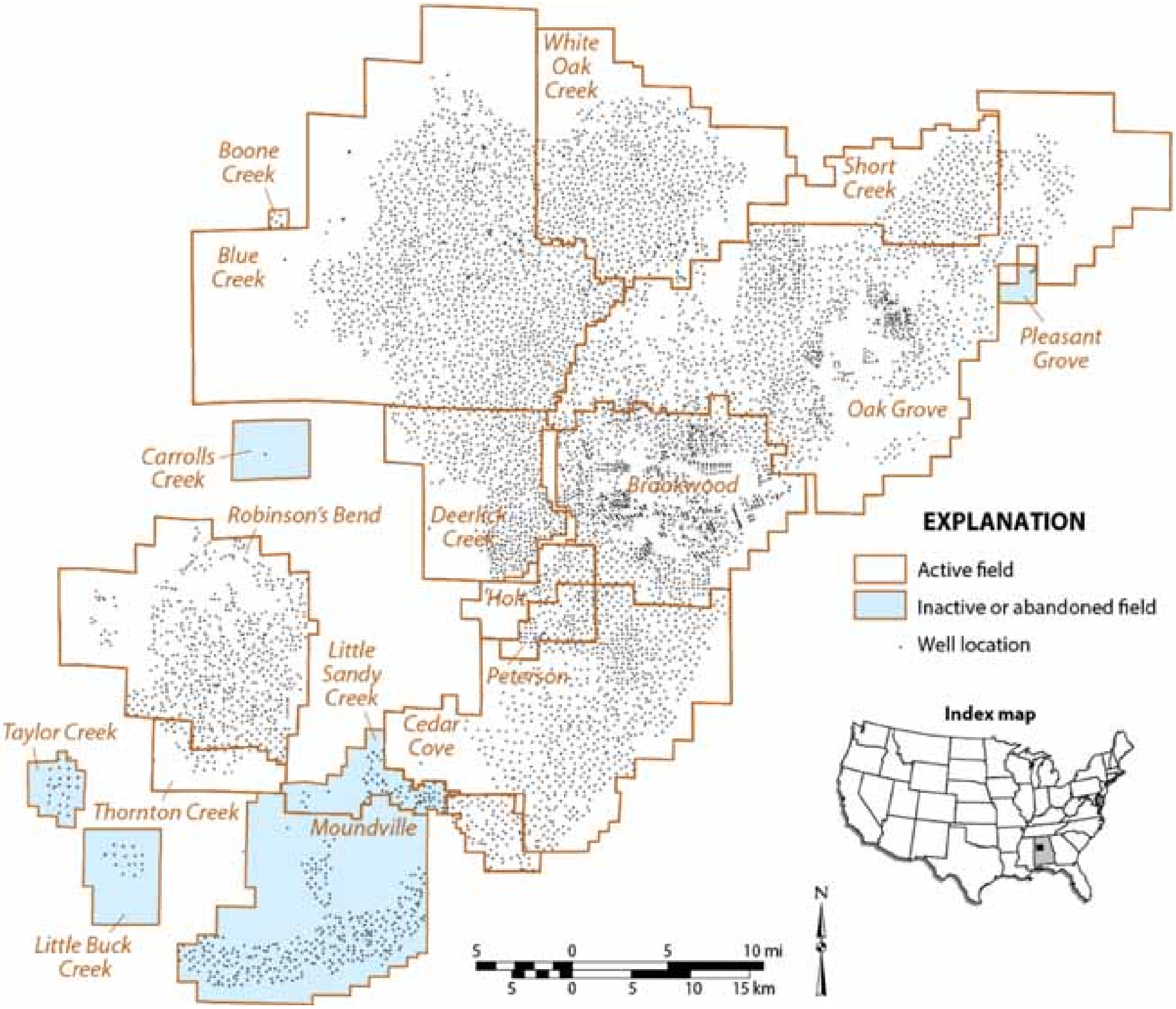


Figure 3.—Coalbed methane fields of the Black Warrior Basin, Alabama.

The CBM resource base in the Black Warrior basin is estimated to be between 10 and 20 Tcf (Hewitt, 1984; McFall and others, 1986). Cumulative CBM production stands at 2.1 Tcf, and Hatch and Pawlewicz (2007) have estimated that an additional 4.6 to 6.9 Tcf may be recoverable. Cumulative water production from the Black Warrior CBM play now exceeds 1.6 billion barrels (bbl), and annual production was higher than 69 million bbl (MMbbl) in 2011. Water production has been rising since 2001 in response to renewed expansion of the CBM industry in Alabama

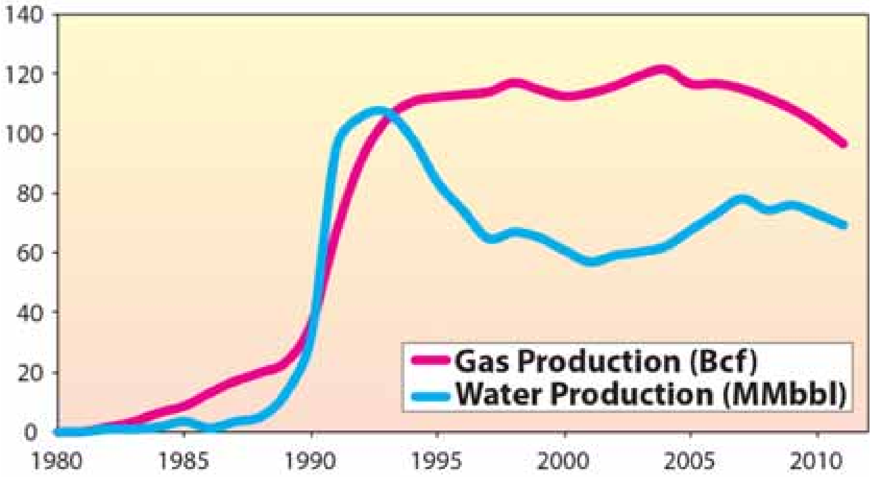


Figure 4.—Chart of annual gas and water production from Black Warrior CBM reservoirs.

(fig. 3). Until recently, the rate of increase was greater than 5 MMbbl/yr, demonstrating that water management issues continue to be of high concern. Wells at peak production produce an average of 1.3 bbl of water per Mcf of gas, and total water production from individual wells can exceed 800,000 bbl (Pashin, 2010b).

Water Management Practice

CBM is largely a hydrodynamic natural gas play, thus understanding basin hydrology is essential for developing a viable strategy for exploration and reservoir management (Pashin and others, 1991; Ayers and Kaiser, 1994; Scott and others, 1994; Scott, 2002). In major CBM regions, such as Black Warrior and San Juan basins, recharge along basin margins is a dominant control on water chemistry, reservoir pressure, gas composition, and gas saturation in coal (Pashin and others, 1991, Ayers and Kaiser, 1994; Scott and others, 1994; Pashin, 2007, 2008, 2010a) (fig. 4). Variation of the composition of reservoir fluids has had a strong influence on the producibility of CBM and the ways produced water has been managed in the Black Warrior basin (Ortiz and others, 1993; Pashin and Hinkle, 1997; Pashin 2007).

All produced water is currently disposed in streams, but a range of water management technologies has been employed, and yet others may be applicable. Underground injection has in the past augmented instream disposal, particularly where produced water is highly saline (Raymond, 1991; Ortiz and others, 1993; Pashin, 2010b). Much of the produced water has TDS content lower than 3,000 mg/L and can potentially be put to beneficial use within and outside the CBM industry. For example, municipal water is now used instead of formation water for hydrofracturing of CBM wells because of scrutiny by environmental agencies. Artificial wetlands may be used to treat produced water, and an experimental program is being conducted in Blue Creek Field by Clemson University, Chevron U.S.A., Incorporated, and the National Energy Technology Laboratory of the U.S. Department of Energy.

This study employed a multidisciplinary approach to the evaluation of CBM reservoirs in the Black Warrior Basin. Accordingly, a broad range of analytical methods were used to assess the geologic and hydrologic framework of the basin and to identify viable strategies for water management. The next section of the report summarizes these methods. After that, the discussion focuses on the geologic and hydrodynamic framework of the basin. Next, the geochemistry of the produced water and gas is characterized. The discussion then shifts to the petrology of the host strata, which records ancient fluid conditions that may have impacted the composition of the produced fluids. The report then considers the production characteristics and life cycles of the CBM wells. In the final section, the results of these analyses are synthesized to identify the options that are available for the management of produced water, as well as to suggest which technologies hold the most promise for implementation.

EXPERIMENTAL METHODS

A battery of field and laboratory techniques was used to assess geology and water management strategies in the Black Warrior CBM play. Evaluation of stratigraphy, geologic structure, and basin hydrology required the collection and analysis of a broad range of subsurface data from well logs and the files of the GSA and the State Oil and Gas Board of Alabama (OGB). Samples of produced water and gas were collected at wellheads and were analyzed in the geochemical laboratories of the GSA and the U.S. Geological Survey (USGS). Petrologic analyses were performed on vein fills in core to determine mineralogy and the stable isotopic composition of calcite. Production data were compiled from OGB files and were analyzed statistically, temporally, and geospatially. A geographic information system (GIS) was then developed to assist understanding the spatial and temporal relationships between fluid production and disposal and to assist in the identification of viable water management strategies. Detailed explanations of the methodology used in this study are given in the following sections.

Stratigraphic and Structural Methods

Stratigraphic and structural data were collected from geophysical well logs available at the State Oil and Gas Board of Alabama. All wells in this report are identified by State Oil and Gas Board of Alabama permit numbers. Geological and engineering parameters are reported in a combination of Imperial and metric units to maintain consistency with the ways data are reported in geophysical well logs and to maintain consistency with common usage by operators in the region.

Gamma-density logs were correlated using standard stratigraphic procedures. Regionally correlable stratigraphic markers, including major marine flooding surfaces and coal seams, were used to identify coal zones and named coal seams where applicable. To facilitate subsurface mapping, stratigraphic, structural, and well-location data from 6,762 wells were compiled into a spreadsheet. Well locations were plotted using the latitude and longitude values in the OGB database. Stratigraphic data include the depth of the top of each coal zone and net coal thickness in each coal zone. Coal thickness was determined using high-resolution density logs, which typically have a scale of 1 inch equals 25 feet. Depending on the logging tool and recording apparatus, the accuracy of these logs ranges from 0.1 to 0.5 foot. Coal beds thinner than 1 foot are seldom completed for gas production and were thus excluded from the thickness determination to provide a reliable approximation of the quantity of coal that functions as reservoir.

Structural data include bed elevation and fault-cut information. The elevation of each cycle boundary was computed by subtracting depth from the appropriate structural datum, which for CBM wells is typically ground level or the elevation of the kelly bushing. Faults also were identified as wells were correlated. Normal faults were identified on the basis of missing section, whereas reverse faults were identified on the basis of repeated section. Depth, elevation, and vertical separation were determined and recorded for each fault cut identified. Vertical separation was determined by the thickness of missing or repeated section. Uncertainty in the location of each fault cut was quantified, and the juxtaposed coal zones were identified and recorded.

Maps of coal thickness and geologic structure were made using Petra software. Maps were gridded and contoured in Petra using a minimum curvature algorithm. The map grids have a cell size of 820 feet (about 15 acres), which provides the high resolution required to ensure that well data are honored. A net coal isolith map of the Black Creek through Brookwood coal zones was made using a contour interval of 10 feet. A structural contour map of the top of the Pratt coal zone was made using a contour interval of 100 feet. Fault-cut information was used to determine bed-fault intersections, but where well control is inadequate, fault and fold traces were compiled from the records of the GSA and OGB. Locations of faulted wells, elevation changes of coal-zone markers, and anomalous interval thicknesses were all used to find and project faults. The final stages of interpretation were to make structural cross sections showing fold and fault geometry and to make a structural contour map showing the elevation of the top of the Pratt coal zone and the locations of mappable fault traces.

Hydrologic and Geochemical Methods

A series of techniques were used to characterize the hydrodynamics of the Black Warrior CBM play. Data include porosity and permeability as determined from cores and well tests. Fracture networks also were characterized because joints, cleats, and fault zones are the principal flow conduits in Black Warrior CBM reservoirs. Reservoir pressure was determined using data from geophysical well logs; the data were compiled in a spreadsheet with the stratigraphic and structural data. Minimum reservoir pressure was determined from well depth and water-level information recorded in the headers of well logs or interpreted from resistivity and gamma-ray profiles. Where possible, water level data were augmented by gauged pressure data that is obtained by operators when wells are completed. Fresh water exists at depth throughout much of the CBM fairway (Pashin and others, 1991; Ellard and others, 1992), so reservoir pressure was estimated using a freshwater hydrostatic gradient of 0.433 psi/ft (pounds per square inch per foot). Once data were compiled, the hydrostatic pressure gradient for each well was computed, pressure-depth plots were made, and a map of hydrostatic pressure gradient was made in Petra.

This research draws on a database that includes 206 analyses of the geochemistry of produced water. These data include physical and aggregate water properties, as well as the concentrations of major ionic compounds, metallic and nonmetallic constituents, and organic constituents. Produced water samples were collected between 2010 and 2012 at wellheads. Field parameters (conductivity, pH, turbidity) were recorded using a Horiba U50 Multi Water Quality Checker. Raw water was collected in the instrument's sample vessel, and the instrument was inserted into the vessel for analysis. The tool was calibrated using Horiba calibration fluid, distilled water, and pH 4 and 7 standard solutions before each sampling trip.

Samples were prepared for laboratory analysis at the Geological Survey of Alabama, the University of Alabama (UA), and the U.S. Geological Survey (USGS). Raw water was collected in two 250 ml Whirl-Pak bags as backup and to determine TSS. For filtered samples, water was passed through glass fiber prefilters and 0.45-μm filter membranes using a plastic-vacuum-hand pump. The filtered water was decanted into a series of Whirl-Pak bags, polyethylene bottles, and glass bottles. A series of unfiltered samples also was collected in a similar set of receptacles. Some receptacles and samples were treated with H_2SO_4, NaOH, and HNO_3 as prescribed by standard sampling procedures for the various analytes. All samples were chilled to ~4° C in coolers for transport to the laboratory.

In the laboratory, a Dionex 4000i ion chromatograph was used to determine the concentrations of Br, F, NO_3, PO_4, and SO_4 with precision exceeding 0.06 mg/L. A Perkin-Elmer 3000 DV ICP-MS was used to determine many metallic and nonmetallic constituents, including Ag, Al, B., Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, SiO_2, Sn, Sr, Ti, V, and Zn, with precision varying between 1 μg/L and 1 mg/L depending on the analyte. A Perkin-Elmer 5100PC GFAAS was used to quantify key trace elements (As, Cs, Pb, Rb, Sb, Se, and Ti) with precision exceeding 2.0 μg/L, and a Perkin-Elmer 2380 CVAAS was used to determine Hg with a sensitivity of detection of 0.010 μg/L. TOC was determined using a Shimadzu TOC-5000A analyzer. Alkalinity, Cl, CN, F, NH_3, NO_2, P, Phenolic compounds, and TKN were determined using a Technicon Autoanalyzer. All determinations were made using third-party quality control samples and using standard procedures specified by the U.S. Environmental Protection Agency and the U.S. Geological Survey. For quality control, replicate analyses were run on selected samples, and ionic concentrations were checked for charge balance. Reproducibility of measurements was high, with error < 2 percent for most analytes. Additional samples were collected and processed by the U.S. Geological Survey for GC-MS analysis of the organic compounds and selected inorganic compounds in the produced water, including DOC, extractable hydrocarbons, volatile fatty acids, PO_4, and NH_4 using the analytical methods described by Orem and others (2007) and in a supplemental file that is included with this publication.

Wellhead gas samples were collected from 103 well sites using an Isotube sampling system. The samples were sent to Weatherford Laboratories for geochemical analysis. Analysis of gas composition included the determination of the quantities of hydrocarbon (C_1-C_6) and nonhydrocarbon gases (He, Ar, O_2, N_2, CO_2). Composition was determined by gas chromatograph with analytical precision of +/- 5 percent for most gases and of +/- 10 percent for $C_{4\text{-}6}$ hydrocarbons. Oxygen concentrations were used to correct the analyses for atmospheric contamination. Stable isotope analysis of methane was performed on the gas samples and included $\delta^{13}C_1$ and δD determinations. Isotopic determinations were made on a GC-IRMS unit with analytical precision of 0.3‰ for $\delta^{13}C_1$ and 3.0‰ for δD.

Geochemical data from the water and gas analyses were compiled in a spreadsheet and incorporated into a Petra database that contains a broad range of geological information, including well locations, stratigraphic data, and structural data. Bubble maps were made in Petra that show variation of water chemistry and gas composition in the study area. Major ionic concentrations were plotted on Piper diagrams to classify the formation water, and stable isotopic data were cross-plotted to help interpret the origin of the coalbed gas. Compositional data also were plotted against other geological and geochemical variables, such as coal rank parameters and TDS, to determine basic geologic controls on water and gas composition. Summary tables are included in this paper, and supplemental files containing the basic data are bundled in this PDF document.

Petrologic Methods

Petrologic research focused primarily on mineral cements, and to a lesser extent on framework rock composition. The distribution and quantity of epigenetic minerals was determined in core samples, polished slabs, and thin sections of coal, sandstone, and shale. The primary emphasis was on mineral identification, mineral habit, and cement stratigraphy. Basic tools that were used include petrographic microscopes at the GSA, as well as a scanning electron microscope at the UA. Typical and diagnostic features were identified and documented using digital microphotography.

Mineral cements provide valuable information on the geochemical evolution of sedimentary basins, including hydrodynamic and methanogenic processes in organic-rich strata (e.g., Budai and others, 2002; Pitman and others, 2003). Fracture-filling calcite was extracted from 22 long cores distributed among the Black Warrior CBM fields. Samples were extracted by hand and by drill from veins (i.e., joint and fault-related fracture fills) in sandstone and shale and from cleats in coal. Stable isotopic analysis was performed to determine $\delta^{13}C$ and $\delta^{18}O$ values for the calcite cement. Isotopic composition was measured at UA with a GasBench-IRMS system using a method similar to that described by Debajyoti and Skrzypek (2007). Isotope values are expressed relative to the VPDB scale by use of the NBS-19 standard. Maps were constructed to demonstrate geographic variation of the stable isotopic composition of mineral cement.

Production Analysis

The OGB maintains a comprehensive database of gas and water production from CBM wells in the Black Warrior basin. Production curves for selected wells were generated analyzed graphically and statistically to determine basic decline characteristics for gas and water, and understand the basic production lifecycle, and to understand the relationship of well performance to regional geology and hydrogeology. Peak and cumulative production values for gas and water were extracted from the OGB database. The data were analyzed statistically to understand how wells perform over the short- and long-term. Statistical analysis included the construction of probability plots showing the range and frequency of cumulative and peak production values. In addition, regression analysis was performed to determine the relationship of peak production to cumulative production.

Maps of peak, annual, and cumulative gas production were made in Petra. Production values for each well were plotted as color-coded bubbles, which proved to be an effective way to display regional variation of well performance, as well as local variability. Comparison of production maps with geologic, hydrologic, and chemical data helped determine where different water management and gas production issues exist and helped the project team develop water management solutions. Maps of annual production were made to show snapshots of gas and water production rates at various times in the history of the Black Warrior CBM industry. These maps demonstrate how production patterns have changed through time, help identify areas where specific production issues have existed, and provide a basis for predicting future production trends and the water management strategies that best fit those trends.

Strategy Development

The previous sections highlight the geologic, hydrologic, geochemical, and production data and methodology required to make informed water management decisions. Developing management strategies requires synthesis of results in a way that is accessible to decision makers. This approach enables evaluation of existing practices, identification of ways practices can be improved, and the proposition of new and alternative practices that focus on the beneficial uses of produced water. This effort centers on optimization of production and water handling operations to minimize the environmental impact of produced water while ensuring that CBM reserves can be booked and delivered to market at reasonable cost.

Key questions to be answered by this approach are as follows: What is the environmental impact of instream disposal where formation water is fresh, and will this strategy remain viable in the future? What is the impact of instream disposal of saline formation water? Can production operations be optimized to increase gas recovery and minimize stream loading where saline formation fluid is produced? Is subsurface disposal of produced fluid a viable strategy to facilitate increased pumping rates, and hence increased gas recovery, where saline formation water is produced? Are there ways that produced water can be processed and transported at reasonable cost that will increase production capacity while maintaining or improving environmental quality? Answering these questions employed a volumetrically driven GIS approach using Petra and Arc/Info software that considers production life cycles, water chemistry, water processing techniques, and water management infrastructure. An essential part of this approach was identifying wells that are allocated to specific water processing facilities and National Pollutant Discharge and Elimination System (NPDES) discharge points. This method enabled understanding of the impact of production operations on the quality of surface water through time. The GIS system is incorporated into this report as a supplemental data package that can be loaded into Petra, which is a petroleum-based GIS system that is widely deployed by the oil and gas industry.

The final step in this study was to use the GIS to help identify beneficial uses for produced water that can reduce environmental impact and can ensure that CBM can be produced at reasonable cost. Key questions relating to beneficial use are: What beneficial uses for produced water exist within the CBM industry that can aid drilling, completion, stimulation, and production operations? What industrial uses for produced water exist outside the CBM industry, and are any of those uses candidates for early deployment? What types of agricultural uses exist for produced water, and are waters with different chemistry candidates for deployment in different agricultural sectors? What opportunities exist for municipal use of produced water, including domestic water supply and drought relief, and what types of processing and transportation infrastructure will be required to realize this potential?

GEOLOGIC FRAMEWORK

The Black Warrior Basin is a late Paleozoic foreland basin in Alabama and Mississippi (Thomas, 1985a, 1988, 1995) (fig. 1). The basin encompasses a triangular region that is bordered on the southeast by the Appalachian orogen, on the southwest by the Ouachita orogen, on the northwest by the Mississippi Valley graben, and on the north by the Nashville Dome. Coal-bearing strata of the Pennsylvanian-age Pottsville Formation are exposed in the northeastern part of the basin, and the basin is buried below Mesozoic-Cenozoic strata of the Gulf of Mexico Basin in the southwestern part.

The CBM fields are situated near the southeastern margin of the basin along the frontal structures of the Appalachian orogenic belt (e.g., Pashin and Groshong, 1998; Groshong and others, 2009, 2010) (fig. 5). Pottsville strata are exposed in the northeastern part of the CBM development area and are overlain with angular unconformity by poorly consolidated Cenozoic strata in the southwestern part. This section of the report establishes the geologic framework of Pottsville CBM reservoirs. This framework is the principal determinant of the quantity, quality, and variability of the fluids produced from Pottsville coal seams. Discussion begins with a summary of Pottsville stratigraphy and sedimentation and continues with a characterization of the structural and tectonic framework. The section concludes with a summary of the burial and thermal history of the region.

Stratigraphy and Sedimentation

Economic coal and CBM resources are in Upper Carboniferous (Lower Pennsylvanian) strata of the Pottsville Formation. The lower Pottsville Formation is dominated by sandstone and contains few economic coal seams. By contrast, the upper Pottsville Formation contains the bulk of the economic coal resources in the basin, including the major mining targets and all of the proven CBM reservoirs (figs. 6, 7). Upper Pottsville coal seams are distributed through a stratigraphic section that is generally between 2,000 and 4,500 feet thick and is composed

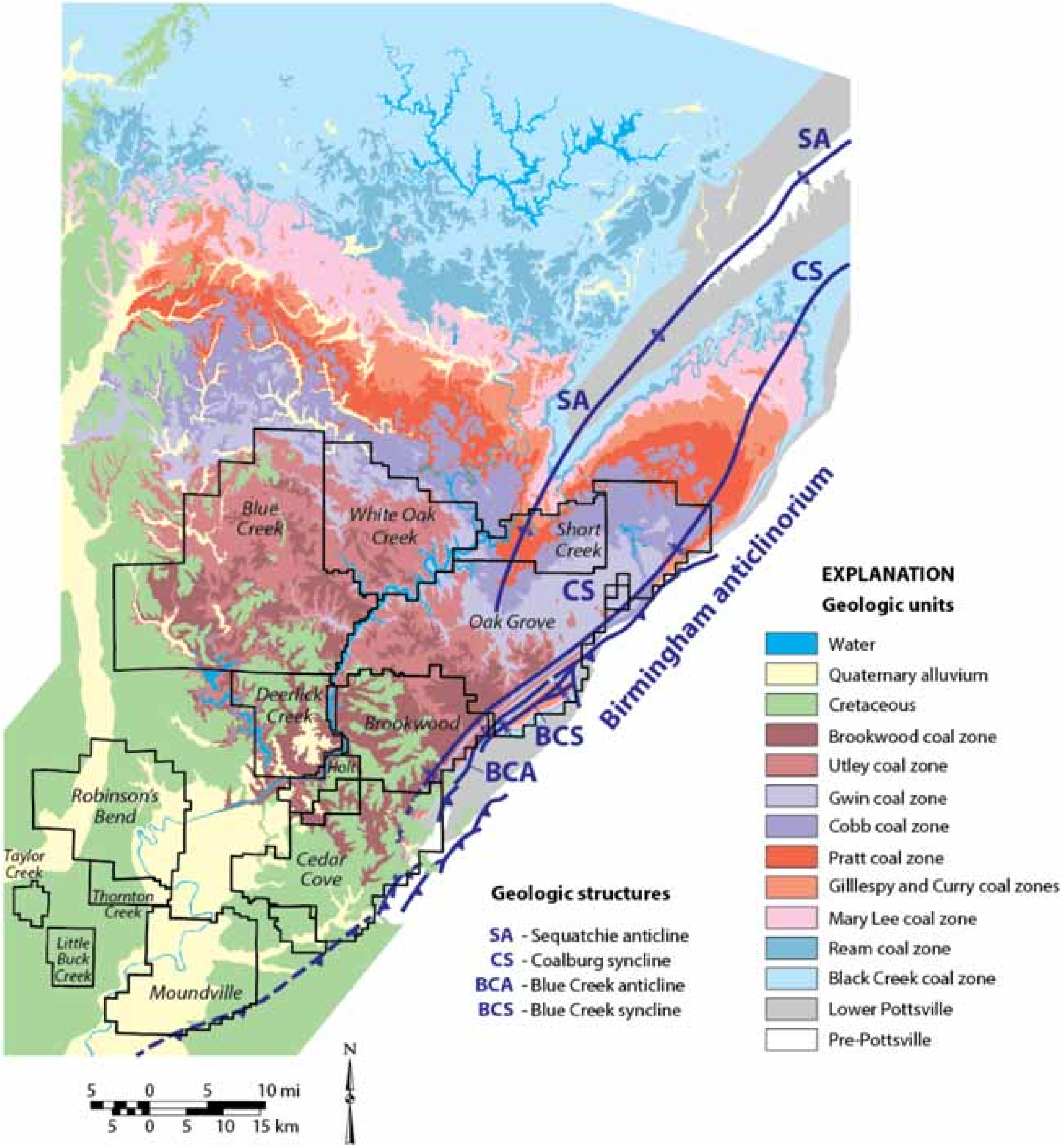


Figure 5.—Geologic map of the eastern Black Warrior Basin showing outcrop areas of Pottsville coal zones, major geologic structures, Cretaceous cover strata, and the locations of CBM fields.

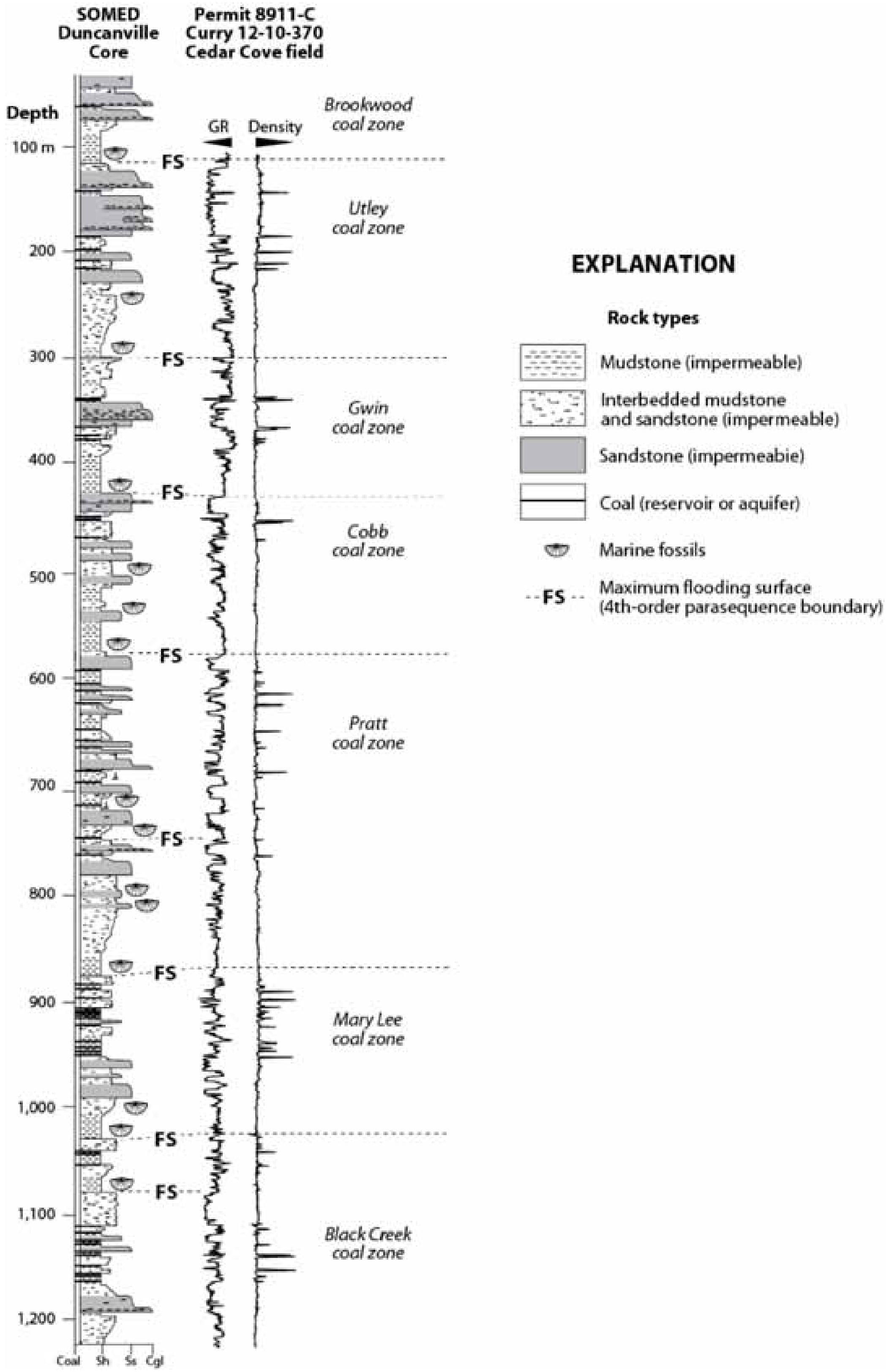


Figure 6.—Graphic core log and geophysical well logs showing stratigraphy of the upper Pottsville Formation in the Black Warrior CBM fields.

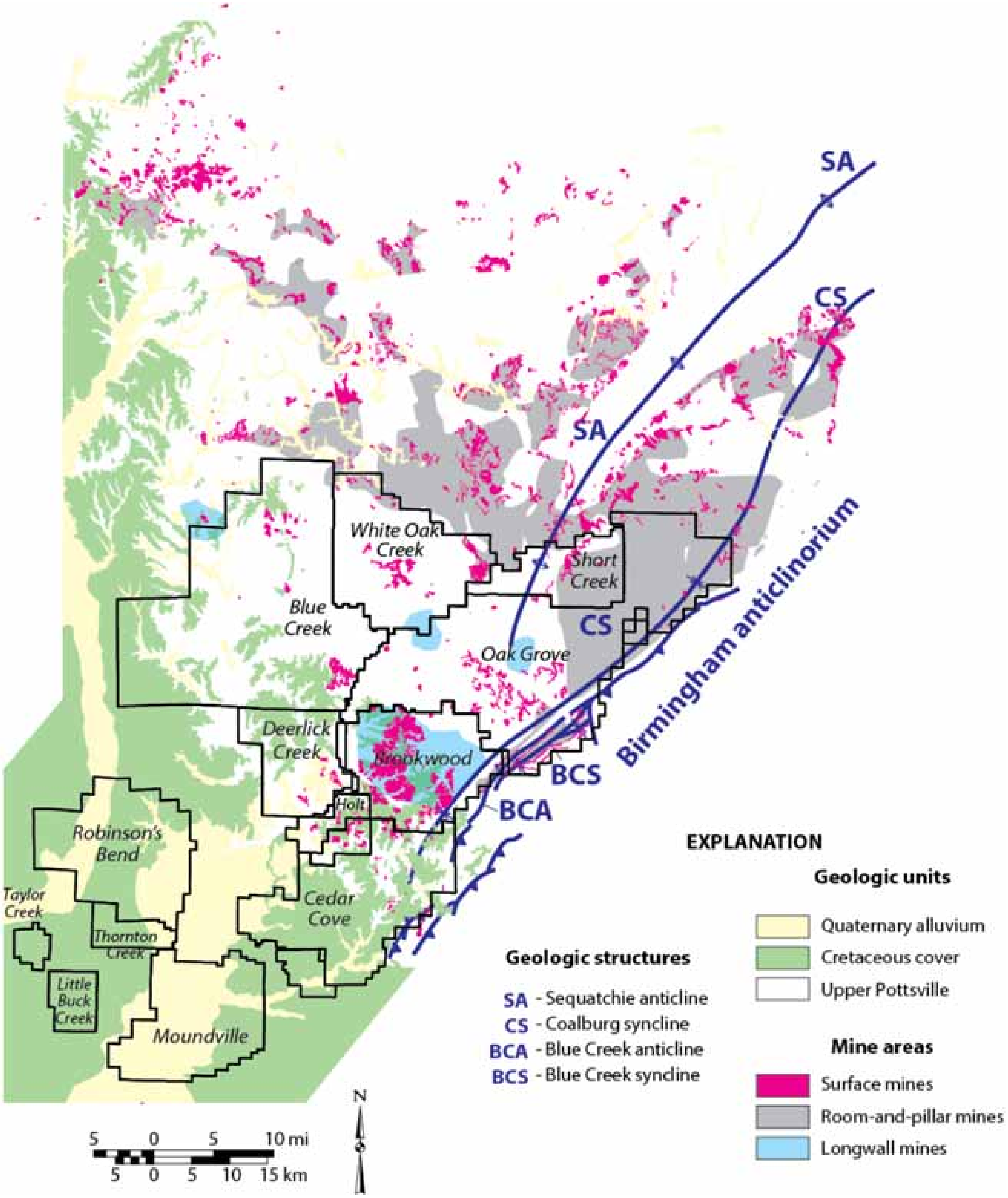


Figure 7.—Map showing distribution of coal mines in relationship to major geologic structures, CBM fields, and Cretaceous cover in the eastern Black Warrior Basin.

principally of shale and sandstone. Seam thickness ranges from less than 0.1 foot to more than 10 feet, and beds as thin as 1 foot are routinely completed for production.

The vast majority of the CBM wells in the Black Warrior Basin are standard vertical wells that are completed in the Black Creek through Pratt coal zones; younger coal zones are commonly perforated in the southwestern CBM fields. Collectively, the completed zones are combined into a single pool that is designated by the OGB as the Pottsville Coal Interval. Five to eight seams have been completed in most wells within the study area, although some wells in the southwestern part of the development area produce from more than 20 seams. The bulk of the wells have been hydrofractured in multiple stages with each stage corresponding to a coal zone. The most common completion fluid is nitrogen foam, although many wells have been hydrofractured with water or gel, and hydraulic fractures are typically propped with 40- to 80-mesh sand. Water is produced through tubing, whereas gas is produced through the annular space between tubing and casing and is commingled from all coal zones. Typical completion depths are between 500 and 2,500 feet, and vertical wells are most commonly drilled with 40-80 acre spacing. Horizontal and gob wells are drilled in conjunction with deep longwall coal mining operations in Brookwood and Oak Grove fields. Virtually no water is produced from the mine-related wells, which are thus excluded from this investigation.

Cyclicity, depositional environments, and sequence stratigraphy.—McCalley (1900) recognized stratigraphic clusters of coal seams, which he called coal groups, that could be correlated across the eastern Black Warrior basin. These coal groups, properly termed coal zones in modern usage, were the basis for most later subdivisions of the Alabama Pottsville (Butts, 1910, 1926; Culbertson, 1964; Metzger, 1965). Butts (1926) recognized evidence for numerous marine transgressions and regressions during Pottsville deposition. During the late 1960's and 1970's, the Alabama Pottsville was central in the development of facies models for Appalachian coal-bearing strata (Ferm and others, 1967; Horsey, 1981; Rheams and Benson, 1982; Ferm and Weisenfluh, 1989). Wanless (1976) made brief mention of cyclicity in the Pottsville Formation, but basinwide depositional cycles were confirmed fairly recently (Pashin and others, 1991; Pashin, 1994a, b, c; Gastaldo and others, 1993). Pashin (1994b, 2004) and Pashin and Raymond (2004) suggested that high-frequency glacial eustasy was the dominant mechanism that drove depositional cyclicity in the Pottsville.

Pottsville depositional cycles are internally heterogeneous (fig. 8). The basal surface of each cycle is typically sharp; marine fossils are concentrated above this surface. The shale above the fossil concentrations is typically between 30 and 300 feet thick and contains burrows and scattered shells. Pottsville sandstone and conglomerate varies from gray litharenite containing low-grade metamorphic rock fragments to pale quartzarenite (Mack and others, 1983). Pottsville litharenite is impermeable, or tight, whereas the sublitharenite and quartzarenite are commonly permeable (Pashin and others, 1991). Lithic sandstone is in places thicker than 150 feet and includes progradational foresets and a variety of channel fills. Most of the quartzose sandstone was deposited basinward of the tight sandstone and forms fining-upward successions 30 to 200 feet thick. Importantly, reservoir-quality sandstone in the upper Pottsville is restricted to areas northwest of the CBM fields. Each cycle is capped by a lithologically heterogeneous coal zone containing one or more coal beds that are intercalated with shale and sandstone.

The cycles are flooding surface-bounded depositional units that can be interpreted as parasequences according to the terminology of Vail (1987) or genetic stratigraphic sequences according to the terminology of Galloway (1989). The surfaces at the base of the Pottsville

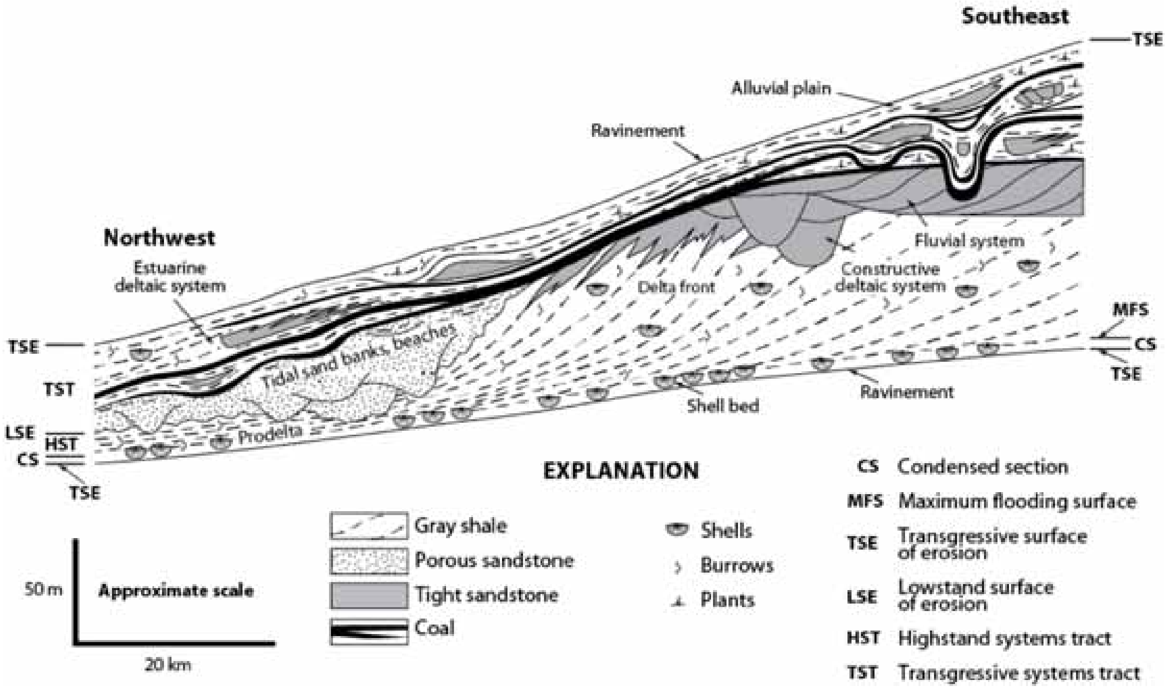


Figure 8.—Idealized depositional cycle in the upper Pottsville Formation of the Black Warrior Basin (modified from Pashin, 1994a, 2004).

cycles are interpreted as transgressive surfaces of erosion, or ravinements, and the overlying fossil concentrations mark condensed sections that formed at maximum flooding (Liu and Gastaldo, 1992; Pashin, 1998) (fig. 8). The coarsening-upward shale-sandstone intervals above the fossil concentrations record deltaic progradation during highstands of sea level (e.g., Gastaldo and others, 1993). Lithic sand is compositionally and texturally immature and was shed rapidly from the Appalachian orogen into the foreland basin. Quartzose sandstone was derived locally by marine reworking of lithic sand (Mack and others, 1983), and recent petrologic investigations indicate transport of sand from remote sources (Moore, 2012). The quartzose sandstone was apparently deposited following lowstands of sea level in tidal sand banks and beach-barrier systems (Hobday, 1974; Gastaldo and others, 1993; Pashin, 1994a, 1998). The coal zones accumulated in diverse coastal-plain settings from highstand into the early stages of marine transgression (Pashin, 1998). The sandstone and conglomerate units associated with the coal beds include a broad range of fluvial and tidal-flat deposits, and the shale units include associated flood-basin and mudflat environments (Rheams and Benson, 1982; Pashin and others, 1991; Demko and Gastaldo, 1996). Coal beds are the products of peat swamps and represent equatorial wetlands that flourished on the Pottsville coastal plain (Eble, 1990; Pashin, 1994a).

Coal thickness and distribution.—Pottsville strata thicken southeastward into an area called the Moundville-Cedar Cove depocenter, which is in the southern part of the study area (fig. 9). The interval from the top of the Black Creek coal zone to the top of the Gwin coal zone is just over 1,000 feet thick in the northern part of the study area and exceeds 2,500 feet in the depocenter. The thickness and percentage of sandstone in the upper Pottsville increases toward the depocenter, as does the number of coal seams in each coal zone (Pashin, 1994b; Pashin and Raymond, 2004). The depocenter is interpreted to be an area of increased subsidence that formed in response to thrust and sediment loading in the Appalachian orogen (Pashin, 1994b, 2004). An abundance of lithic sandstone in the depocenter indicates that it was a major receptacle of fluvial-deltaic sediment.

Net completed coal thickness in the Black Creek through Brookwood coal zones also increases toward the Moundville-Cedar Cove depocenter (fig. 10). Less than 10 feet of coal is present in parts of White Oak Creek, Robinson’s Bend, and Taylor Creek fields. Low net coal values in the mining areas of Brookwood and Oak Grove Fields reflect wells reaching total depth in the Mary Lee coal zone rather than any depositional factor. Net coal thickness exceeds 40 feet in much of the Moundville-Cedar Cove depocenter, and in parts of Moundville Field, net coal thickness is greater than 70 feet. Southeastward thickening of upper Pottsville strata reflects

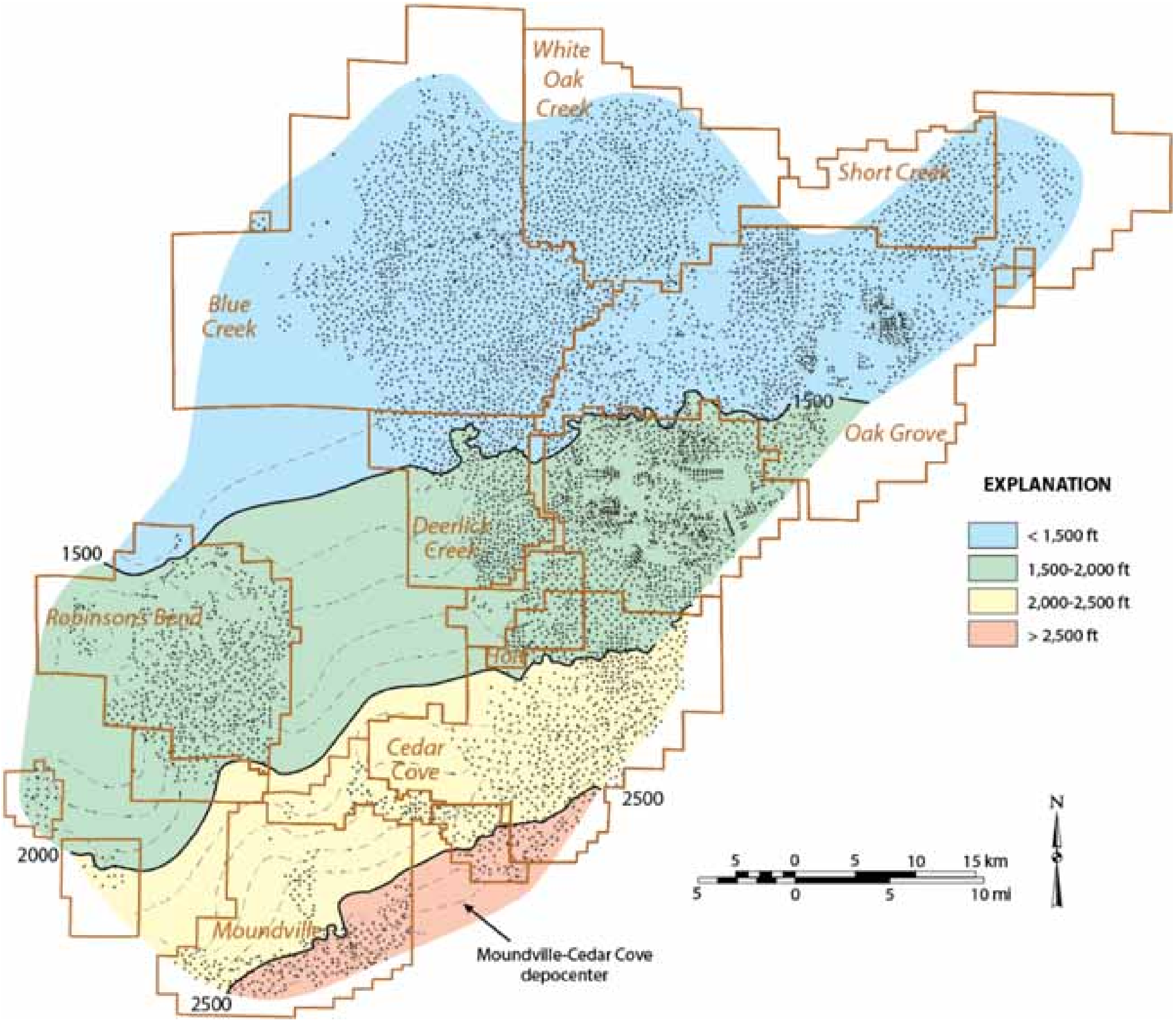


Figure 9.—Isopach map of the Black Creek through Gwin coal zones in the Black Warrior CBM fields.

subsidence of the Moundville-Cedar Cove depocenter during the early stages of Appalachian orogenesis (Pashin, 2004). Coal thickness trends reflect not only subsidence of the depocenter, but the development of a coastal plain that supported peatland environments adjacent to the uplifting Appalachian orogen.

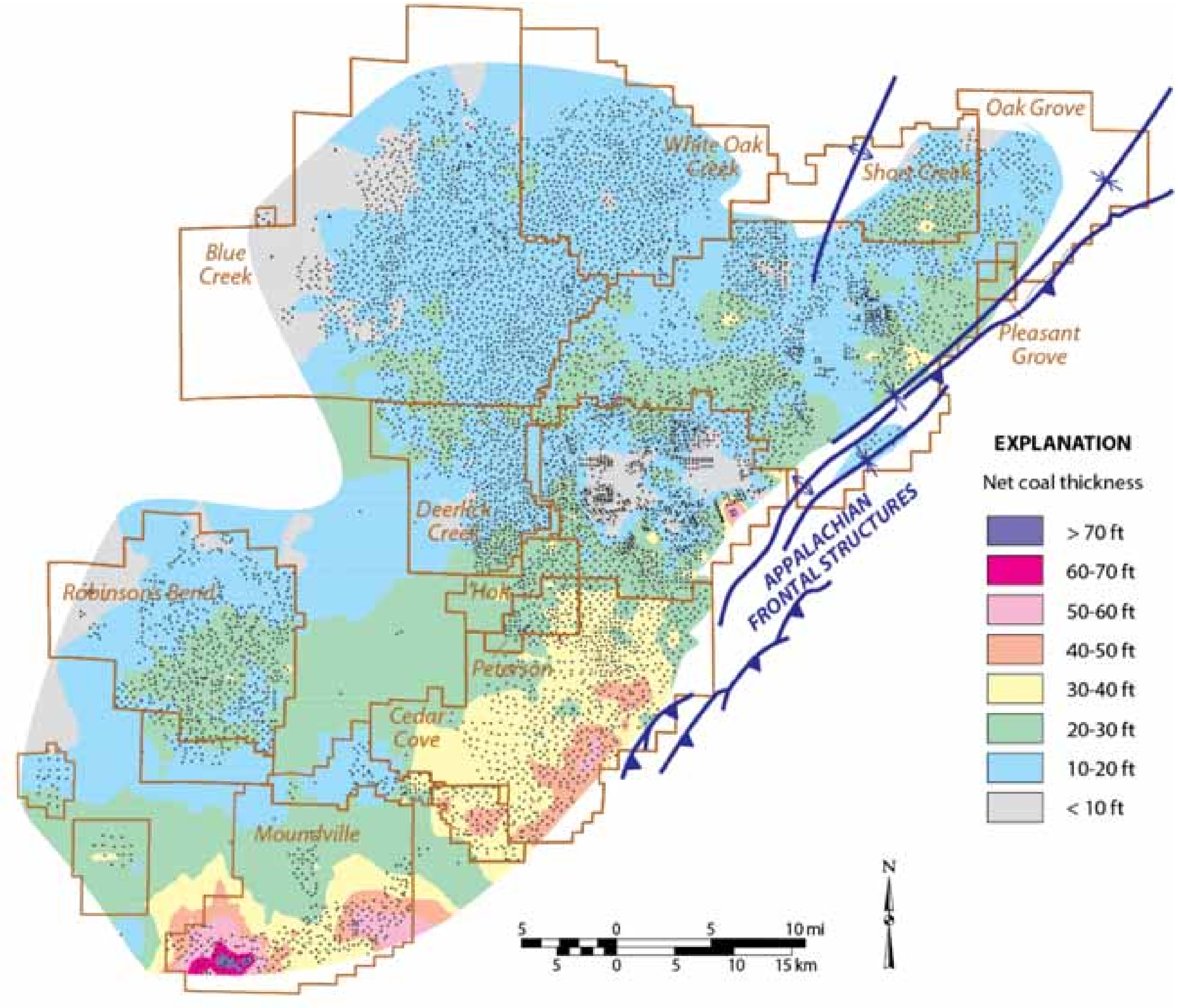


Figure 10.—Net coal isolith map of Pottsville Coal Interval in the Black Warrior CBM fields. Coal seams thinner than 1 foot are generally too thin to complete for production and are thus excluded from the map.

Cretaceous cover strata.—Upper Cretaceous strata of the Tuscaloosa Group disconformably overlie Paleozoic strata in much of the Black Warrior Basin (figs. 5, 7). The Tuscaloosa Group is composed primarily of weakly consolidated sandstone and conglomerate with some significant interbeds of shale and claystone. Tuscaloosa strata in the CBM fields post-date the Black Warrior Basin and form the updip fringe of the Gulf of Mexico Basin. These strata form a sedimentary wedge that thickens southwestward from a feather-edge in Brookwood Field to more than 900 feet in Little Buck Creek and Taylor Creek Fields. Sandstone and conglomerate in the Tuscaloosa Group constitute a major aquifer that is a vital source of potable water in much of Alabama. Accordingly, protection of this valuable resource is of great importance in areas of CBM development.

Structure and Tectonics

Folding, faulting, and fracturing modify the geometry, continuity, and hydraulic conductivity of coal-bearing strata. Tectonic deformation of the Pottsville Formation began during deposition and continued after deep burial (Weisenfluh and Ferm, 1984; Thomas, 1988; Pashin, 1994c, 1998; Pashin and Groshong, 1998). Major structures in the Pottsville Formation include the compressional folds and thrust faults of the Appalachian thrust belt and horst and regional graben systems of the foreland basin (figs. 5, 11). All of these structures are truncated at the sub-Cretaceous unconformity, which dips southwestward and records late-stage tilting of the basin (Kidd, 1976; Pashin and others, 1991). Strata in the Pottsville Formation lack matrix permeability to water, thus virtually all flow is through natural fractures (Pashin and others, 1991). Natural fractures in the Pottsville include joints, cleats, and fault-related shear fractures (Ward and others, 1984; Pashin and others, 1999).

Appalachian folds and thrust faults.—Pashin and Groshong (1998) suggested that large-scale folds and faults influence coalbed methane production by determining the abundance and openness of natural fractures. The eastern Black Warrior basin can be characterized most simply as a southwest-dipping homocline upon which folds and faults have been superimposed

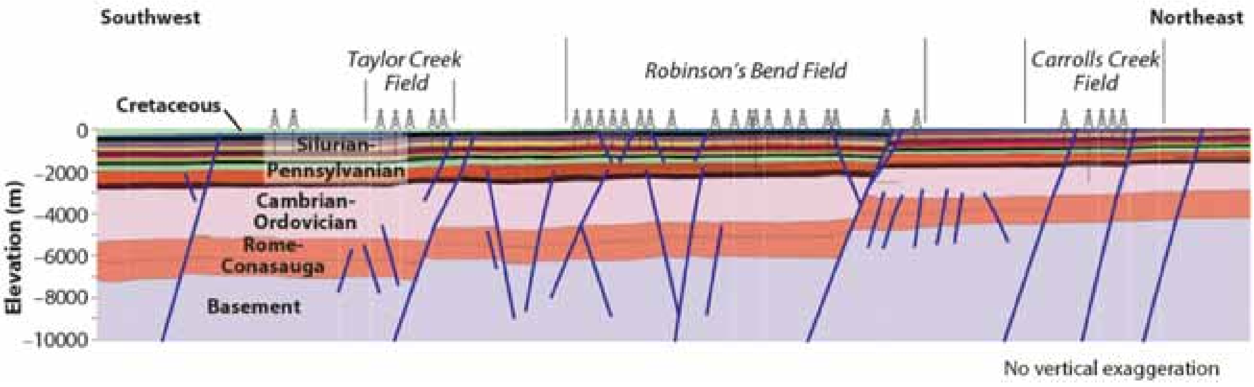


Figure 11.—Structural cross section showing thick-skinned normal faults in the Black Warrior Basin (modified from Groshong and others, 2010).

(Thomas, 1988) (fig. 12). Folds of the Appalachian thrust belt have deformed the southeast margin of this homocline and include the Sequatchie anticline, the Coalburg syncline, and the Blue Creek anticline. The Sequatchie anticline is a prominent frontal structure of the Appalachian orogen in Alabama and Tennessee; it plunges southwestward, terminating in northern Oak Grove Field. In Oak Grove Field, the Sequatchie anticline is a broad, open detachment fold with an interlimb angle of 178° and about 400 feet of structural relief (Pashin, 1994c; Pashin and Groshong, 1998).

Structures along the southeast margin of the coalbed methane development area include northeast-striking folds associated with the forelimb of the Birmingham anticlinorium (fig. 12). The anticlinorium is a broad, anticlinal structure that is detached in Cambrian shale and brings Cambrian-Ordovician carbonate rocks to the surface (Osborne and others, 1989; Thomas, 2001). The Coalburg syncline is a flat-bottomed structure that shares common limbs with the Sequatchie anticline and Birmingham anticlinorium (Blair, in Semmes, 1929) and has an axial trace that follows the southeast margin of the coalbed methane fairway. The southeast flank of the Coalburg syncline is vertical in places and has been overthrust in part by Cambrian-

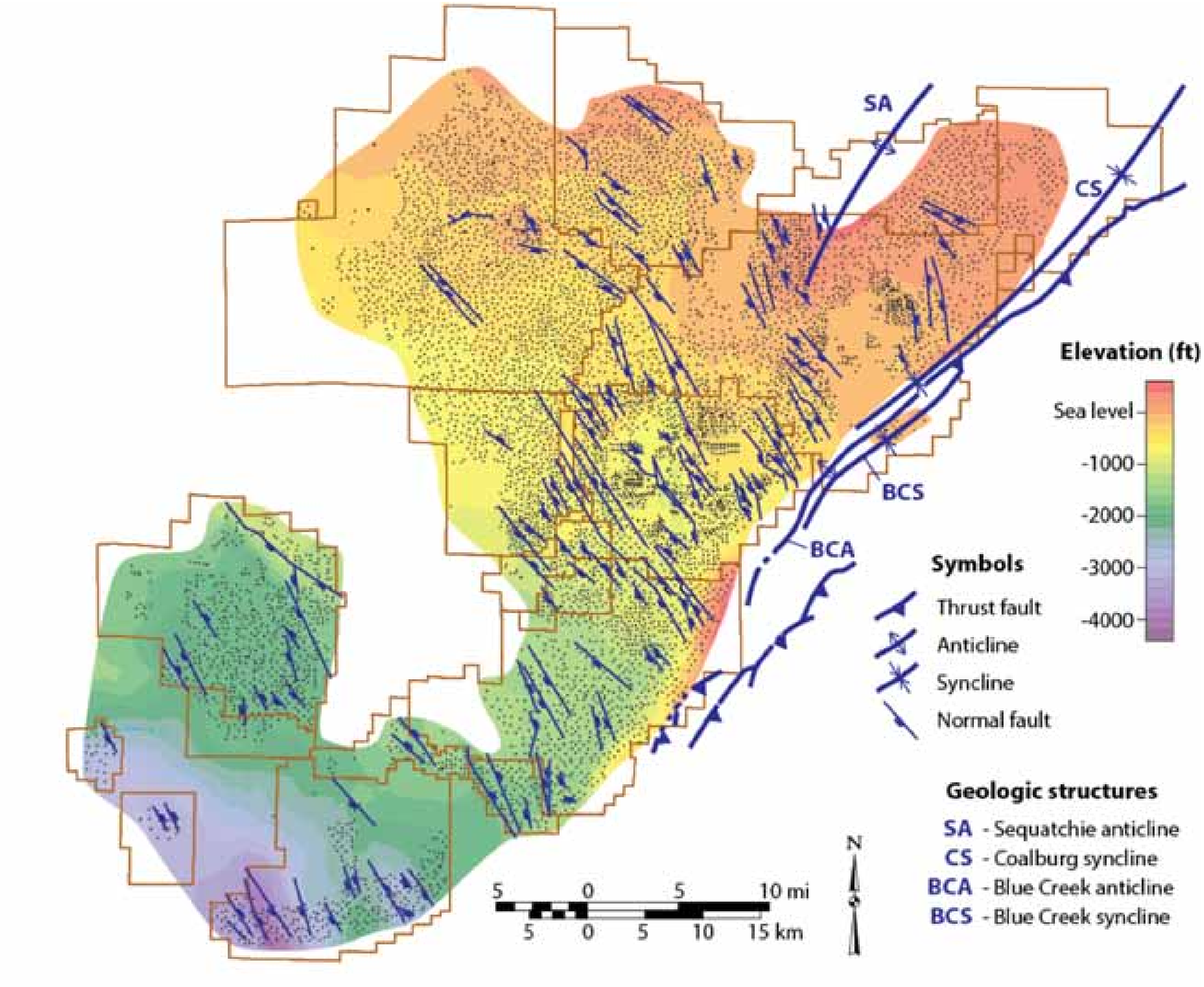


Figure 12.—Structural contour map of the top of the Pratt coal zone showing locations of folds, thrust faults, and normal faults in the Black Warrior CBM fields.

Ordovician carbonate rocks (Butts, 1910, 1927; Osborne and others, 1989). Thus, the southeastern margin of the basin adjacent to the CBM fields can be characterized as part of a footwall syncline in the forelimb of the Birmingham anticlinorium.

The Blue Creek anticline is an arcuate structure that strikes northeast, following the southeast boundaries of Oak Grove and Brookwood fields (fig. 12). The forelimb of the structure locally dips steeper than 50° NW and is thought to be a major recharge zone that has fed freshwater deep into the Pottsville Formation through coal beds and fractures exposed on the flank (Pashin and others, 1991; Ellard and others, 1992; Pashin, 2007) (fig. 13). The Blue Creek anticline is thought to have formed above a blind detachment in Mississippian-age siliciclastic rocks (Thomas, 1985b; Cates and Groshong, 1999). Pottsville strata occur in both limbs of the anticline, and the Mary Lee coal zone is exposed in the forelimb within a mile of where it is degassed at depth.

Horst and graben systems.—The southwest-dipping homocline of the Black Warrior basin is broken by normal faults that generally strike northwest (figs. 11, 12, 14). Trace length of the subsurface-mappable faults ranges from about 1 to 8 miles. Fault strike averages about N. 30° W. and changes across the region from N. 7° W. in eastern Oak Grove Field to N. 54° W. in Robinson's Bend Field. Dip of the faults is generally between 50 and 70°, and the faults form horst-and-graben systems in which about 60 percent of the faults dip southwest. The faults are effectively planar or are composed of planar segments with sharp bends (figs. 11, 12). Vertical separation is typically less than 250 feet. In the southwestern fields, however, vertical separation exceeds 750 feet along a fault in northeastern Robinson's Bend Field and approaches 1,000 feet along a fault in southwestern Moundville Field.

The major fault in northeastern Robinson's Bend Field marks the edge of a large half graben that extends into crystalline basement (Groshong and others, 2009) (fig. 11). The normal faults compose subparallel horsts and grabens in a corridor stretching from Moundville Field to Brookwood and Deerlick Creek fields. From Deerlick Creek Field northeastward, balanced structural modeling and surface mapping indicate that the normal faults are thin-skinned, having formed above a basal detachment in the lower Pottsville Formation (Wang and others, 1993; Smith, 1995; Cates and Groshong, 1999) (fig. 15). Regional extension is thought to be the

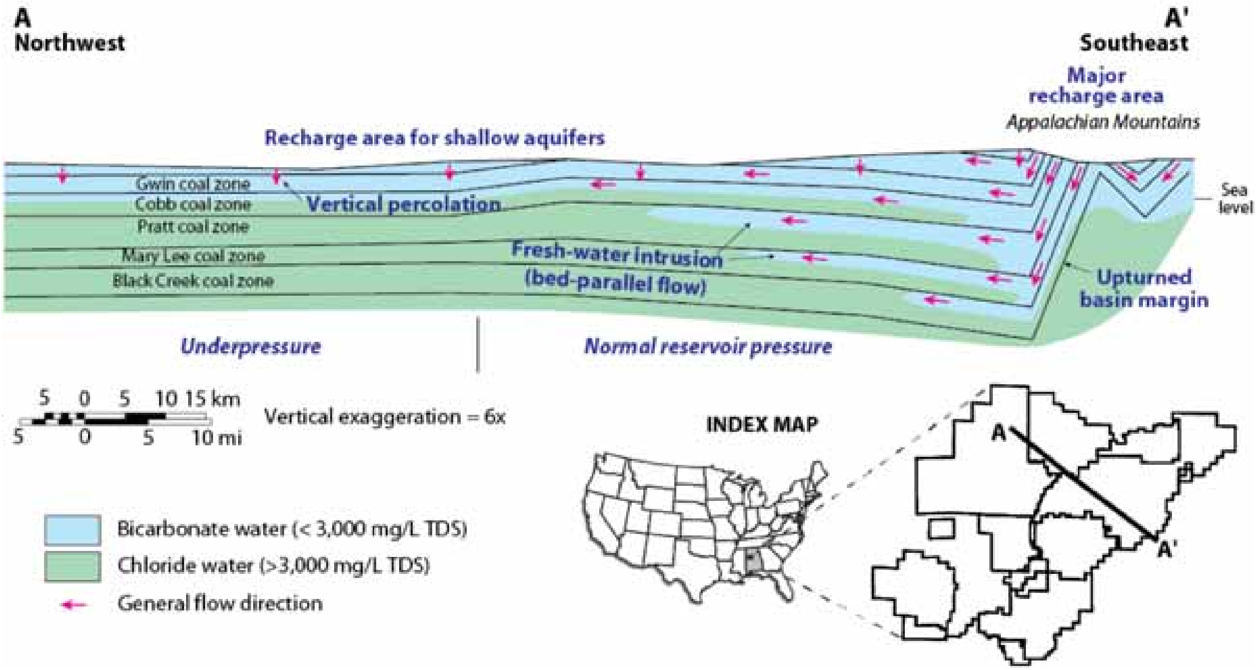


Figure 13.—Hydrodynamic model showing structurally upturned strata that accept meteoric recharge along the southeastern margin of the Black Warrior Basin (modified from Pashin and McIntyre, 2003).

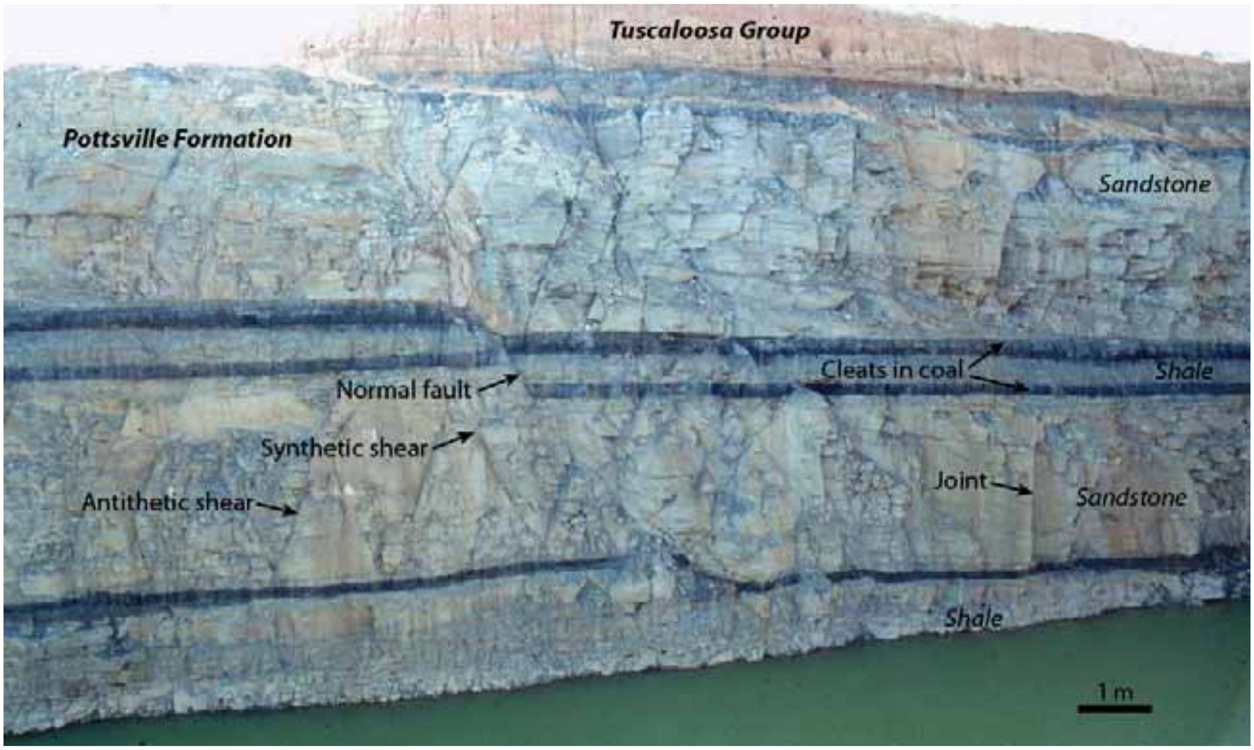


Figure 14.—Mine highwall showing exposed normal fault and associated natural fractures in the Brookwood coal zone of the upper Pottsville Formation.

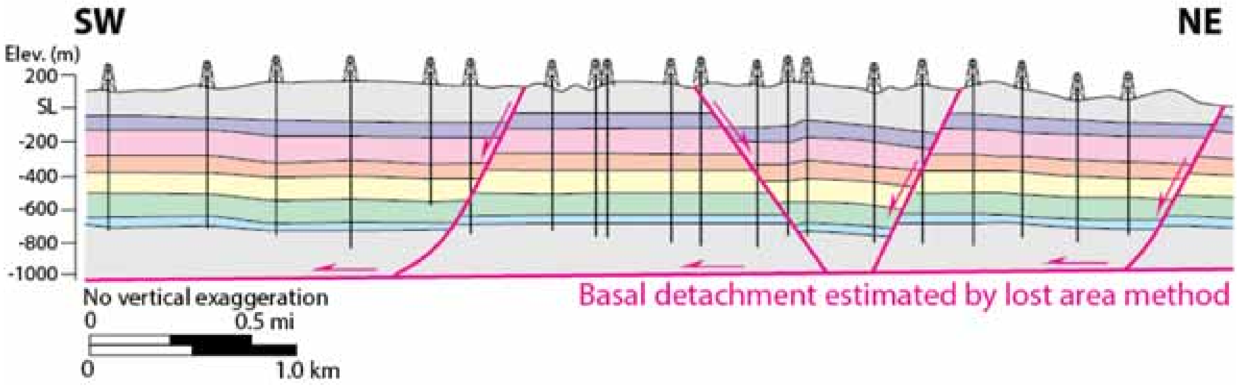


Figure 15.—Structural cross section showing interpretation of thin-skinned normal faulting and associated folding in Deerlick Creek Field (modified from Wang and others, 1993).

product of flexural extension associated with thrust and sediment loading in the Ouachita orogenic belt (Pashin and Groshong, 1998; Groshong and others, 2010).

Fault patterns are distinctly en echelon in the northeastern part of the study area, forming right-stepping patterns that indicate sinistral shear (Butts, 1910, 1927; Pashin, 1994c) (fig. 12). The Sequatchie anticline terminates at a north-south trending swarm of en echelon normal faults in central Oak Grove Field, which Pashin (1994c) interpreted as a transtensional tear fault system marking the edge of the Sequatchie detachment block. Thus, the northeastward trend toward en echelon faulting is thought to reflect a kinematic linkage between regional flexural extension and Appalachian folding.

Mesozoic cover.—A structural contour map of the base of the Tuscaloosa Group demonstrates that the unconformity surface separating the Pottsville Formation from the Mesozoic-Cenozoic cover of the Gulf of Mexico Basin dips southwest (Kidd, 1976) (fig. 16). Cretaceous strata are absent northeast of Brookwood and Blue Creek Fields. Between an elevation of 300 and 600 feet above sea level, outliers of Cretaceous strata predominate. A short

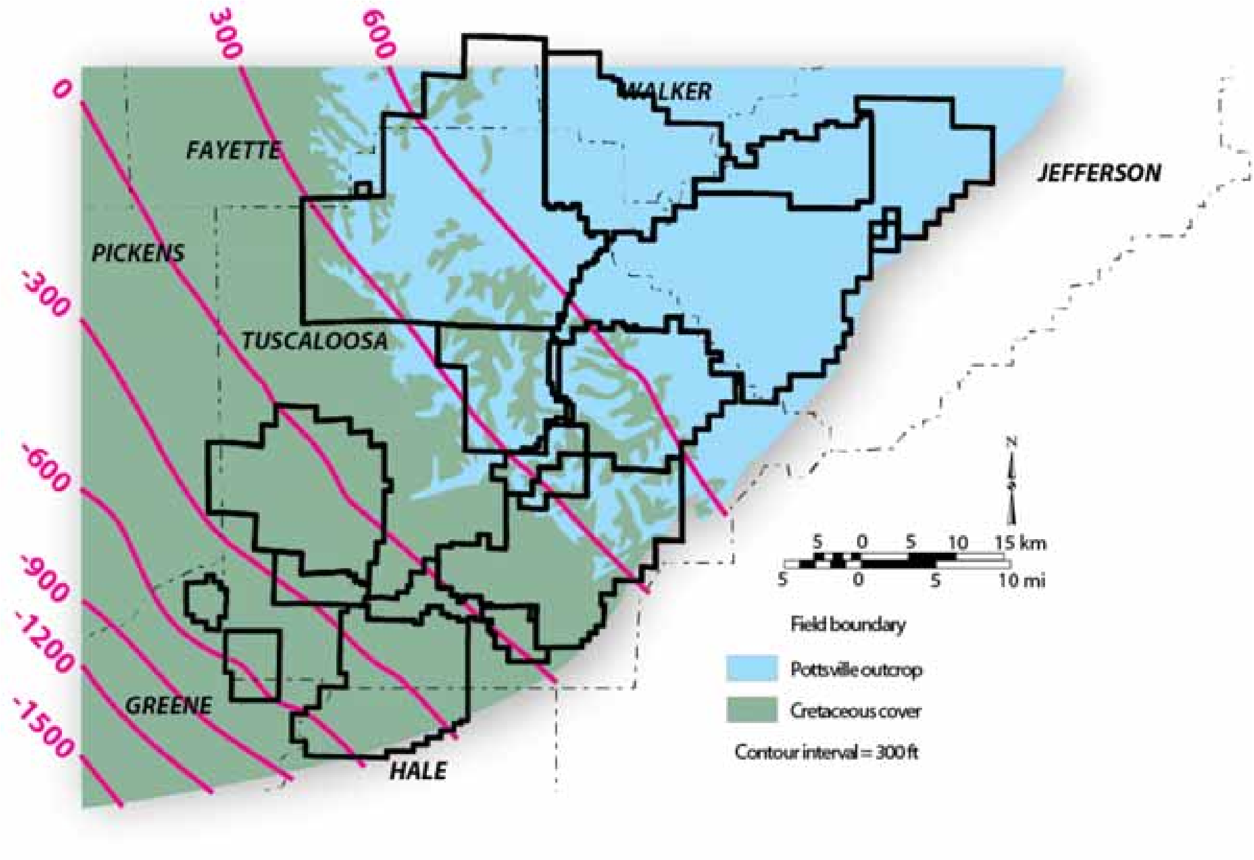


Figure 16.—Structural contour map of the base of the Paleozoic-Cretaceous disconformity surface in the area of the Black Warrior CBM fields (modified from Kidd, 1976).

distance southwest of the 300-foot contour, the Pottsville Formation is buried below continuous Cretaceous cover. In the southwestern coalbed methane fields, the Mesozoic section is locally thicker than 900 feet, and the top of the Pottsville lies more than 600 feet below sea level. Dip of the unconformity increases southwestward and is less than 1°.

All normal faults in the Black Warrior basin terminate at the sub-Cretaceous unconformity (Thomas, 1988; Groshong and others, 2011) (fig. 11). Therefore, no structural reactivation of the faults has taken place since the Tuscaloosa Group was deposited. Increasing southwest dip indicates that structural movement associated with Cretaceous reburial of the Black Warrior basin was dominated by southwestward tilting and flexure related to development of the Gulf of Mexico passive margin and subsidence of the Mississippi Embayment.

Fracture networks.—Upper Pottsville strata in the Black Warrior CBM fields have effectively no matrix permeability to water, thus flow is concentrated along natural fractures. Fracture systems in the Pottsville Formation are diverse and include joints, cleats, and fault-related shear fractures (figs. 14, 17, 18). Joints are simple opening-mode fractures. Vertical joints are widespread in shale and sandstone and are typically spaced between 1 and 30 feet. Closely spaced joints in coal (about 0.2 to 1 inch) are called cleats and are a primary control on aquifer and reservoir quality in the Pottsville Formation. Joint systems in the Pottsville tend to be strata-bound (Pashin and others, 2004, 2008); that is, the upper and lower tips of the fractures tend to be at or near the upper and lower contacts of the host shale, sandstone, or coal bed. Fracture spacing in shale and sandstone increases logarithmically with bed thickness. McFall and others (1986) and Pashin and others (1999) observed that cleat spacing decreases markedly as coal rank increases.

Joint systems in the Pottsville Formation constitute orthogonal sets of vertical fractures composed of systematic joints and cross joints (Ward and others, 1984; Pashin and others, 1999, 2004, 2008) (fig. 17). Systematic joints are planar fractures that can have surface traces on the order of 100 m. Cross joints are shorter than systematic joints, tend to strike perpendicular to systematic joints, have irregular surfaces, and commonly terminate at intersections with systematic joints. In coal, systematic joints are referred to as face cleat, and cross joints are called butt cleat (fig. 18). Systematic joints and cleats have distinctive orientations in the study area (Ward and others, 1984) (fig. 19). Joints in sandstone and shale can be subdivided into a

Figure 17.—Photograph of jointed mudstone below the Gwin coal zone in Oak Grove Field (modified from Pashin and others, 2004).

regional joint system and a localized joint system that is restricted to the area containing Appalachian folds (fig. 19A). Systematic joints of the regional joint system strike with a vector mean azimuth of N. 47° E., whereas systematic joints of the fold-related system strike with a vector mean azimuth of N. 64° W. Cleat systems can similarly be subdivided into a regional cleat system and a localized system that is restricted to the southeast margin of the Black Warrior basin (fig. 19B). Face cleats of the regional cleat system strike with a vector mean azimuth of N. 62° E., which is 15° east of the regional systematic joints. Face cleats in the localized fracture system along the southeast margin of the basin strike with a vector mean azimuth of N. 36° W.

Joints and cleats in the Pottsville Formation are commonly mineralized (Pashin and others, 1999; Pitman and others, 2003). Calcite is the dominant fracture-filling mineral in shale and

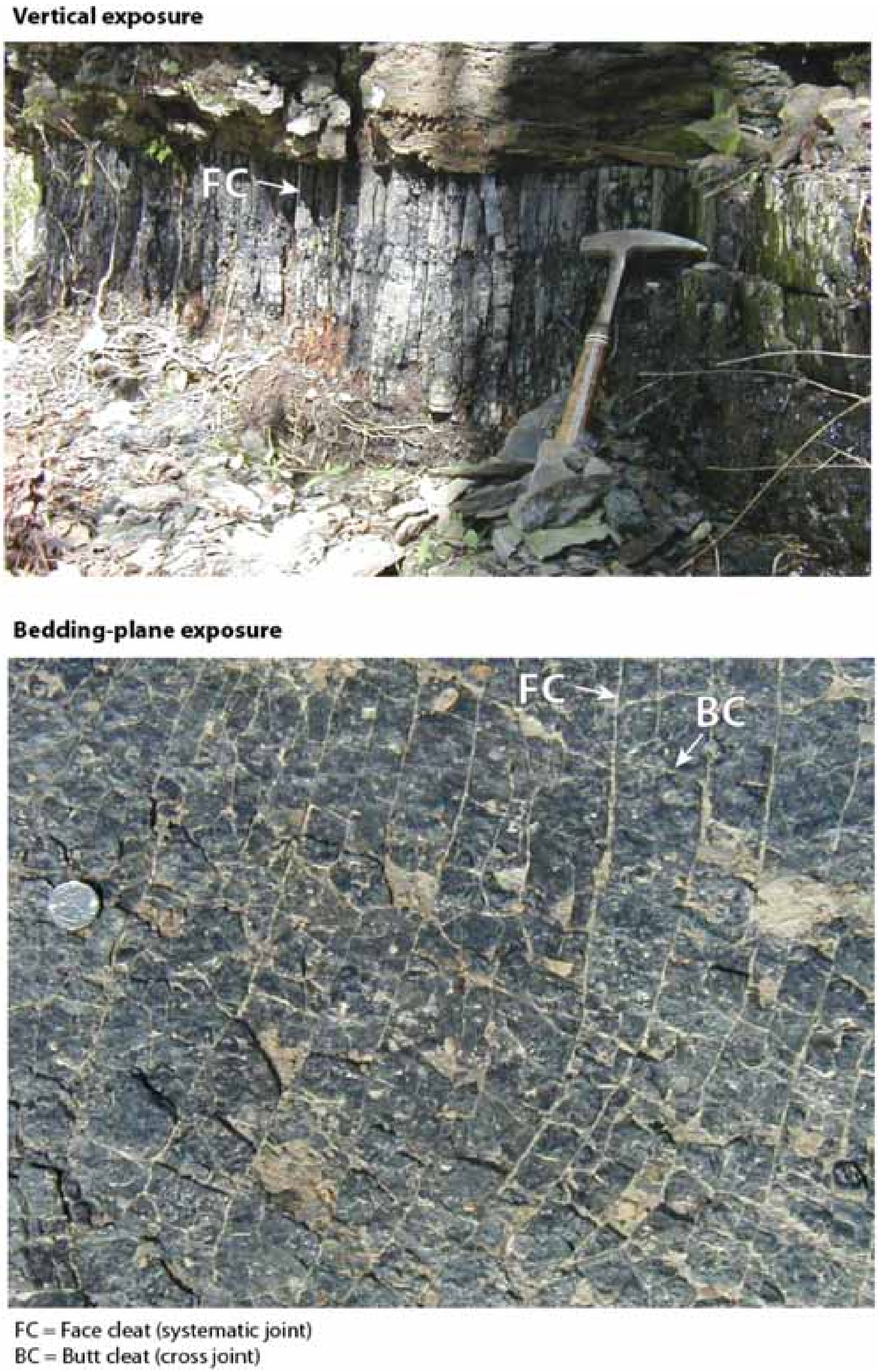
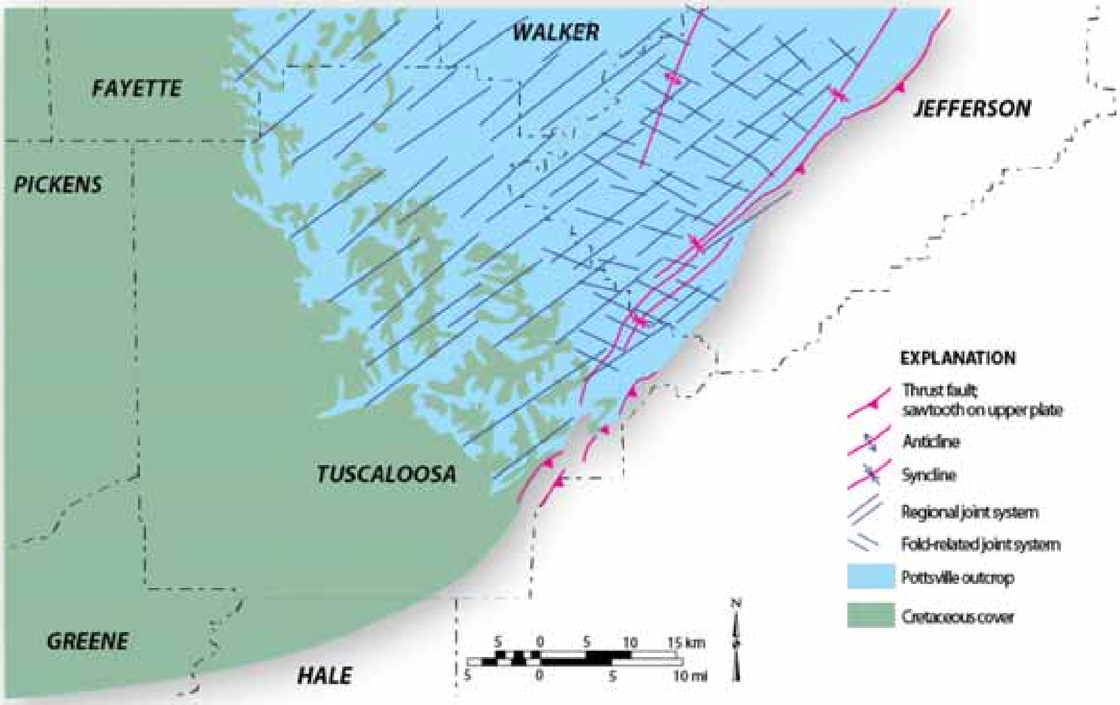


Figure 18.—Outcrop exposures of cleated coal (modified from Pashin and others, 2008).

A. Joint orientation



B. Cleat orientation

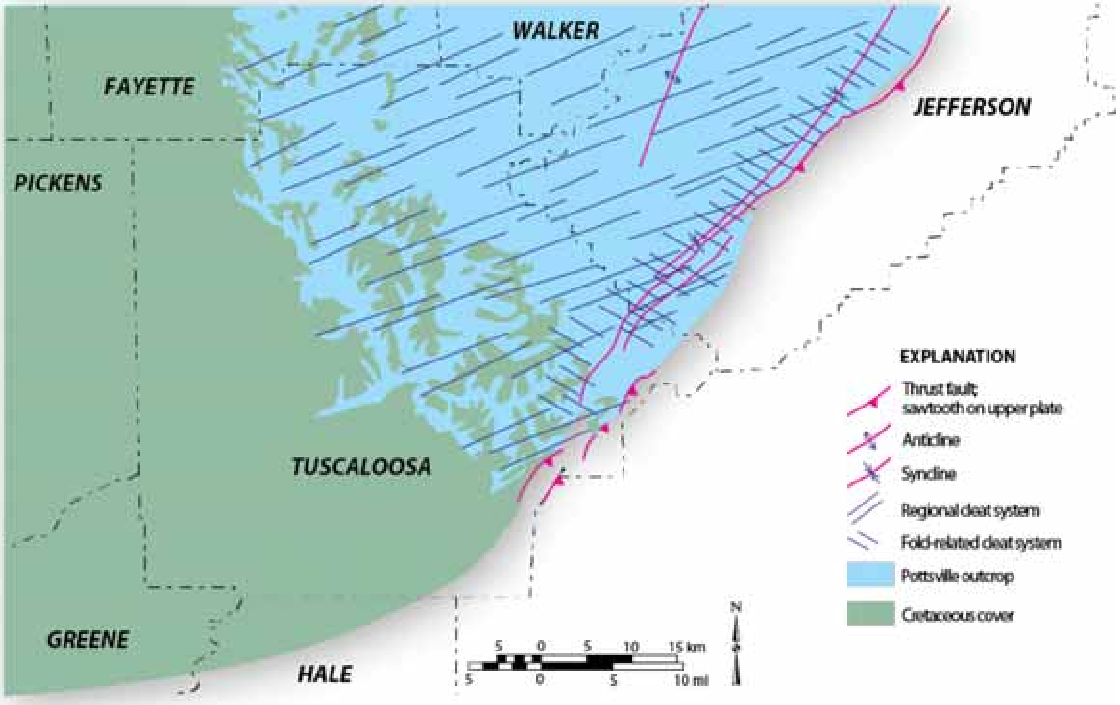


Figure 19.—Fracture orientation in the eastern Black Warrior basin (modified from Ward and others, 1984; Pitman and others, 2003).

sandstone, whereas pyrite and calcite are common in coal. Fracture-filling minerals generally have a patchy distribution and seldom completely fill fractures. Accordingly, the mineral fills are generally not considered major obstacles to fluid flow, and in places may help prop open fractures that would otherwise be closed.

Dipping and slickensided shear fractures are abundant within 10 m of normal faults (Pashin and others, 1991) (fig. 14). These fractures form crisscrossing networks and can be subdivided into synthetic and antithetic shears. Synthetic shears dip parallel to the associated fault, whereas antithetic shears dip opposite to the associated fault. Faults and the associated shear-fracture systems cut across bedding and thus are possible avenues for hydrologic communication between reservoir coal beds and the surface. In a study of gas seeps in the Black Warrior basin, Clayton and others (1994) investigated a number of exposed normal faults and found a significant gas seep along one fault in Oak Grove Field. However, Pitman and others (2003) observed pervasive cementation of coal cleats within 10 m of normal faults in the Black Warrior basin, which appears to preclude flow in coal along large parts of many faults.

Burial and Thermal History

Coal in the Pottsville Formation is bright-banded and ranges in rank from high volatile B bituminous to low volatile bituminous in the CBM fields (Blair, in Semmes, 1929; Telle and Thompson, 1987; Winston, 1990a, b; Levine and Telle, 1989; Pashin and others, 1999). The Mary Lee coal zone is of high volatile B bituminous rank in the western part of the study area, and rank increases toward the east and southeast (fig. 20). High volatile A bituminous coal forms a broad belt extending from Deerlick Creek Field northward through Blue Creek and White Oak Creek fields. A large, elliptical area containing medium and low volatile bituminous coal is

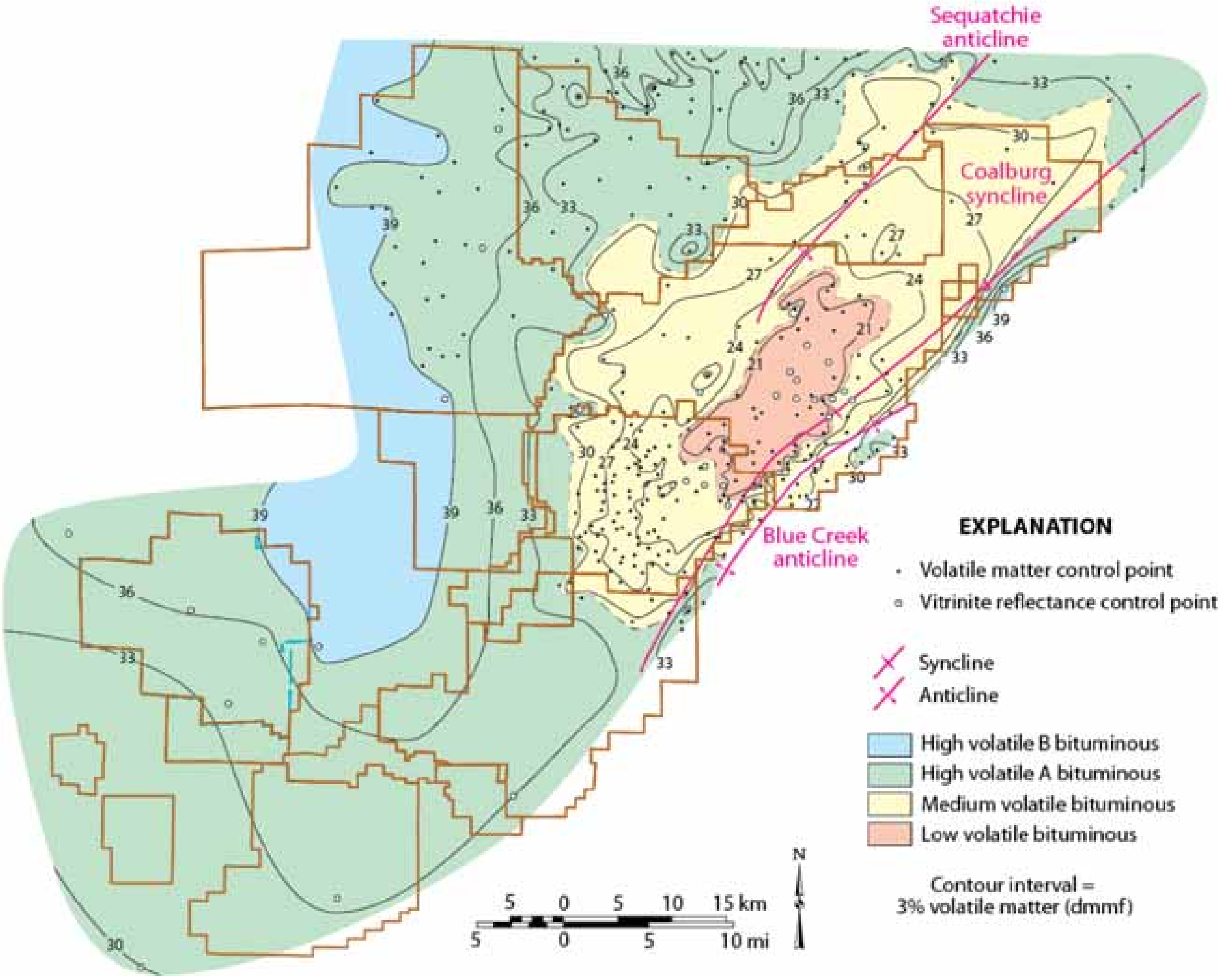


Figure 20.—Map of coal rank in the eastern Black Warrior Basin (modified from Pashin and others, 2009).

developed in Oak Grove and Brookwood fields and forms the heart of Alabama's metallurgical coal industry. Isovols cross-cut structure, indicating that the rank pattern is post-kinematic and reflects regional variation of geothermal gradient rather than simple burial depth (Telle and others, 1987; Pashin and others, 1999). Explanations of the rank pattern include thermal upgrading from orogenic expulsion of warm fluid (Winston, 1990a, b) and increased overburden related to an eroded thrust sheet (Thomas and others, 2008).

Pottsville strata were buried rapidly after deposition, apparently reaching maximum burial during Permian time (Telle and Thompson, 1987; Carroll and others, 1995) (fig. 21). A protracted interval of post-orogenic unroofing extended into the Mesozoic, and Pottsville strata were probably near modern burial depth by the end of Jurassic time. The coal-bearing strata were again buried during Cretaceous time as the Tuscaloosa Group was deposited. Some time after the end of Tuscaloosa deposition, erosion recommenced, thereby exposing Pottsville strata in the northeastern part of the basin.

Lopatin modeling indicates that major thermal maturation occurred near maximum burial during late Paleozoic orogenesis (Telle and Thompson, 1987; Carroll and others, 1995) (fig. 21). Thermal maturation apparently continued during the early stages of regional uplift and unroofing but was probably complete by the Early Jurassic. Coal of high volatile A bituminous and higher rank has been heated enough to have generated large amounts of thermogenic natural gas, whereas lower rank coal is submature with respect to thermogenic gas generation.

During unroofing, upper Pottsville strata cooled to temperatures lower than 80°C, which are favorable for subsurface biotic activity (e.g., Shurr and Ridgley, 2002; Flores, 2008). In basins that have been uplifted substantially and cooled, coal is expected to be greatly undersaturated with thermogenic gas (Scott and others, 1994; Bustin and Bustin, 2008) (fig. 22). Accordingly, Pottsville coal seams would be greatly undersaturated unless native thermogenic gas was augmented by migrated gas or late-stage biogenic gas. As Pottsville strata were exposed, freshwater infiltration by meteoric processes apparently facilitated microbial activity, including late-stage microbial methanogenesis (Pitman and others, 2003; Pashin and others, in press). Indeed, augmentation of thermogenic gas with late-stage microbial gas to be an essential process

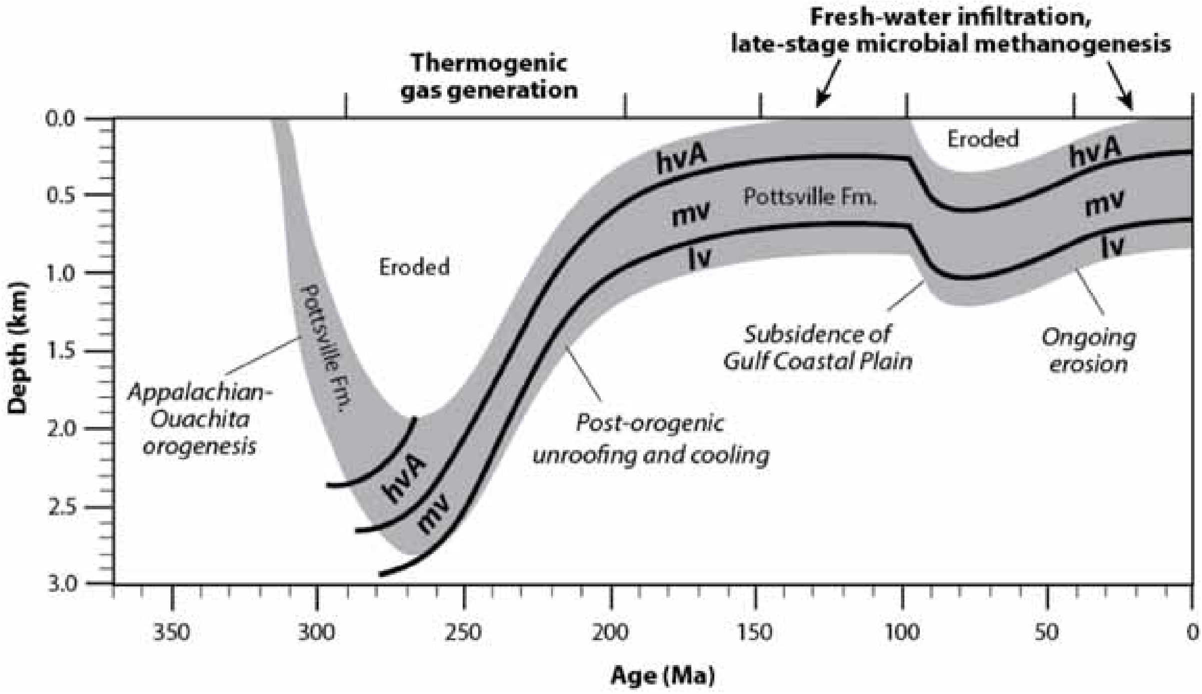


Figure 21.—Burial history curve showing major thermal and hydrodynamic events in the eastern Black Warrior Basin (modified from Pitman and others, 2003).

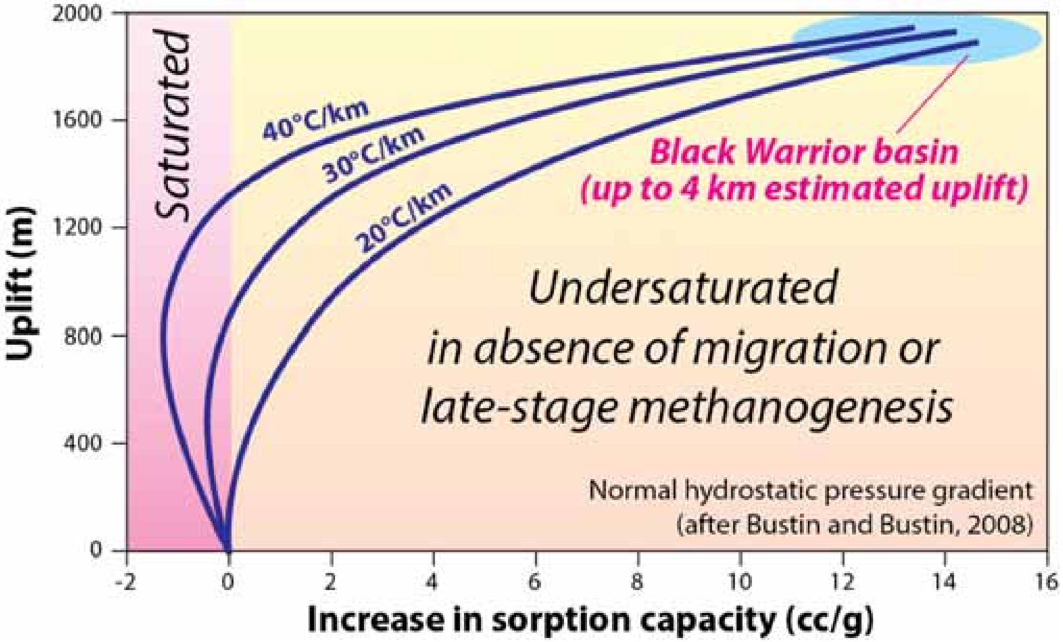


Figure 22.—Plot showing impact of regional uplift, erosion, and cooling on thermogenic gas saturation in coal. This is plot predicts that the Black Warrior Basin should be strongly undersaturated with thermogenic gas (modified from Bustin and Bustin, 2008).

for charging coal with gas in sedimentary basins that have been uplifted and deeply eroded (e.g., Scott and others, 1994; Scott, 2002; Bustin and Bustin, 2008; Pashin, 2007, 2010a).

BASIN HYDRODYNAMICS

Simply stated, hydrodynamics is the study of fluids in motion. Considering the complex geologic history of sedimentary basins as well as the importance of dewatering for CBM production, hydrodynamics is central for understanding the characteristics of CBM reservoirs (e.g., Kaiser, 1993; Scott, 2002; Pashin, 2007; Pashin and others, in press). Three fundamental hydrogeologic variables are permeability, reservoir pressure, and water chemistry. Permeability and pressure gradients determine how, where, and at what rate fluid flows in the subsurface. Geochemistry is the ultimate determinant of water quality and further affects the viability of the microbial consortia that generate late-stage biogenic gas in many CBM basins. Accordingly, the following sections focus on permeability, reservoir pressure, bulk geochemistry, and fluid flow.

Permeability

Upper Pottsville sandstone in the CBM fields typically has microdarcy-class permeability (Pashin and Hinkle, 1997), and shale has nanodarcy-class permeability (Clark and others, 2013). For this reason, virtually all flow of water through the Pottsville Coal Interval takes place through natural fractures. The close spacing of cleats in coal relative to joints in shale and sandstone gives coal the best aquifer and reservoir properties of any rock type in the Pottsville Coal Interval. On the basis of slug tests, the Pottsville can be considered a poorly transmissive system with permeability between 0.1 and 100 md at reservoir depth (McKee and others, 1988; Pashin and others, 2010). McKee and others (1988) discovered that permeability in coal of the

Pottsville Formation is highly stress-sensitive and decreases downward from nearly a Darcy at the ground surface to tens of millidarcies or less below 1,000 feet (fig. 23).

Discrete fracture network (DFN) modeling and well testing indicate that the vertical decrease in the permeability of coal has significant consequences for coalbed methane production. Transmissivity is a function of permeability and bed thickness, and the discrete network models of Pashin and others (2004, 2008) show that shallow coal beds in the Pratt, Cobb, and Utley coal zones are significantly more transmissive than joints in adjacent strata. By comparison, beds in the Black Creek zone, which is about 2,000 feet deep, have lower transmissivity than fractures in adjacent shale and sandstone beds.

The results of pressure buildup tests in Oak Grove and Blue Creek fields (Koenig, 1989; Pashin and others, 2010) are consistent with the DFN models. Pressure buildup results in the Pratt coal zone provide evidence for permeability anisotropy that is strongly elongate in the face cleat direction (fig. 24). This reflects the high transmissivity of coal relative to adjacent strata and indicates that flow is primarily in coal. In contrast, test results from the Black Creek coal zone indicate reduced permeability anisotropy in the systematic joint direction. This result reflects the limited transmissivity of coal deeper than 2,000 feet and suggests that hydraulic communication took place with fractures in adjacent strata. However, multizone pressure monitoring indicates that no significant communication exists among coal zones.

Faults cut across bedding (figs. 14, 25) and are thus of concern as potential pathways for cross-formational flow. Observations of fault-related deformation in the field indicates that shear fractures in sandstone locally extends more than 300 feet away from some fault planes. By comparison, deformation of shale tends to be concentrated in narrow zones within 10 feet of the major faults. Accordingly, the symmetry of shear fracture networks around the faults depends on

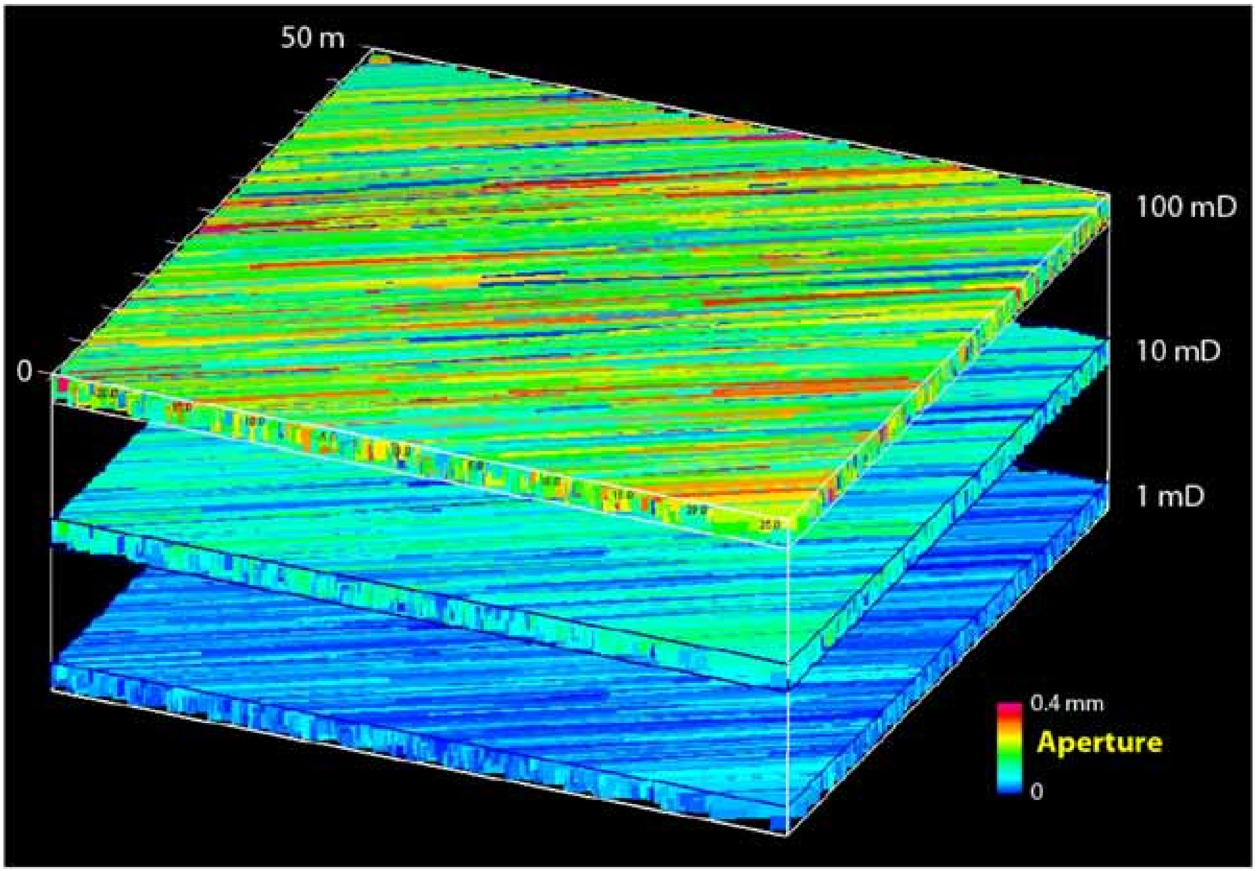


Figure 23.—Discrete fracture network model of face cleat in coal showing relationship of fracture aperture to permeability (modified from Pashin and others, 2008). Permeability in Pottsville coal of the Black Warrior Basin typically decreases from about 100 millidarcies in shallow reservoir coal seams to less than 1 millidarcy beyond a depth of 2,000 feet.

the rock types that are juxtaposed by the fault. For example, where like rock types are juxtaposed, the deformation zone is fairly symmetrical. Alternatively, where different shale and sandstone are juxtaposed, the deformation zone is highly asymmetrical, reflecting the different deformation habit of the rock types. This asymmetry tends to channel flow parallel to bedding, thus helping limit cross-formational hydraulic communication (Pashin and others, 2008).

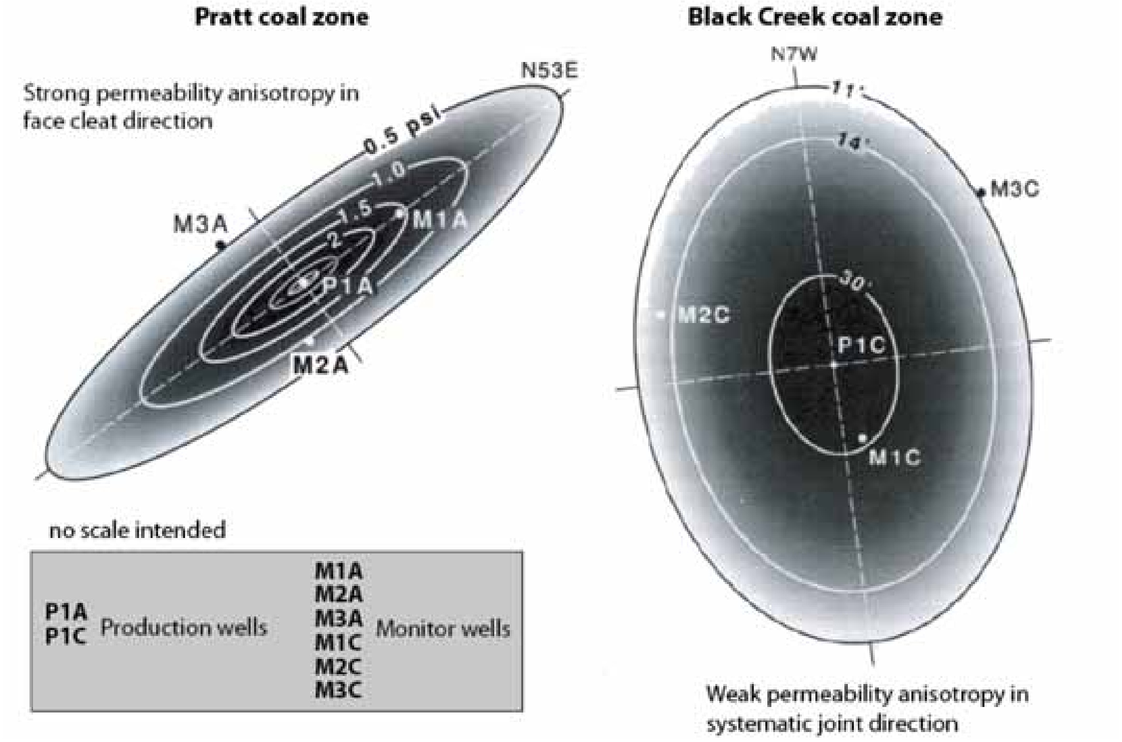


Figure 24.—Results of pressure buildup testing in the Pottsville Coal Interval at the Rock Creek test site, Oak Grove Field (modified from Koenig, 1990). Note control by cleating of permeability anisotropy in shallow, permeable Pratt coal and control of anisotropy by jointing in adjacent strata in deep, low-permeability Black Creek coal.

Reservoir Pressure

Reservoir pressure includes lithostatic and hydrostatic components, both of which are of critical concern in coalbed methane production (Pashin and McIntyre, 2003). Lithostatic and hydrostatic stress combine to influence macroporosity and permeability in coal, which is much more stress-sensitive than other rock types (McKee and others, 1988). Moreover, lowered hydrostatic pressure is the principal mechanism by which gas flows to the wellbore. Examination of bulk density logs indicates that lithostatic pressure gradients in the Pottsville Formation are about 1.1 psi/ft and in the Tuscaloosa Group are about 1.0 psi/ft. Salinity of formation water in the Pottsville Formation is commonly below that of seawater, so minimum hydrostatic pressure

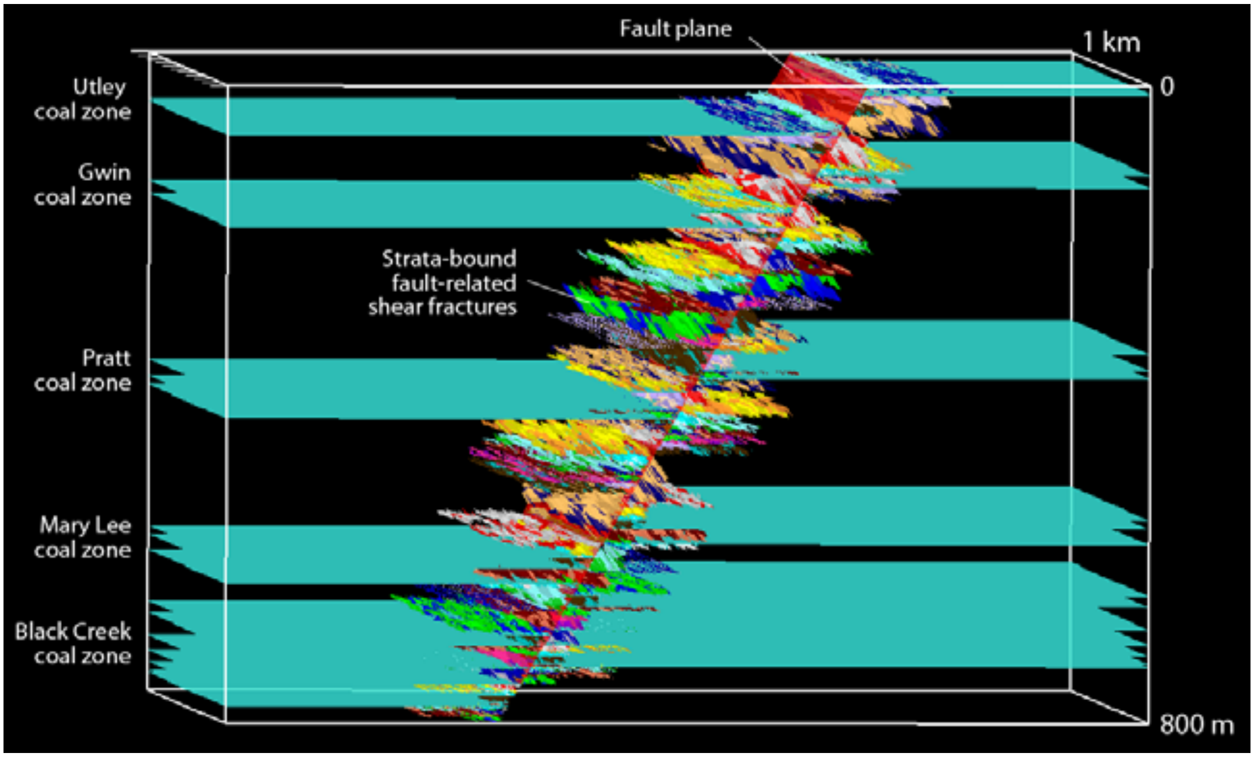


Figure 25.—Discrete fracture network of fault-related fracturing in the Pottsville Coal Interval (modified from Pashin and others, 2008). Asymmetry of fracture distribution around faults is caused in large part by juxtaposition of narrow shear zones in shale with broad fracture zones in sandstone.

can be estimated readily from water-level data using a freshwater hydrostatic gradient of 0.43 psi/ft. Effective stress can be estimated by subtracting the hydrostatic pressure gradient from the lithostatic gradient (McKee and others, 1988).

Water-level data are available from 2,174 wells (fig. 26). These data indicate that the pre-completion hydrostatic pressure gradient in the Black Warrior coalbed methane fairway varies from normal (0.43 psi/ft) to abnormally low (<0.05 psi/ft). A pressure-depth plot indicates that pressure gradients prior to production have a bimodal population distribution. Wells with a hydrostatic pressure gradient less than 0.20 psi/ft can be classified as extremely underpressured; those with a higher gradient are normally pressured to moderately underpressured. Extremely

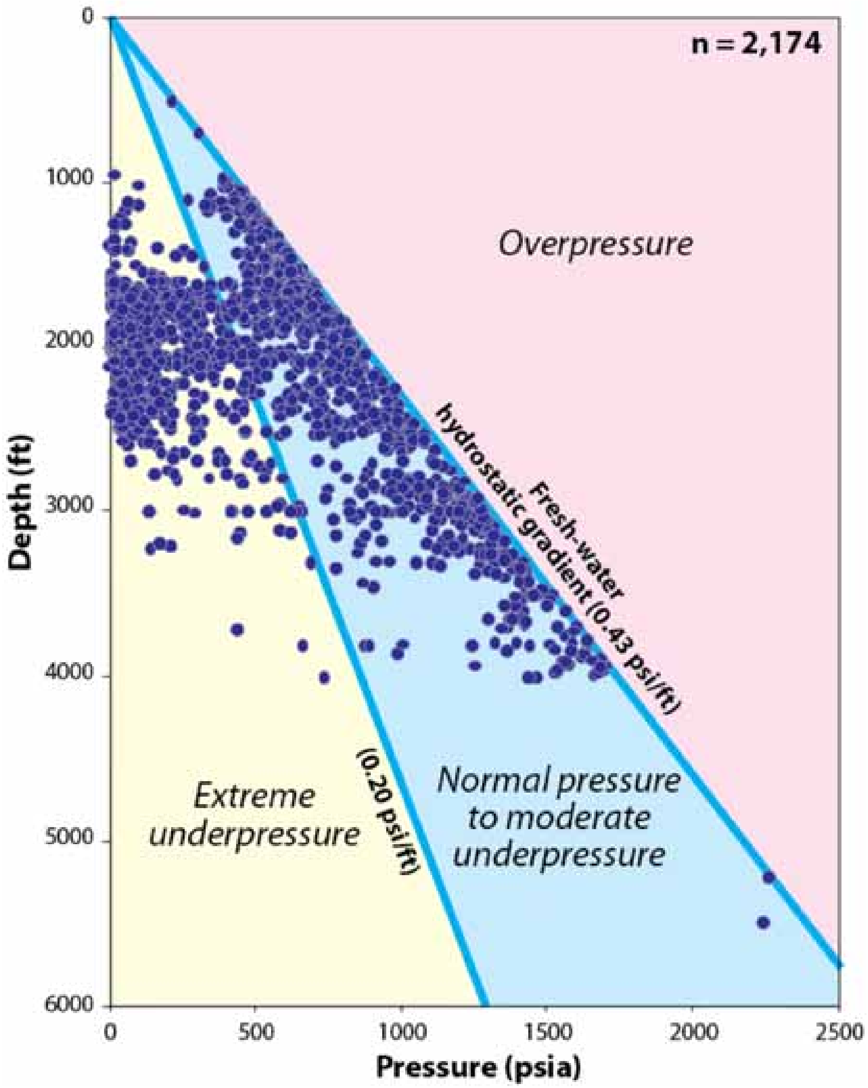


Figure 26.—Pressure-depth plot based on water levels in CBM wells showing normal hydrostatic pressure to extreme underpressure in the Pottsville Coal Interval.

underpressured wells cluster about a median of 0.05 psi/ft, and normally pressured to moderately underpressured wells cluster about 0.39 psi/ft. Wells with normal pressure to moderate underpressure exist at all bottom-hole depths, whereas extremely underpressured wells cluster between 1,500 to 2,500 feet. Gauging data from Blue Creek Field indicate that virgin reservoir pressure varies significantly among coal zones (Pashin and others, 2010). In this area, the Black

Creek and Pratt coal zones were normally pressured prior to completion, whereas the Mary Lee coal zone was significantly underpressured, having a hydrostatic gradient below 0.30 psi/ft.

Water-level data are available from most active CBM fields and can be used to map minimum hydrostatic pressure gradient and minimum pressure prior to degasification in the northeastern part of the coalbed methane fairway (fig. 27). Wells with near-normal hydrostatic pressure gradients span large areas of Cedar Cove, Deerlick Creek, Blue Creek, and Oak Grove Fields. Large areas of underpressure are in Brookwood, Oak Grove, Blue Creek, and White Oak Creek fields. Other pockets of significant underpressure exist in parts of Holt, Peterson, Deerlick Creek, Blue Creek, and White Oak Creek fields. Although pressure gradient is mappable, in some areas, the gradient can change from less than 0.1 psi/ft to more than 0.3 psi/ft across a 40-acre drilling unit.

Bimodal pressure gradients are typical of compartmentalized hydrologic systems (Bradley and Powley, 1994), and the extreme bimodality of hydrostatic pressure gradients in the Pottsville Formation reflects a combination of anthropogenic and natural factors. Dewatering associated with longwall mining appears to be the primary cause of underpressure in Brookwood and Oak Grove fields. In Brookwood Field, the Blue Creek coal of the Mary Lee zone is mined at a depth of about 2,000 feet, which explains the clustering of extremely underpressured wells at this level (fig. 27). Indeed, caution must be exercised when interpreting water levels, especially in mined areas, because bottom-hole pressure may not be representative of the shallow hydrologic system, where a water table may remain perched above the depressurized zone (Pashin and others, 1991; Pashin and Hinkle, 1997).

Pockets of extreme underpressure in Holt, Peterson, Deerlick Creek, Blue Creek, and White Oak Creek fields are far removed from the underground coal mines and thus appear to be natural.

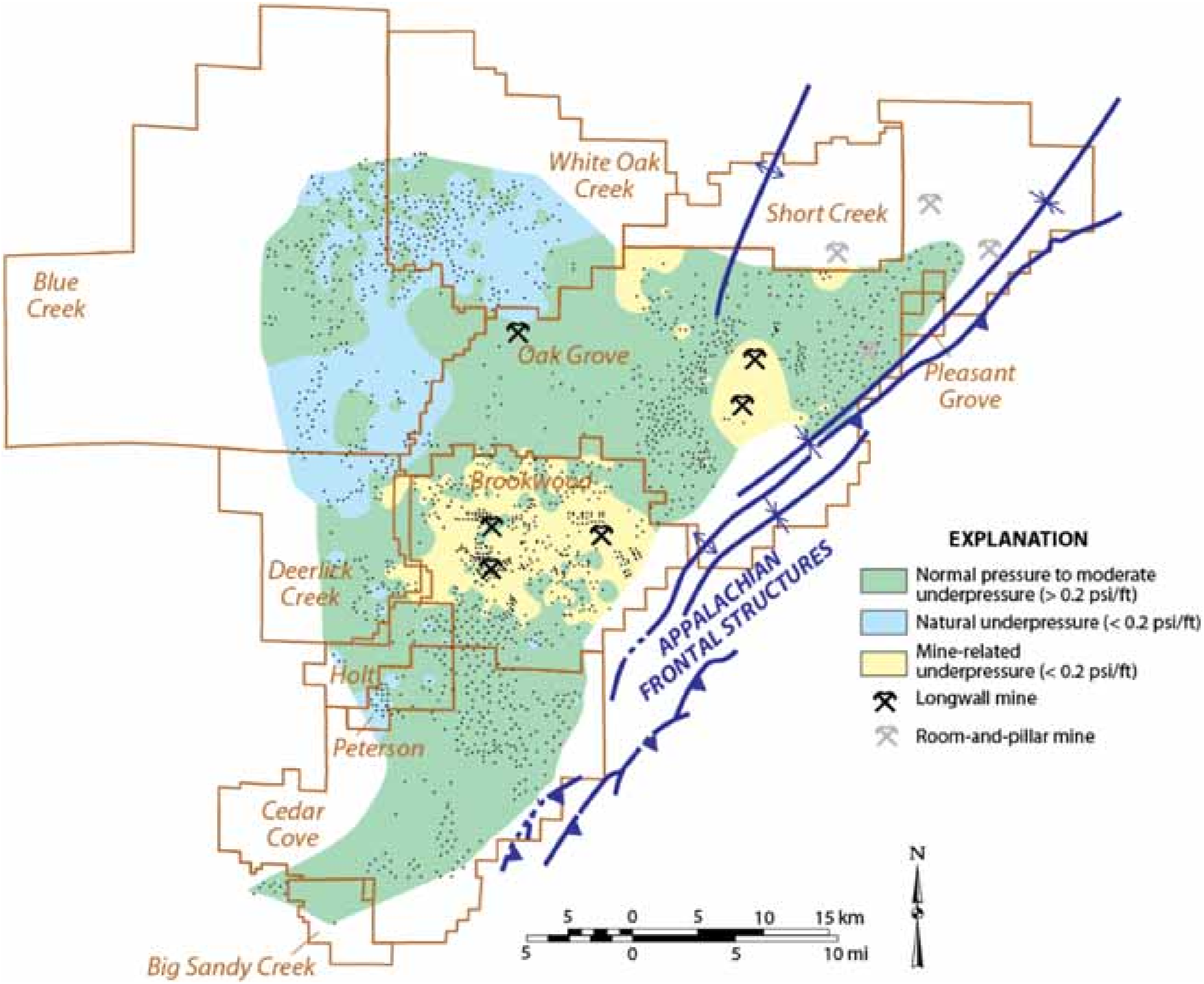


Figure 27.—Map of hydrostatic pressure gradient in the Pottsville showing extreme underpressure in areas of coal mining and natural underpressure basinward of the regional recharge system along the Appalachian frontal structures.

Indeed, the aforementioned gauging results from Blue Creek Field (Pashin and others, 2010) demonstrate that reservoir pressure in the upper Pottsville is in places stratified, with some zones having normal pressure and others having underpressure. Pressure stratification indicates that upper Pottsville coal zones are hydraulically confined and are capable of maintaining separate pressure gradients over geologic time.

After decades of commercial CBM production, upper Pottsville coal seams have been significantly depressurized. Flowing wellhead pressures recorded by surface gauges are generally between 7 and 12 psig, and wellhead shut-in pressures are on the order of 25 psig. Multizone monitoring in a series of observation wells in Blue Creek Field indicates that a range of pressures exist at reservoir depth about 350 feet from an operating well (Pashin and others, 2010). In the Black Creek coal zone, for example, mature reservoir pressure is between 125 and 205 psig. In the Mary Lee zone, pressure is between 25 and 50 psig, and in the Pratt zone, pressure has been depleted to less than 20 psig.

Some degree of underpressure is typical of geologically old sedimentary basins like the Black Warrior basin because rocks and fluids contract and fractures dilate during regional uplift and cooling (Bradley, 1975; Kreitler, 1989). Kaiser (1993) suggested that normal pressure in coalbed methane reservoirs indicates hydrologic connection to recharge areas. The natural underpressure in parts of Blue Creek and White Oak Creek fields (fig. 27) may indicate isolation from recharge areas, free gas in the available pore space, or a tight reservoir condition in which water is unable to flow into the wellbore in the time between drilling and logging. Of the three possibilities, a tight borehole condition is doubtful because coalbed methane production has been highly successful in these fields (Pashin and McIntyre, 2003; Pashin, 2010a). Isolation from recharge is a better explanation, because major variations in hydrostatic pressure across drilling units provides evidence for compartmentalization. Another factor that should be considered in these areas, however, is that significant gas pressure may exist that must be detected by gauges rather than by analysis of water levels.

The heterogeneity of hydrostatic pressure in the Pottsville Formation has significant implications for the distribution of effective stress and permeability. In normally pressured reservoirs, vertical effective stress increases downward at a rate of about 0.7 psi/ft, whereas in completely underpressured reservoirs, coal must bear the full lithostatic load of 1.0 to 1.1 psi/ft. Increased lithostatic load will close fractures and can decrease the ability of coal matrix to transmit gas (Bustin, 1997), thereby potentially degrading reservoir quality. This effect may be mitigated by shrinkage of the coal matrix as gas is desorbed (Harpalani and Schraufnagel, 1990; Levine, 1996; Kroos and others, 2001). Furthermore, where underpressure is related to free gas in fractures, minimal dewatering may be required for economic gas production (Pashin, 2010a).

Although lithostatic stress affects permeability, the flow of gas is induced by changes in hydrostatic pressure. The most obvious evidence for this is that gas is produced as hydrostatic stress is reduced and effective stress is increased. Although fracture aperture and coal fabric respond to effective stress, the internal surface area, or Langmuir volume, of coal is relatively insensitive to stress (Bustin, 1997). Diffusion of gas through the coal structure to free surfaces, such as fractures, is a fundamental control on sorption and desorption (Gamson and others, 1993; Harpalani and Ouyang, 1999), and changing hydrostatic pressure by dewatering apparently stimulates diffusion toward the open spaces where Darcy flow operates.

Geochemistry and Subsurface Flow

Produced water from the Black Warrior CBM fields ranges from nearly potable freshwater to hypersaline water (Pashin and others, 1991; Ellard and others, 1992). Pashin and others (1991) discovered that the formation water is freshest along the frontal structures of the Appalachian orogen (fig. 13). Accordingly, the structurally upturned southeast basin margin has been interpreted as a major recharge area. Indeed, reservoir coal seams come to the surface in the steep forelimb of the Birmingham antinclinorium and the Blue Creek anticline, where they can accept meteoric recharge, and a major freshwater intrusion extends from the basin margin deep into the interior (Pashin and others, 1991, Pashin and others, in press; Pashin, 2007, 2010a).

Recharge of Pottsville strata in the upturned basin margin affects not only the geochemistry of the formation water, but helps support reservoir pressure in the interior of the basin (Pashin and McIntyre, 2003). Indeed, the main area of normal reservoir pressure corresponds with the freshwater intrusion that has been fed by meteoric recharge, and mining areas constitute the only significant pressure sinks in the freshwater intrusion (figs. 13, 27). Natural underpressure northwest of the intrusions indicates loss of pressure support by the freshwater intrusion, and evidence for free gas in this area suggests that hydrodynamic sweep and accumulation of natural gas northwest of the intrusion may be a contributing factor.

Cretaceous cover strata of the Tuscaloosa Group form a world-class, high-yield aquifer (Carlston, 1944; Lee, 1985). These strata intercept meteoric recharge throughout their outcrop distribution and contain potable water throughout the study area. Below Cretaceous cover, however, upper Pottsville strata generally contain saline formation water and only locally contain any evidence of connection to freshwater recharge (Ellard and others, 1992). Results of hydrodynamic analysis provide the basic framework for consideration of the geochemistry of produced water, and the following sections present the detailed geochemistry of produced water and natural gas in the Pottsville Coal Interval.

WATER CHEMISTRY

The geochemistry of produced water from the Pottsville Coal Interval is extremely complex because it has diverse physical and aggregate properties and contains numerous ionic compounds, metallic and nonmetallic substances, nitrogen compounds, and organic compounds.

Understanding the correlations among these compounds and their relationship to the regional geologic and hydrodynamic framework is essential for developing robust water management strategies. Accordingly, this section focuses on characterization of water geochemistry and the complex interrelationships among the various analytes and the regional geologic and hydrodynamic framework.

Physical and Aggregate Properties

The composition of water produced from Black Warrior CBM reservoirs varies from fresh and brackish water that is protected by the Safe Drinking Water Act (< 10,000 mg/L TDS) to basinal brine (TDS > 30,000 mg/L) (fig. 28; table 1). TDS content within the study area ranges from 589 mg/L to more than 61,000 mg/L. The conductivity of the formation water ranges from 718 to 97,700 microSiemens per centimeter (μS/cm) (table 1), which is characteristic of fresh to hypersaline water. Accordingly, conductivity correlates strongly with TDS content with a coefficient of regression of 0.89. Mapping TDS defines the freshwater plumes (TDS < 10,000 mg/L) and saline basinal fluid (TDS > 30,000 mg/L), which extend westward from the frontal Appalachian structures and cover large parts of Oak Grove, Short Creek, White Oak Creek, Brookwood, and Cedar Cove fields (fig. 28). In Brookwood Field, 6 samples within the plumes have TDS > 10,000 mg/L. These pockets of saline water may reflect local sheltering from the regional recharge system by small-displacement normal faults (Pashin and others, 1991). Conversely, isolated samples basinward of the plumes with < 10,000 mg/L TDS may reflect local extensions of the plumes or, alternatively, percolation along faults and fracture zones.

The freshwater plumes exert control over most geochemical parameters in the Pottsville Coal Interval, as is readily apparent in the map of alkalinity (fig. 29). Alkalinity is expressed in

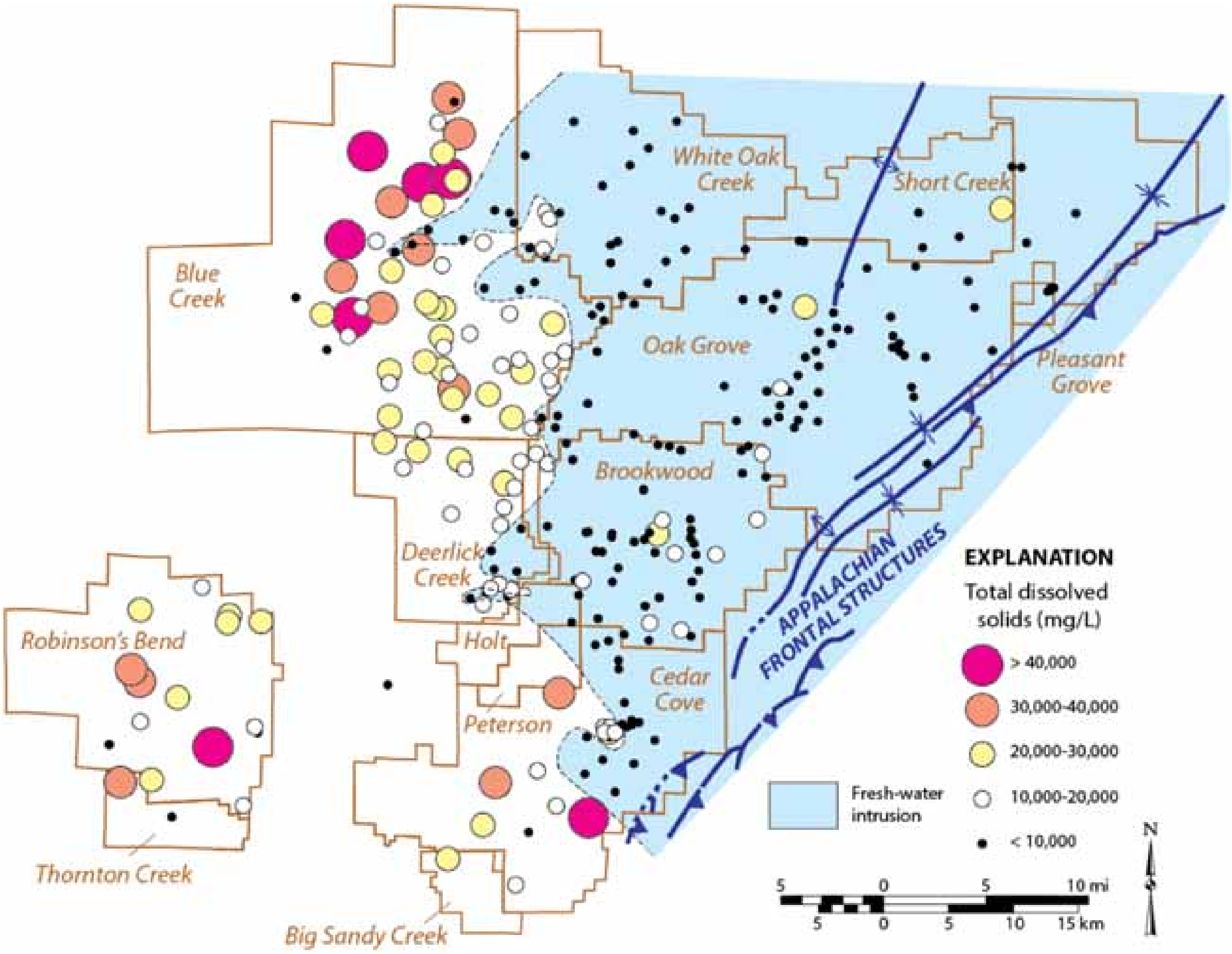


Figure 28.—Map of TDS content of produced water in the active Black Warrior CBM fields.

millequivalents per liter (mEq/L). Alkalinity ranges from 3 to 1,600 mEq/L and has a mean value of 355 mEq/L (table 1). All values higher than 1,000 mEq/L are concentrated in the northeastern corner of the CBM development area, and values higher than 750 mEq/L are clustered in Short Creek, White Oak Creek, and northern Oak Grove fields (fig. 29). Within the freshwater intrusion, Alkalinity is generally greater than 250 mEq/L. West of the plumes, most alkalinity values are less than 250 mEq/L. Hardness, expressed as mg/L $CaCO_3$, ranges from 3 to 6,150 (table 1) and is has an inverse logarithmic relationship to alkalinity with a regression coefficient of -0.75.

Table 1. Summary of selected physical and aggregate properties and major ionic compounds in wellhead water samples from coalbed methane wells in the Black Warrior Basin. Analyses performed in the geochemical laboratories of the Geological Survey of Alabama and the University of Alabama.

Variable	**N**	**Minimum**	**Maximum**	**Mean**	**Standard deviation**
Alkalinity (mEq/L)	206	3	1,600	355	268
COD (mg/L)	206	0	10,500	830	1,022
Conductivity (μS/cm)	205	718	97,700	20,631	20,311
Hardness (mg/L as $CaCO_3$)	206	3	6,150	871	1,124
pH	205	5.3	9.0	7.5	0.6
Total dissolved solids (mg/L)	205	589	61,733	14,319	13,350
Total suspended solids (mg/L)	205	0	2,290	78	206
TKN (mg/L)	206	0	38	6	6
Turbidity (NTU)	203	0	539	74	92
Ca^{2+} (mg/L)	206	0	1,640	218	289
Cl^- (mg/L)	206	11	42,800	9,078	9,478
CO_3 (mg/L)	206	0	64	3	7
HCO_3^- (mg/L)	206	2	1,922	427	324
K^+ (mg/L)	206	0	74	12	12.65
Mg^{2+} (mg/L)	206	0	414	68	85
Na^+ (mg/L)	205	126	16,700	4,353	3,912
SO_4^{2-} (mg/L)	206	0	302	6	25

The pH of the produced water ranges from 5.3 to 9.0, indicating that the water is weakly acidic to strongly basic (table 1). A mean pH of 7.5 indicates that the water, on average, tends to be slightly basic. Interestingly, pH correlates weakly with alkalinity, having a regression coefficient of only 0.38 percent. Mapping pH indicates that the formation water tends to be basic in the freshwater intrusion and acidic to weakly basic west of the intrusion (fig. 30).

Total suspended solids (TSS) content ranges widely from 0 to 2,290 mg/L and averages 78 mg/L (table 1). Values lower than 10 mg/L are concentrated along the northern margin of the CBM play in White Oak Creek, Short Creek, and Oak Grove fields (fig. 31). TSS concentrations exceeding 100 mg/L are clustered in Blue Creek Field in the area where TDS content is highest. TSS consists of coal and sediment fines derived from the country rock, as well as carbonate precipitates associated with the buildup of wellbore scale on casing and around perforations.

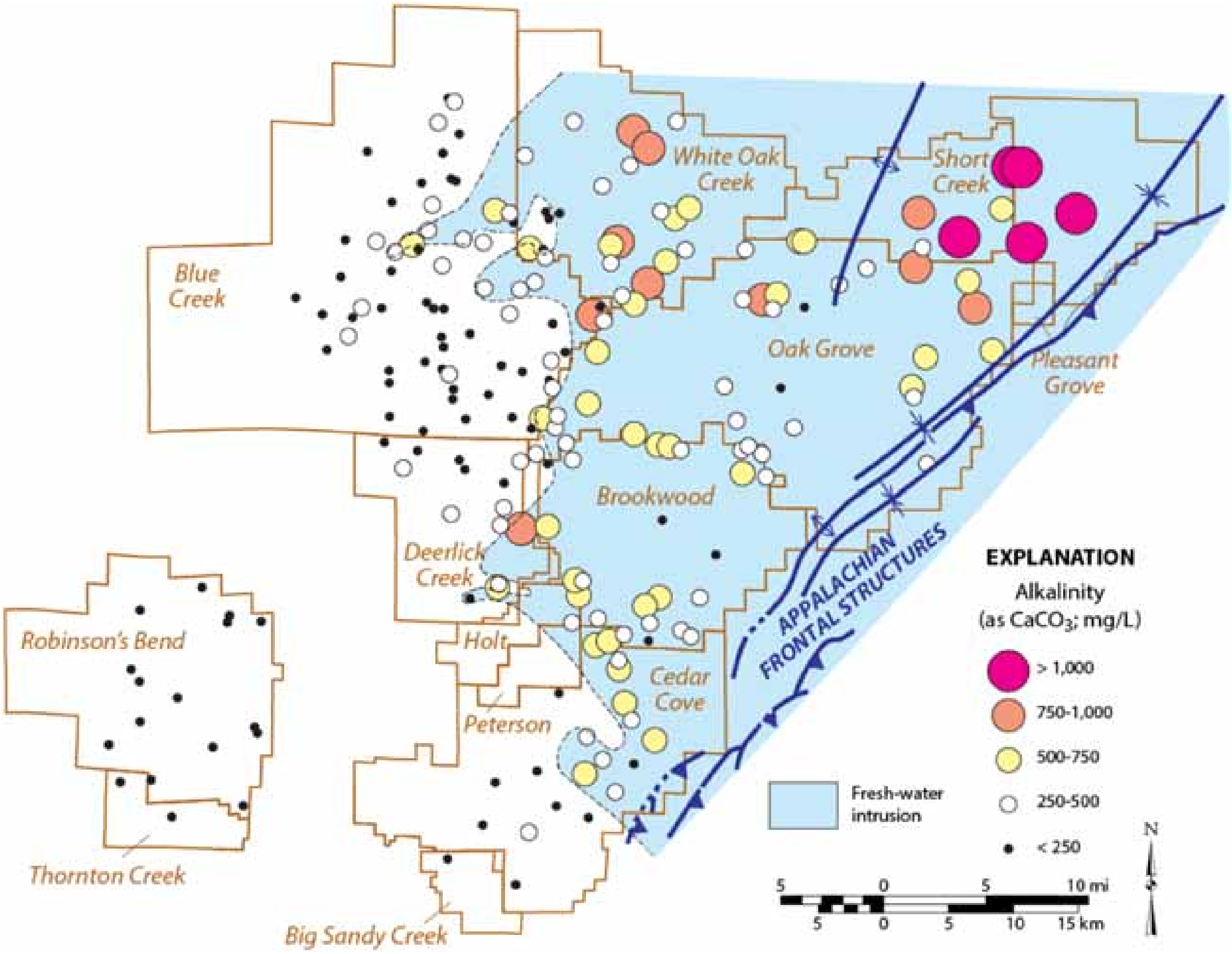


Figure 29.—Map of alkalinity of produced water in the active Black Warrior CBM fields.

Other aggregate properties include chemical oxygen demand (COD), a proxy for dissolved organic compounds in water, and total Kjeldahl nitrogen (TKN), a proxy for dissolved nutrients. COD is typically between 0 and 2,870 mg/L, although a few samples have anomalous values as high as 10,500 mg/L (table 1). COD correlates moderately and positively with TDS (r = 0.52). TKN values range from 0 to 38 mg/L and average 6 mg/L. TKN and TDS correlate with a regression coefficient of 0.85, indicating a strong relationship (fig. 32). An interesting result of this analysis is that the amount of organic matter and nutrients tends to increase with TDS content in the Pottsville Coal Interval.

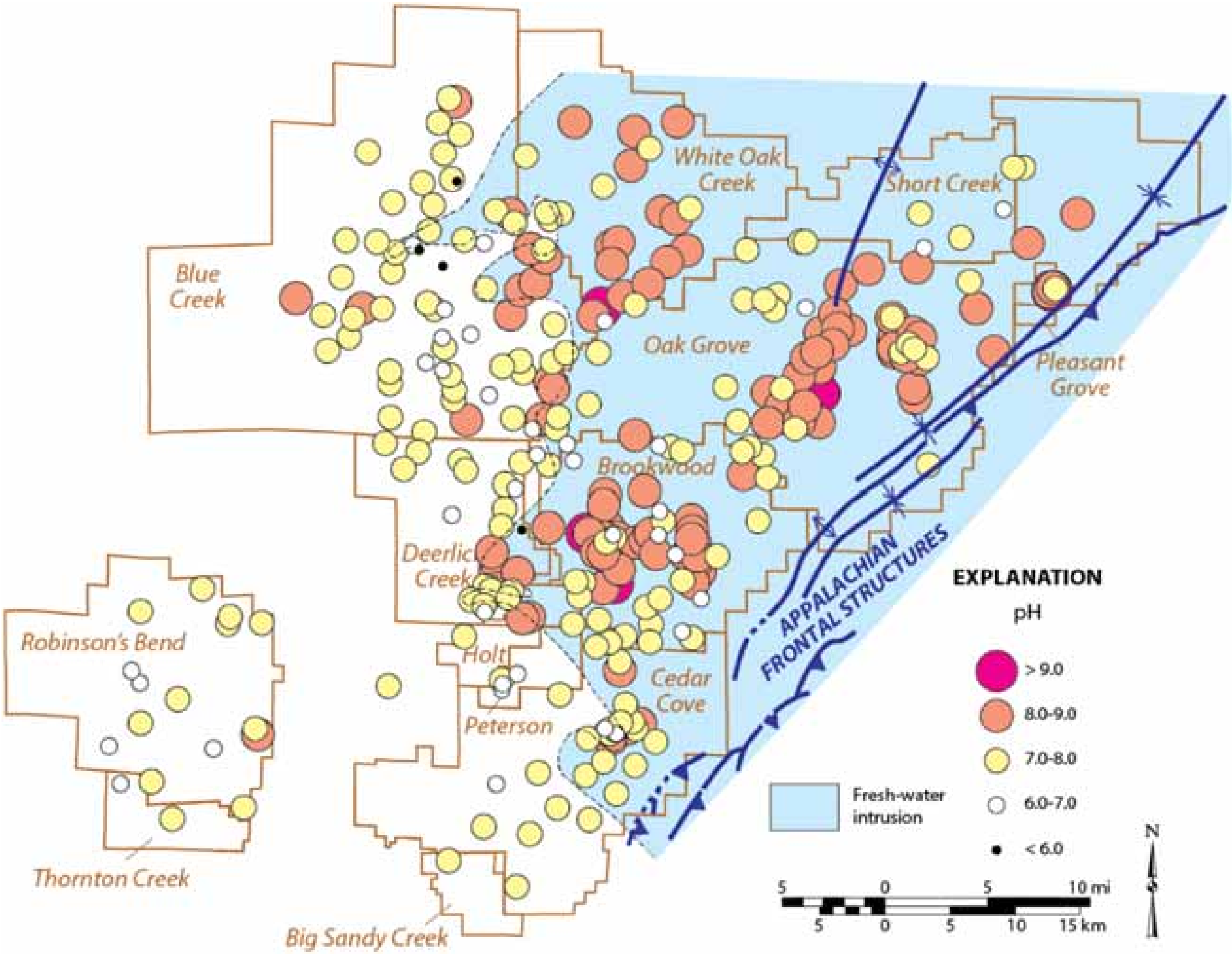


Figure 30.—Map of pH of produced water in the active Black Warrior CBM fields.

Major Ionic Compounds

Major ionic compounds in the produced water are dominated by Cl^-, Na^+, and HCO_3^- (table 1). Piper and Stiff diagrams indicate that the produced water represents a compositional continuum ranging from $NaHCO_3$- to NaCl-type, which is common in many CBM plays (Ayers and Kaiser, 1994; Rice and others, 2000; Rice, 2003; Van Voast, 2003) (figs. 33, 34). A few samples with TDS < 10,000 mg/L contain anomalous concentrations of Ca^{2+}, Mg^{2+}, and SO_4^{2-}. The samples tend to be strongly depleted in CO_3^{2-}, which has a mean concentration of only 3 mg/L (table 1). Elevated CO_3^{2-} concentrations are restricted to the freshwater plumes, particularly

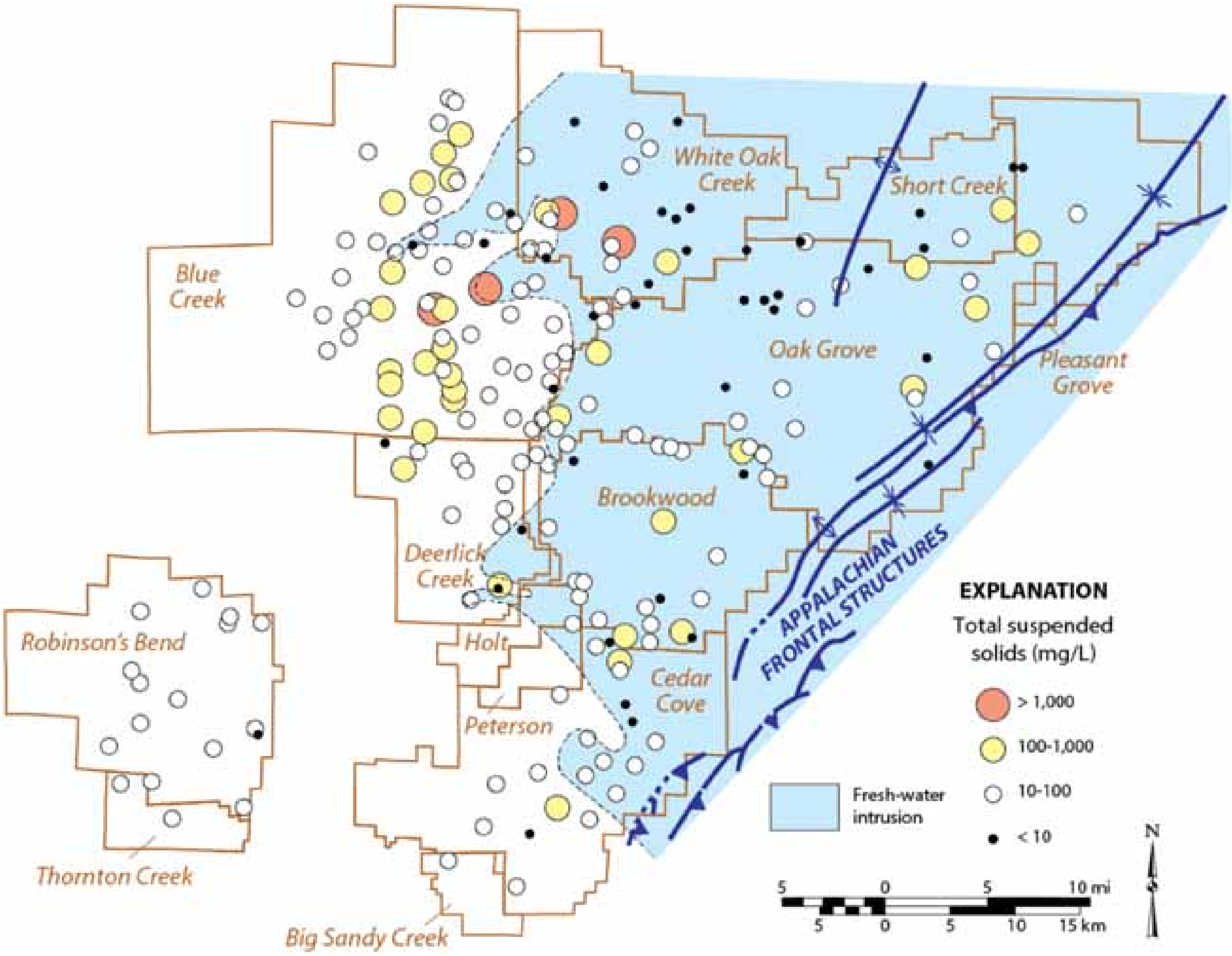


Figure 31.—Map of TSS content of produced water in the active Black Warrior CBM fields.

in Oak Grove and Brookwood Fields (fig. 35). Regression analysis indicates that Cl^- and Na^+ are the principal determinants of TDS content and that HCO_3^- correlates negatively with TDS (fig. 36). To date, the maximum recorded HCO_3^- content in water with TDS > 10,000 mg/L is 807 mg/L, and NaCl-type water predominates where TDS > 3,000 mg/L.

Maps of Cl^-, Na^+, K^+, Mg^{2+}, and Ca_2^+ concentrations (figs. 37-41) are consistent with the TDS map (fig. 28) and demonstrate the impact of the freshwater plumes on water chemistry. Some samples in Robinson’s Bend Field have anomalously low Cl^- concentrations, and comparison with the TDS, Na^+, and HCO_3^- data indicates local infiltration of fresh water and

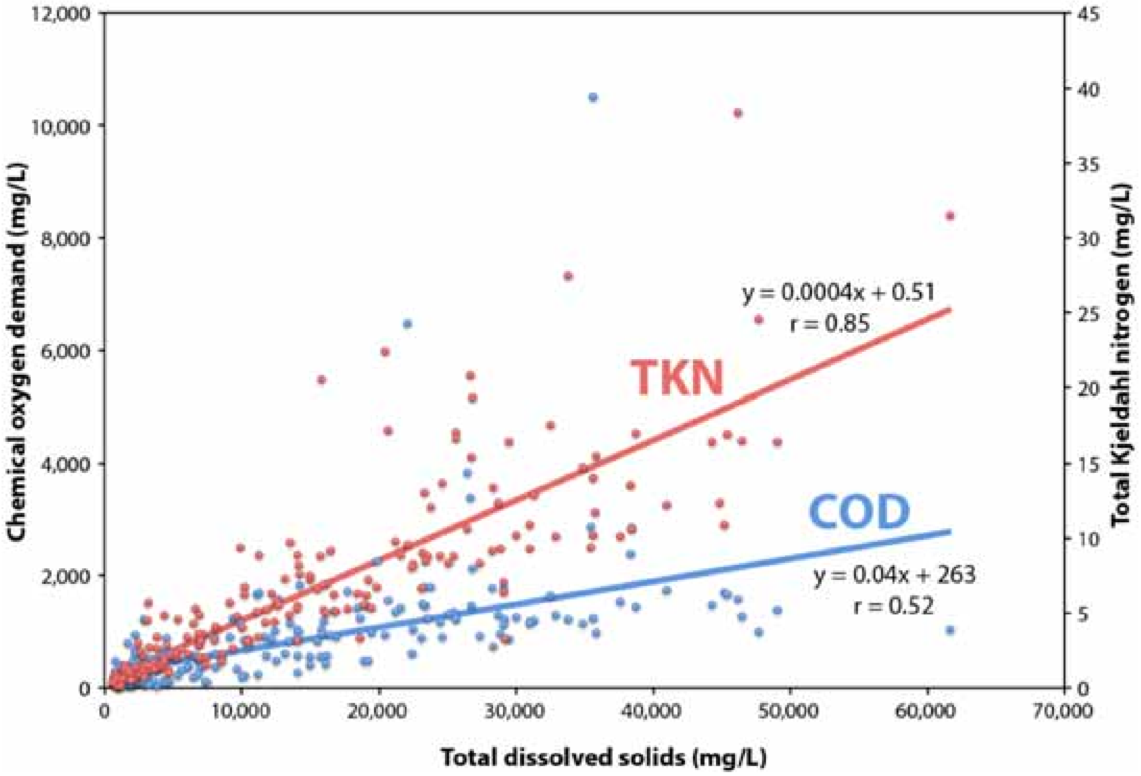


Figure 32.—Map showing relationship of TKN and COD to TDS in produced water from the active Black Warrior CBM fields.

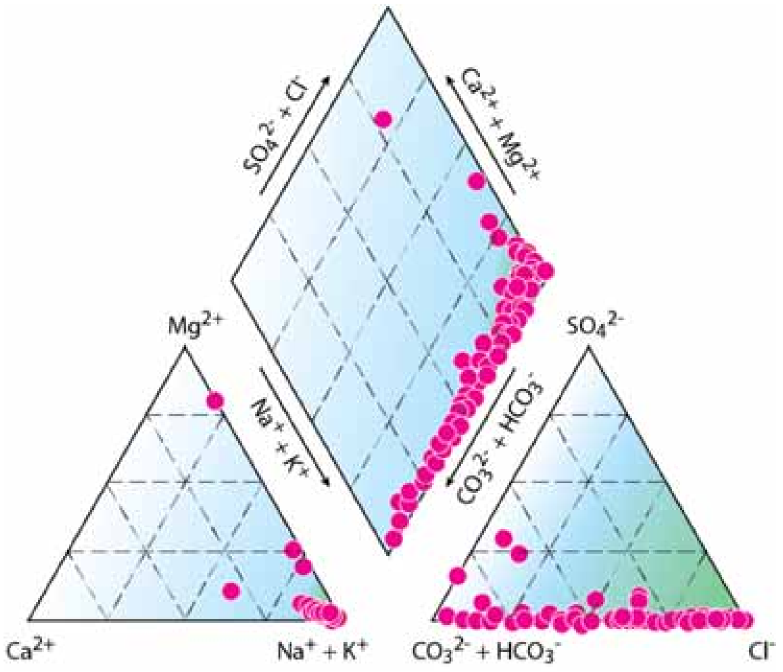


Figure 33.—Piper diagram showing major ionic compounds in produced water from the Black Warrior CBM fields.

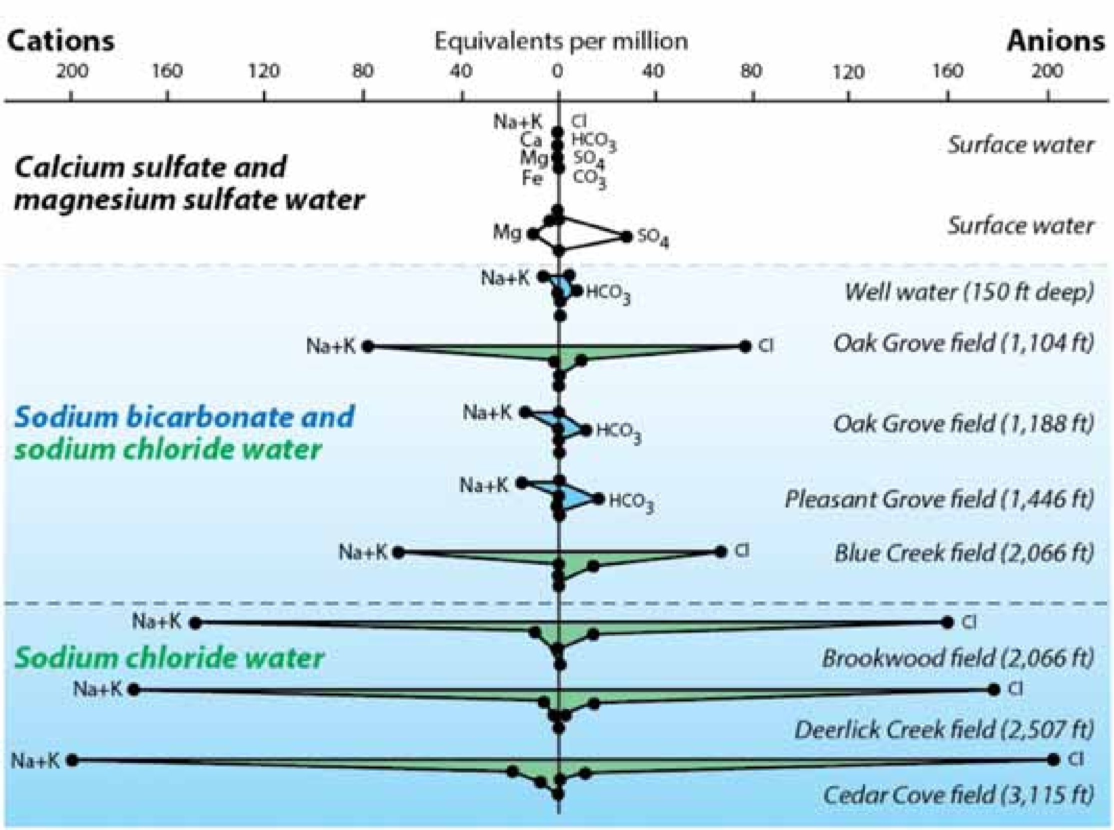


Figure 34.—Stiff diagrams showing variation of major ionic composition of produced water from the Black Warrior CBM fields (modified from Pashin and others, 1991).

perhaps local connection with the Cretaceous aquifer. Mapping HCO_3^- levels establishes an inverse pattern relative to the other maps (fig. 42), reflecting the meteoric origin of the freshwater plumes, in which HCO_3^- is a product of biological activity that is stimulated by freshwater intrusion (e.g., Van Voast, 2003). Sulfate tends to be associated with surface and near-surface water in the Black Warrior Basin (Pashin and others, 1991). Sulfate (SO_4^{2-}) content is generally less than 5 mg/L, but numerous prominent anomalies where concentration exceeds 25 mg/L are scattered about the map (fig. 43). Elevated SO_4^{2-} values are most common in the mine-impacted areas of Brookwood and Oak Grove fields and may reflect draw of near-surface water into the CBM reservoirs. The origin of the other anomalies is less clear and may be related

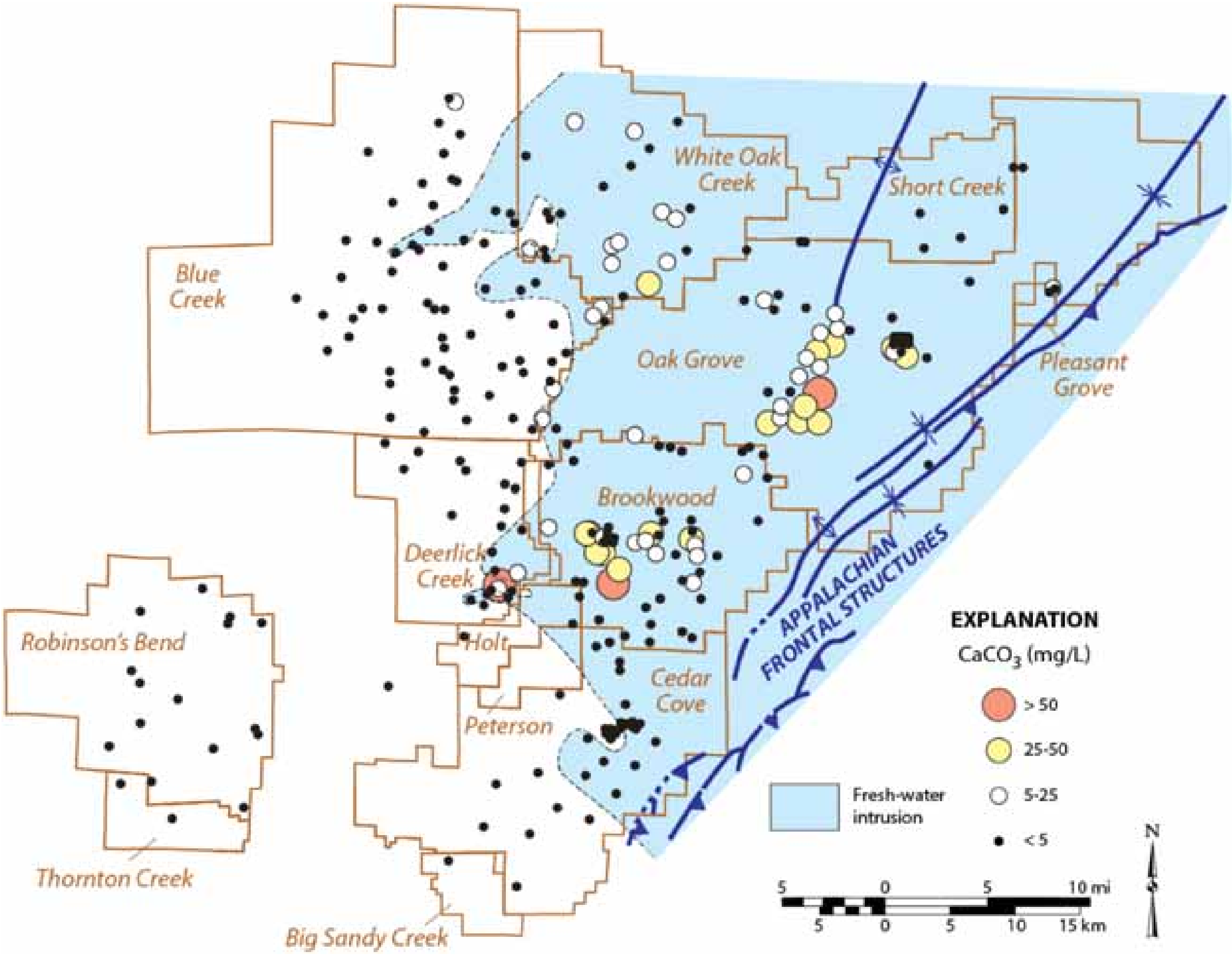


Figure 35.—Map of CO_3^{2-} content of produced water in the active Black Warrior CBM fields.

to localized communication of the CBM reservoirs with shallow groundwater or, alternatively, oxidation of sulfide fines in the water during and after sampling.

Metallic and Nonmetallic Substances

Metallic and nonmetallic substances tend to be minor components of the produced water (tables 2, 3), and virtually all correlate positively with TDS and Cl^- and are thus associated with the native basinal brine. Of these, the most abundant elements are Ba, F, Fe, Li, Mn, and Sr, and

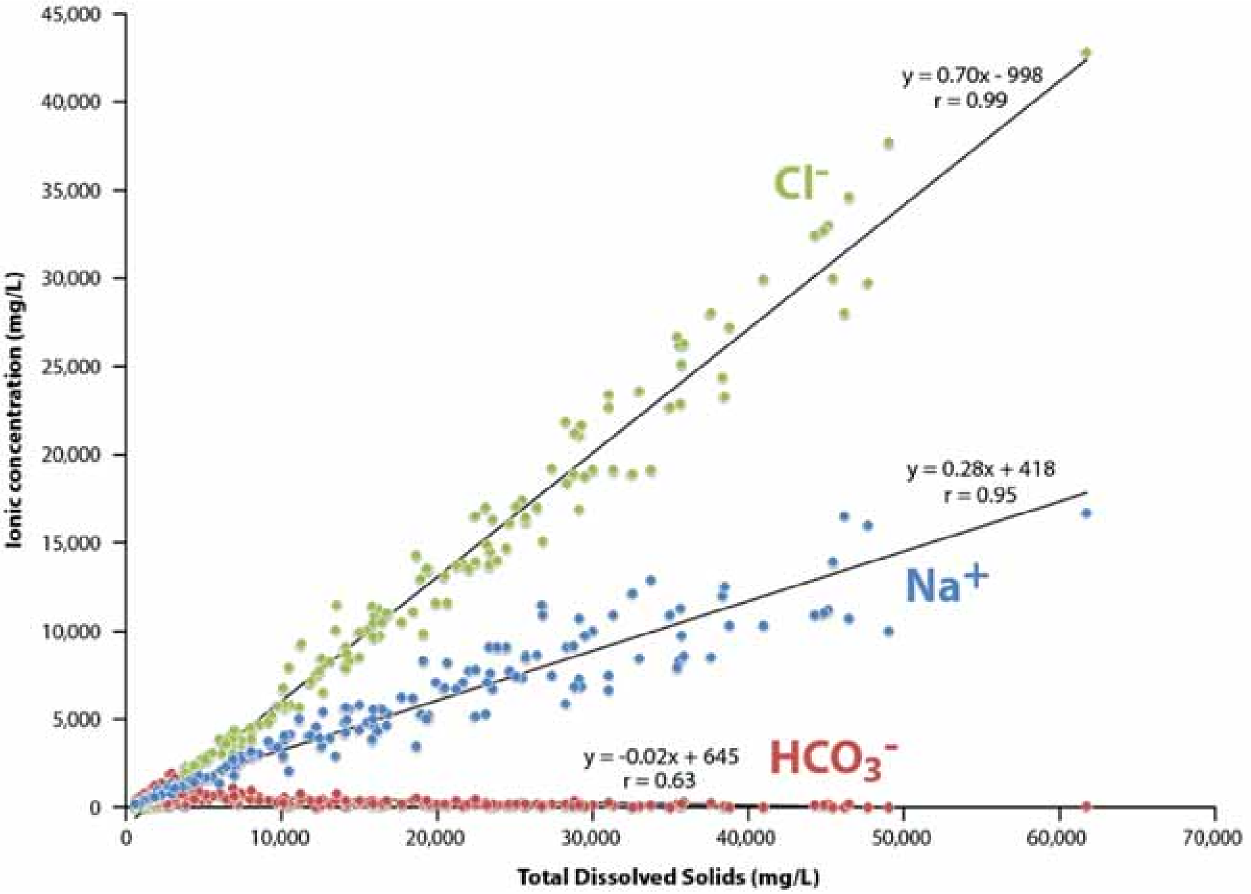


Figure 36.—Plot of chlorine, sodium, and bicarbonate versus TDS content in produced water from Black Warrior CBM reservoirs.

these substances are sufficiently abundant that they should be included in calculations of TDS and evaluation of analytical charge balance.

A wide range of trace elements are present in the produced water, and the concentrations typically correlate positively with TDS and chloride (table 2). Constituents of concern in the water include As, Hg, Pb, and Se. Arsenic (As) is associated with high-sulfur coal in the Black Warrior Basin (Goldhaber and others, 2003), but concentrations in the produced water are generally very low, averaging only 1.8 mg/L. Mercury (Hg) is below detection levels (0.010 μg/L) in all but 29 samples (fig. 44). Maximum values tend to decrease with increasing TDS

Table 2. Summary of metallic and nonmetallic elements in wellhead water samples from coalbed methane wells in the Black Warrior Basin. Analyses performed in the geochemical laboratories of the Geological Survey of Alabama and the University of Alabama.

Substance	**N**	**Minimum (μg/L)**	**Maximum (μg/L)**	**Mean (μg/L)**	**Standard deviation (μg/L)**
Ag	206	0	565	15	61
Al	206	0	99	37	24
As	206	0.0	85.2	1.8	7.7
B	206	0	541	185	123
Ba	206	136	352,000	45,540	60,072
Be	206	0.0	7.7	0.1	0.6
Br	206	0	964	62	113
Cd	206	0	15	1	2
Co	206	0	162	23	30
Cr	206	0	351	2	25
Cs	115	0	72	11	14
Cu	206	0	98	1	9
F	206	0	22,600	6,130	6,570
Fe	206	45	93,100	8,956	14,157
Hg	206	0.000	0.056	0.003	0.009
Li	206	0	8,940	1,157	1,362
Mn	206	6	4,840	245	411
Mo	206	0	83	2	9
Ni	206	0	358	15	32
P	206	0.0	5.8	0.3	0.6
Pb	206	0	250	8	27.4
Rb	115	0	114	13	20
Sb	206	0	22	1	2
Se	206	0	63	2	7
Sn	206	0	9	0	1
Sr	206	15	142,000	11,354	17,748
Ti	206	0	45	3	7
V	206	0	39	1	5
Zn	206	0	278	24	32

content, suggesting an association with recharge along the basin margin. The amount of Pb is lower than 50 μg/L in all but 7 samples, and mean Pb content is only 8 μg/L. Selenium is typically below detection levels (1 μg/L) and has a mean concentration of only 2 μg/L, but 8 samples with TDS > 20,000 mg/L have concentrations above 20 μg/L.

Other metallic and nonmetallic substances include CO_2, PO_4, SiO_2, which are discussed in this paragraph, and a number of nitrogen and organic compounds, which are discussed in the

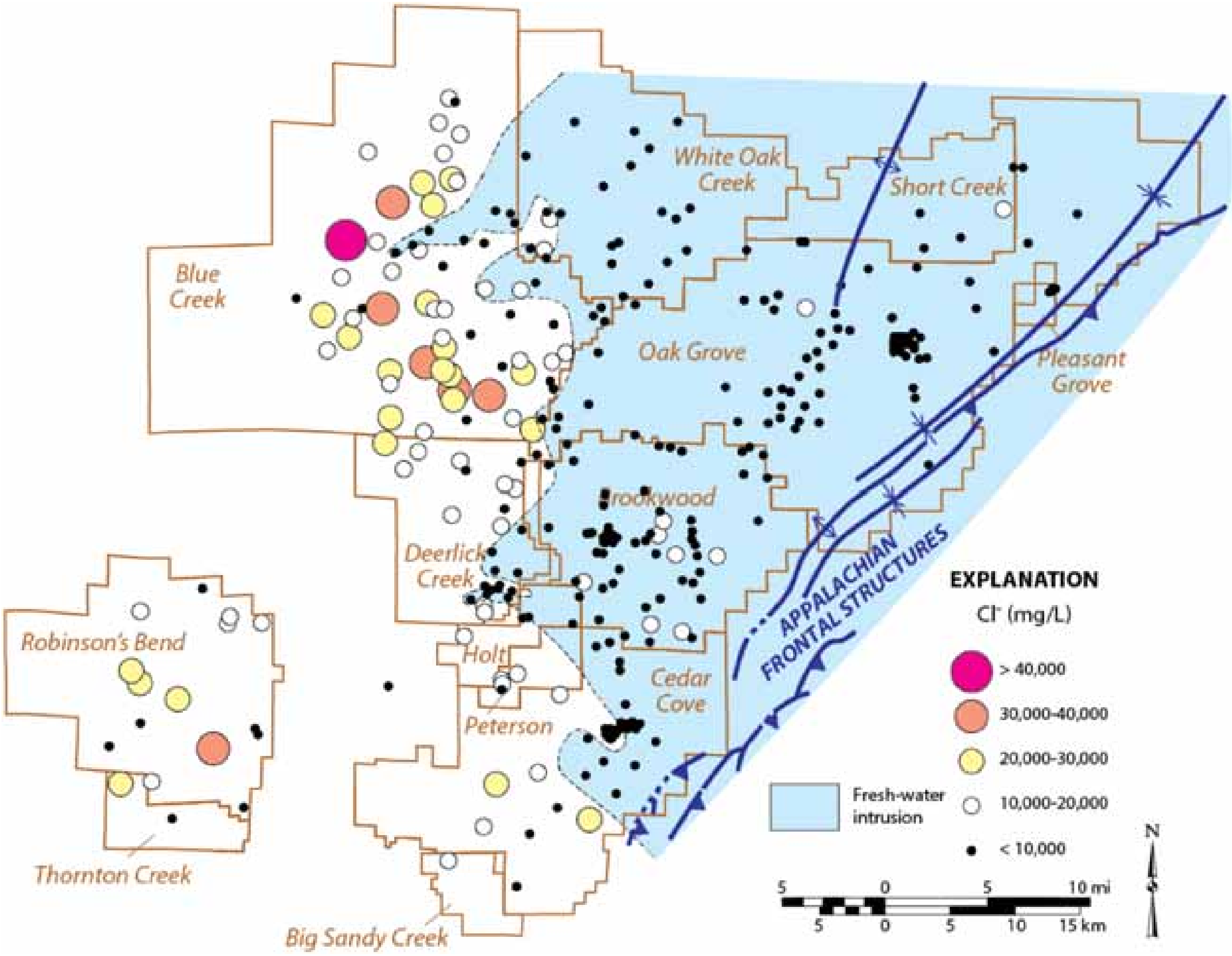


Figure 37.—Map of Cl$^-$ content of produced water in the active Black Warrior CBM fields.

Table 3. Summary of nutrients, organic compounds, and other constituents in wellhead water samples from coalbed methane wells in the Black Warrior Basin. Analyses performed in the geochemical laboratories of the Geological Survey of Alabama, the University of Alabama, and the USGS.

	N	Minimum	Maximum	Mean	Standard deviation
CO_2 (mg/L)	204	0	701	39	85
NH_3 and NH_4^+ as N (mg/L)	206	0	24	5	4
NH_4^+ (mg/L)	58	0	9	4	3
NO_2 (mg/L)	206	0	2.08	0.03	0.20
NO_3 (mg/L)	204	0	127	9	20
PO_4 (μg/L)	58	26	3,570	435	554
SiO_2 (mg/L)	206	1	18	9	3
DOC (mg/L)	55	1	61	3	9
TOC (mg/L)	206	0	103	6	16
Phenolic compounds (μg/L)	206	0	192	10	28

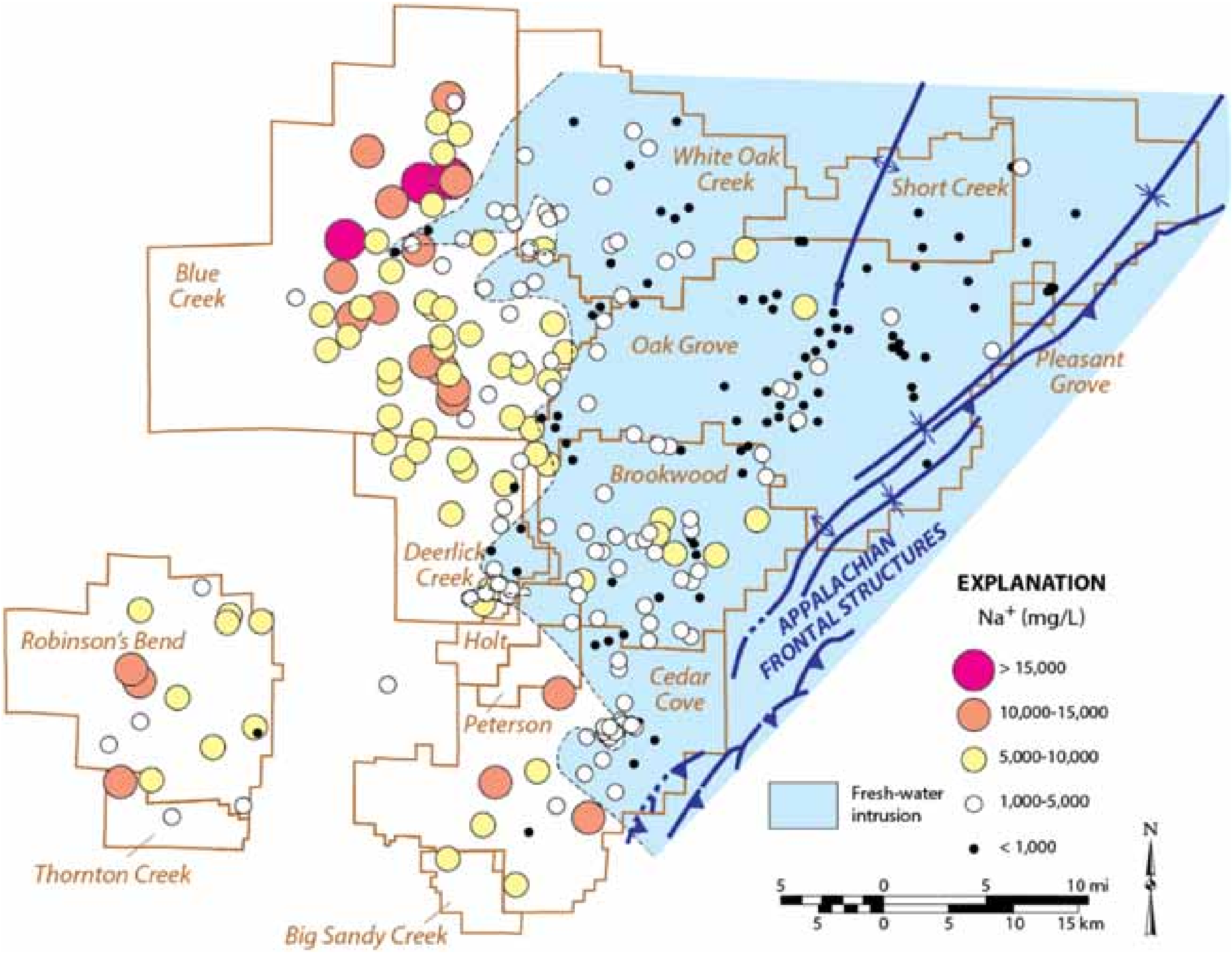


Figure 38.—Map of Na^+ content of produced water in the active Black Warrior CBM fields.

sections that follow (table 3). Dissolved CO_2 concentrations average 39 mg/L and locally exceed 700 mg/L, and no correlations with other parameters are apparent. A map of CO_2 content shows that values exceeding 50 mg/L are clustered in Short Creek Field and in a corridor extending from Blue Creek Field to Brookwood Field (fig. 45). Phosphorus and phosphate concentrations are typically lower than 500 μg/L. Values are locally higher than 3,000 μg/L and do not correlate with each other or with other geochemical variables. Dissolved silica (SiO_2) concentrations range from 1 to 18 mg/L and average 9 mg/L. Silica concentrations reflect the reactivity of host

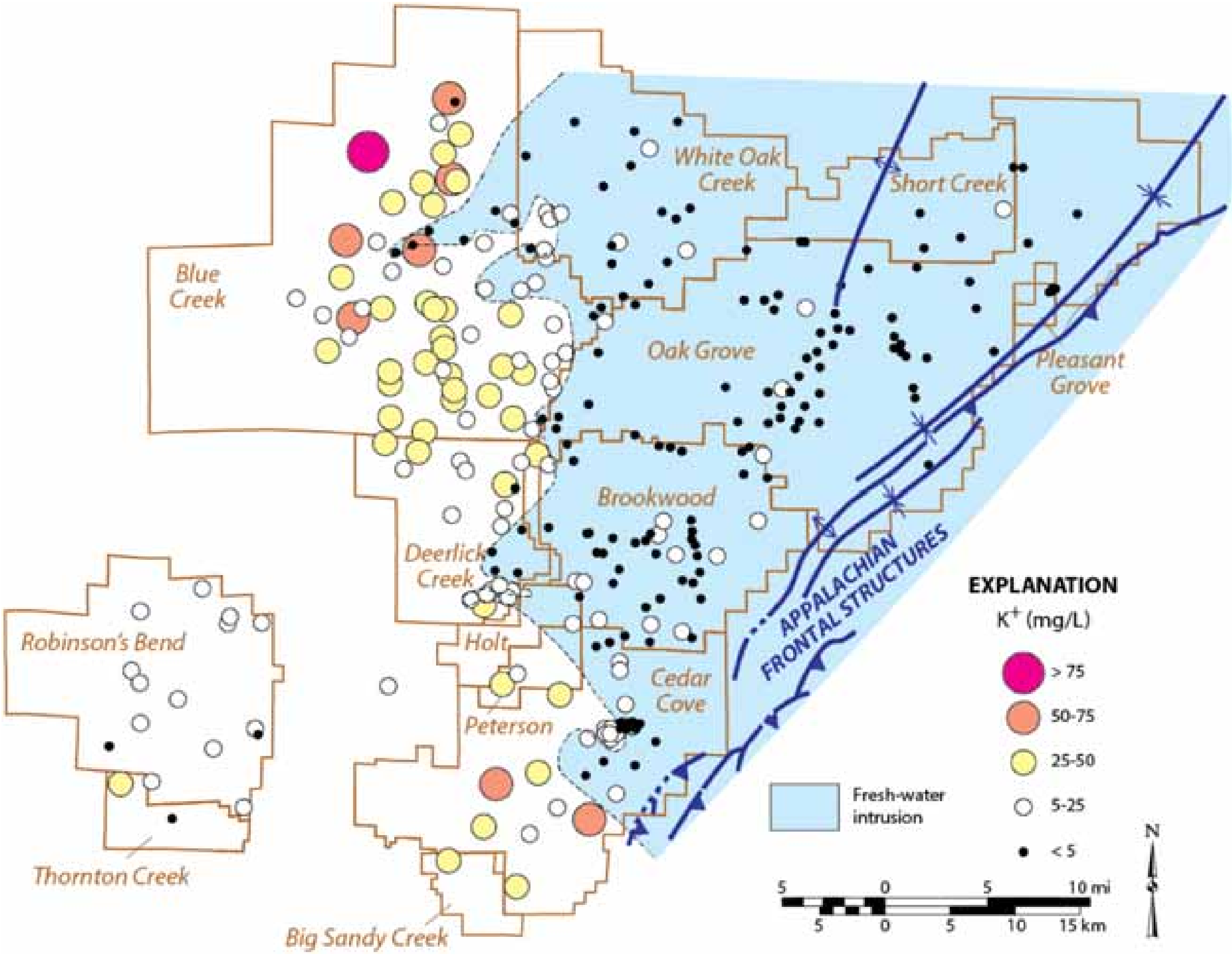


Figure 39.—Map of K^+ content of produced water in the active Black Warrior CBM fields.

formations with the formation water, and no regional trends or significant correlations are apparent.

Nitrogen Compounds

Nitrate (NO_3^-) and ammonia compounds (ammonia and ammonium; NH_3 and NH_4^+ determined as N) are the principal nitrogen-bearing compounds in the produced water (table 3). Nitrate levels are typically lower than 30.0 mg/L and do not correlate with other geochemical parameters. However anomalously high NO_3^- values (36-123 mg/L) were measured in 12

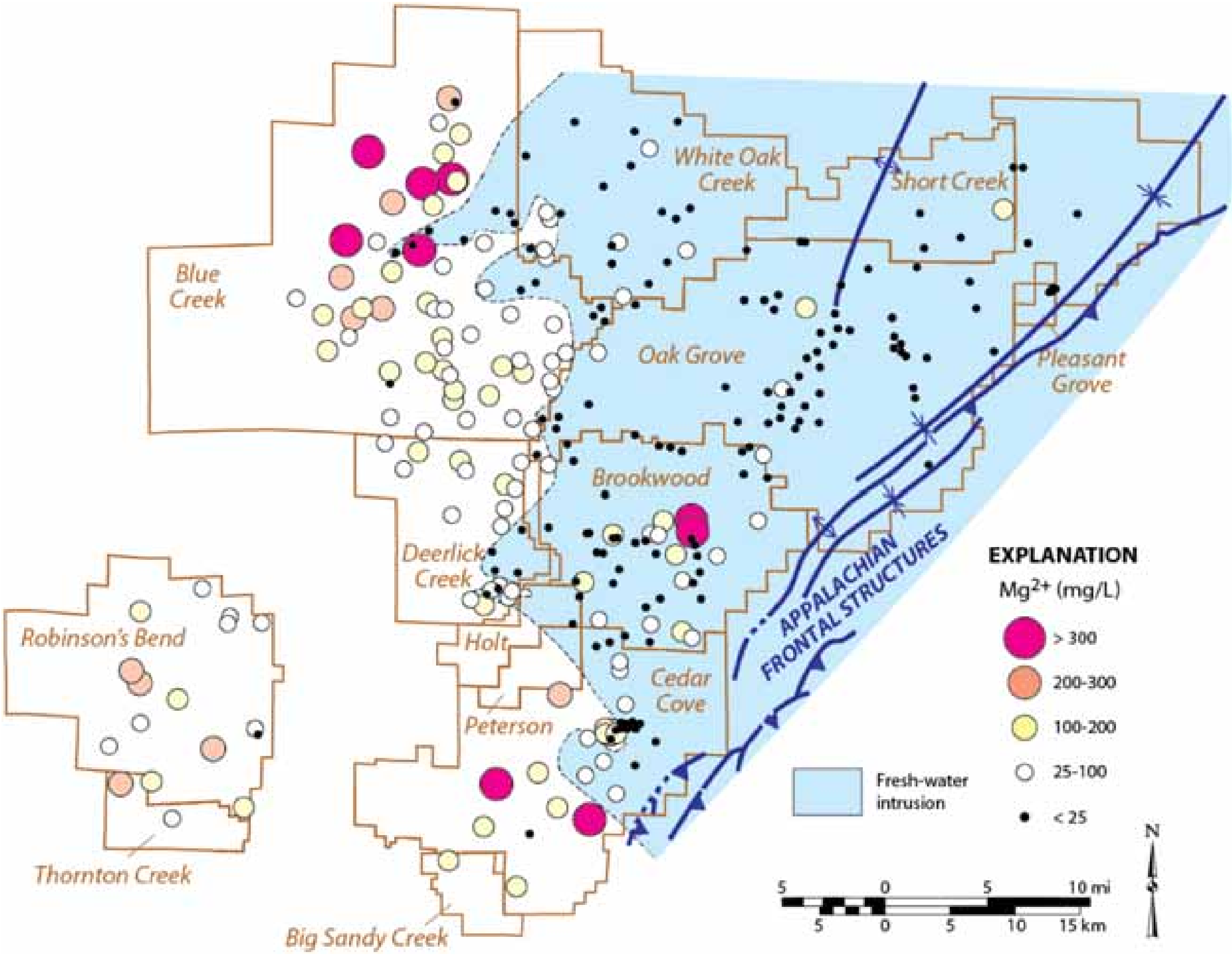


Figure 40.—Map of Mg^{2+} content of produced water in the active Black Warrior CBM fields.

samples, and mapping reveals that elevated values are most common in the distal part of the freshwater intrusion in White Oak Creek Field and west of the intrusion in Blue Creek and Robinson's Bend fields (fig. 46). Nitrite (NO_2^-) concentrations in formation water are typically below detection limits. Where detected, levels are typically lower than 0.30 mg/L. Ammonia and ammonium, by comparison, were detected in all samples, and values range from less than 1 to 24 mg/L (table 3). Ammonium constitutes about 30 percent of the nitrogen compounds in the water. Ammonia + ammonium content correlates strongly and positively with TDS content (fig. 47), and concentrations higher than 5 mg/L are typical of water with TDS > 10,000 mg/L (fig. 48).

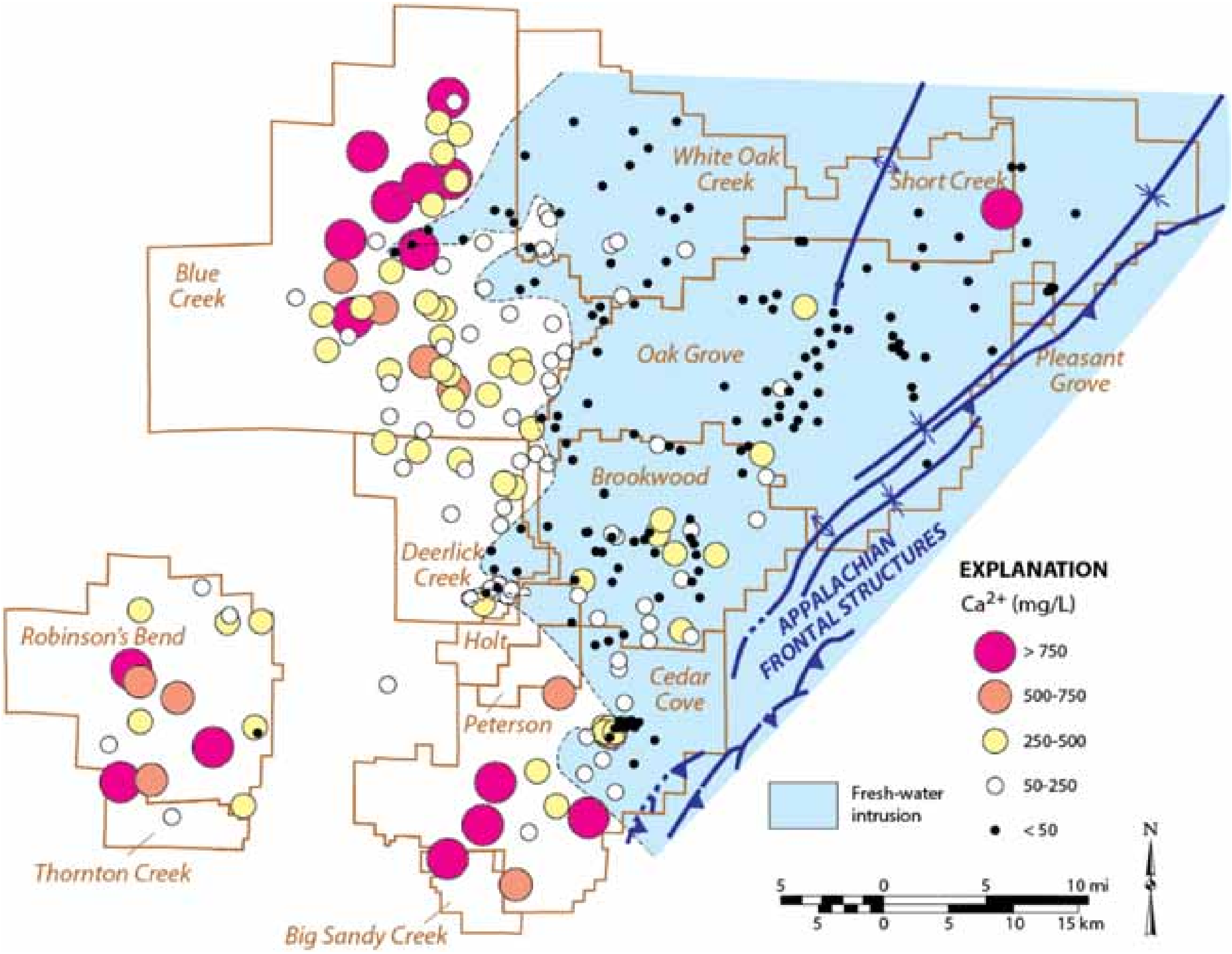


Figure 41.—Map of Ca^{2+} content of produced water in the active Black Warrior CBM fields.

The clear correlation between NH_3 + NH_4^+ and TDS (fig. 47) indicates a strong association with basinal brine, which is surprising for these compounds. Ammonium is known to substitute for K and Na in feldspar and muscovite in metamorphic terranes (Barker, 1964; Eugster and Munoz, 1966; Duit and others, 1986). Ammonia, moreover, has been identified in illite from Carboniferous coal-bearing strata (Juster and others, 1987) and in oil shale (Oh and others, 1988). In the North German Basin, NH_4^+-bearing illite is thought to be a source of N_2 in natural gas (Mingram and others, 2005). Therefore, one explanation for the correlation between NH_3 + NH_4^+ and TDS is ion exchange between minerals and brine. However, Bates and others (2011)

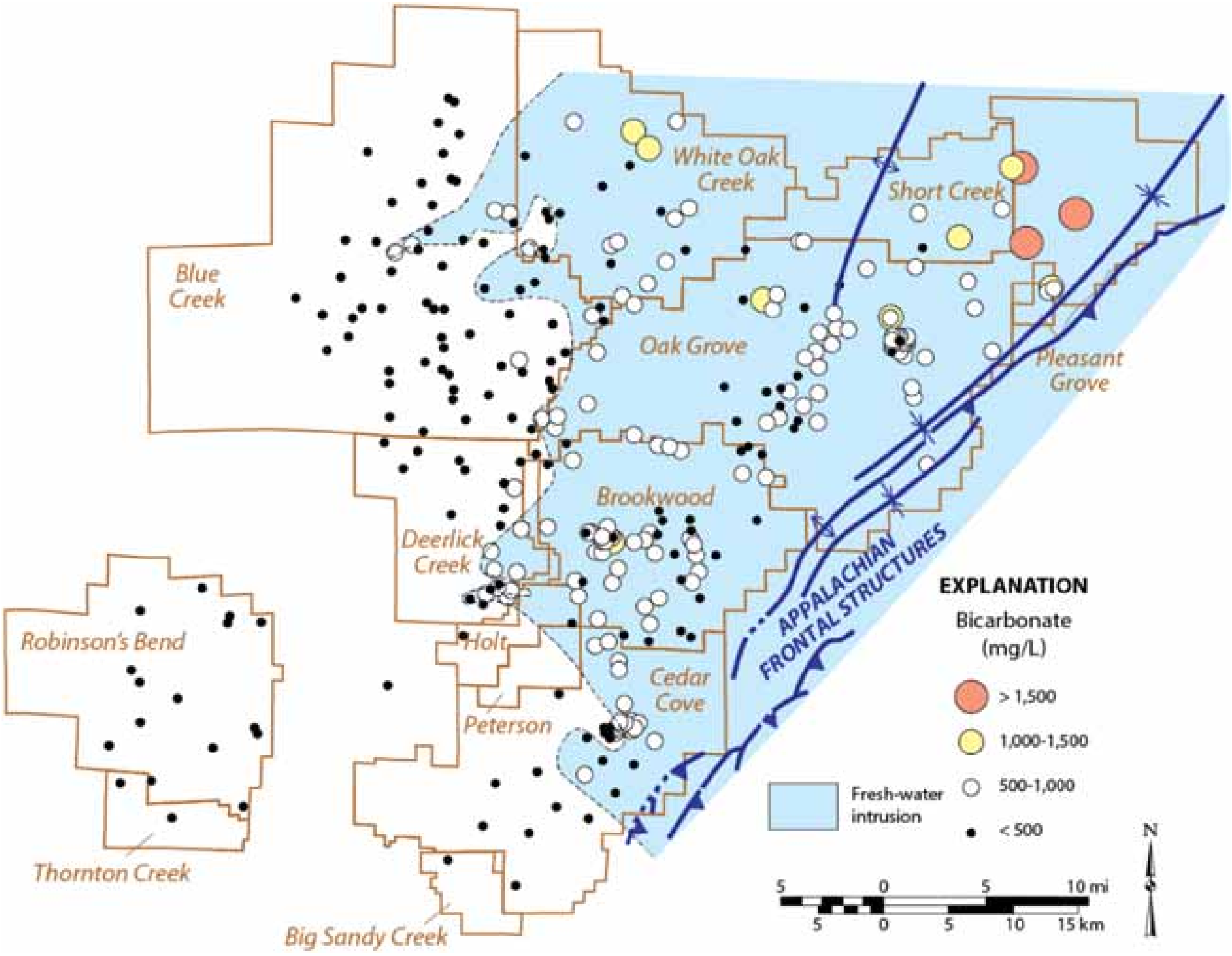


Figure 42.—Map of HCO_3^- content of produced water in the active Black Warrior CBM fields.

attributed NH_4^+ in water produced from subbituminous coal of the Powder River Basin to reaction of formation water with coal. One possibility is that denitrification of organic matter early in the regional coalification history may be the ultimate source of NH_4^+ and NH_3 in the Black Warrior basin, and the distinct association with basinal brine is interpreted to reflect a complex history of nitrogen exchange among organic matter, minerals, and formation water.

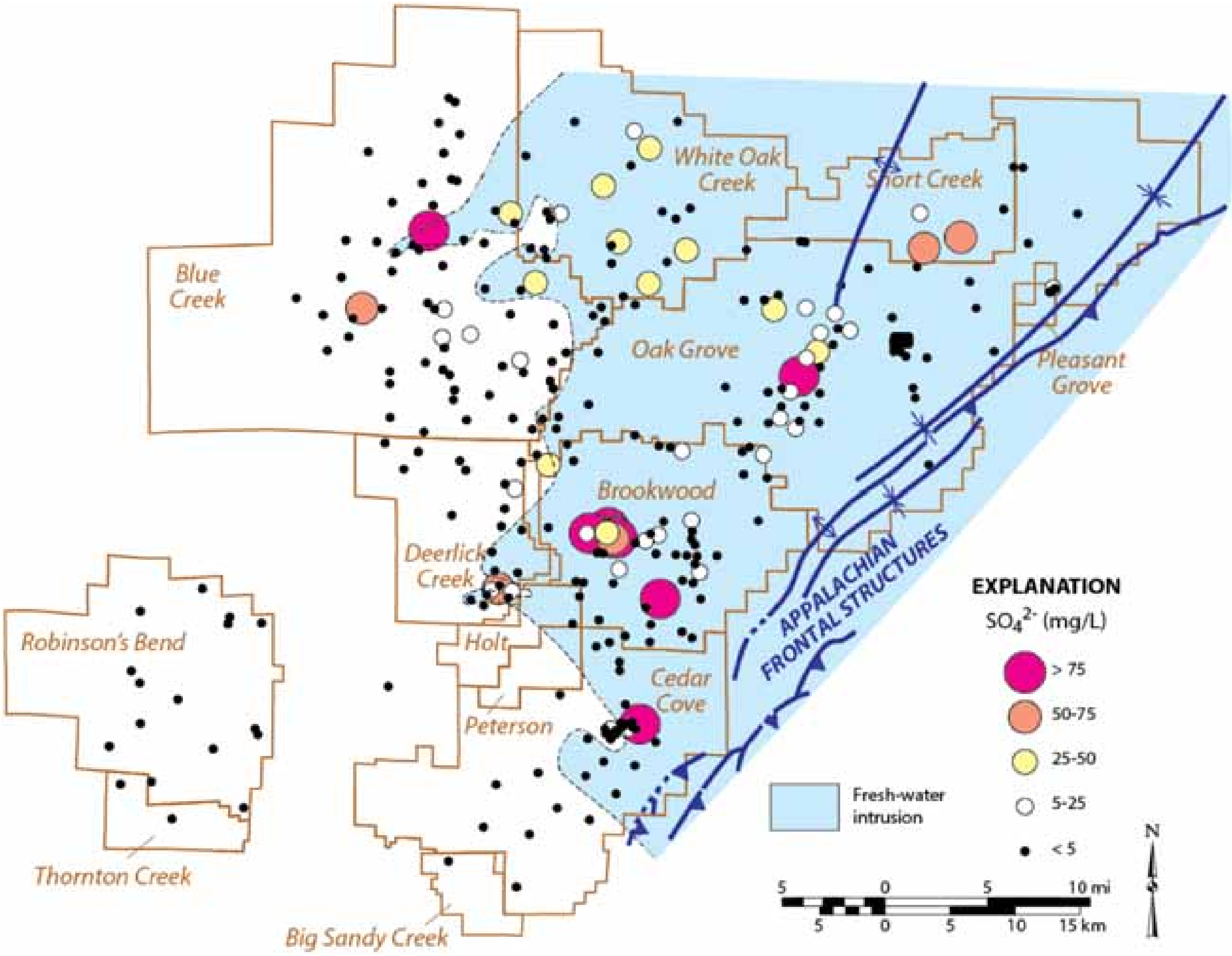


Figure 43.—Map of SO_4^{2-} content of produced water in the active Black Warrior CBM fields.

Organic Constituents

DOC and TOC values in the produced water are typically < 12 mg/L but locally exceed 30 mg/L (table 3). Mean TOC content is 6 mg/L, and most samples have TOC values lower than 4 mg/L. Mapping shows that samples with TOC > 30 mg/L have an erratic distribution (fig. 49). One possibility is that these elevated values are the product of sample contamination by lubricant at the wellhead, specifically the sucker rod and stuffing box. If one discounts these samples, then most of the samples with TOC between 4 and 30 mg/L come from the distal reaches of the freshwater intrusion and the brine-rich area of Blue Creek Field (fig. 50).

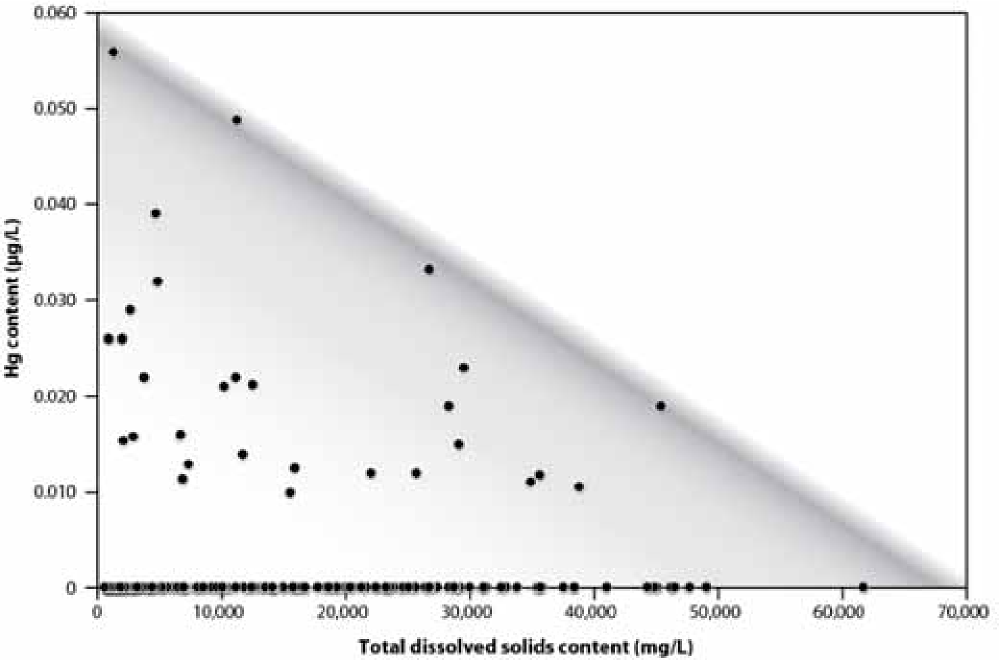


Figure 44.—Plot showing relationship of Hg to TDS content in produced water from the Black Warrior CBM fields.

The produced water has a distinct petroliferous odor, and variety of organic compounds was identified. Organic compounds include a spectrum of aromatic, heterocyclic, and aliphatic hydrocarbons. Indeed, several of the wells from the northwestern part of the study area produce incidental amounts of oil (< 1 bbl/day). Concentrations of aromatic hydrocarbons in the produced water are locally higher than 100 µg/L (fig. 51; table 3). Phenols and polycyclic aromatic hydrocarbons (PAH) form the bulk of the extractable hydrocarbons, which represent a fraction of the total hydrocarbons in the formation water (table 4). Additional extractable hydrocarbons include minor amounts of other heterocyclic, aromatic, and non-aromatic compounds. Overall, the assemblage and concentrations of organic compounds in Black Warrior coal resemble those identified previously in coal-borne water of the Powder River Basin (Orem and others, 2007). The dominant phenols that were identified are 4-(1,1,3,3-tetramethylbutyl)-phenol and 2,4-bis(1,1-dimethylethyl)-phenol. The principal PAH compounds are naphthalic substances. Acetate

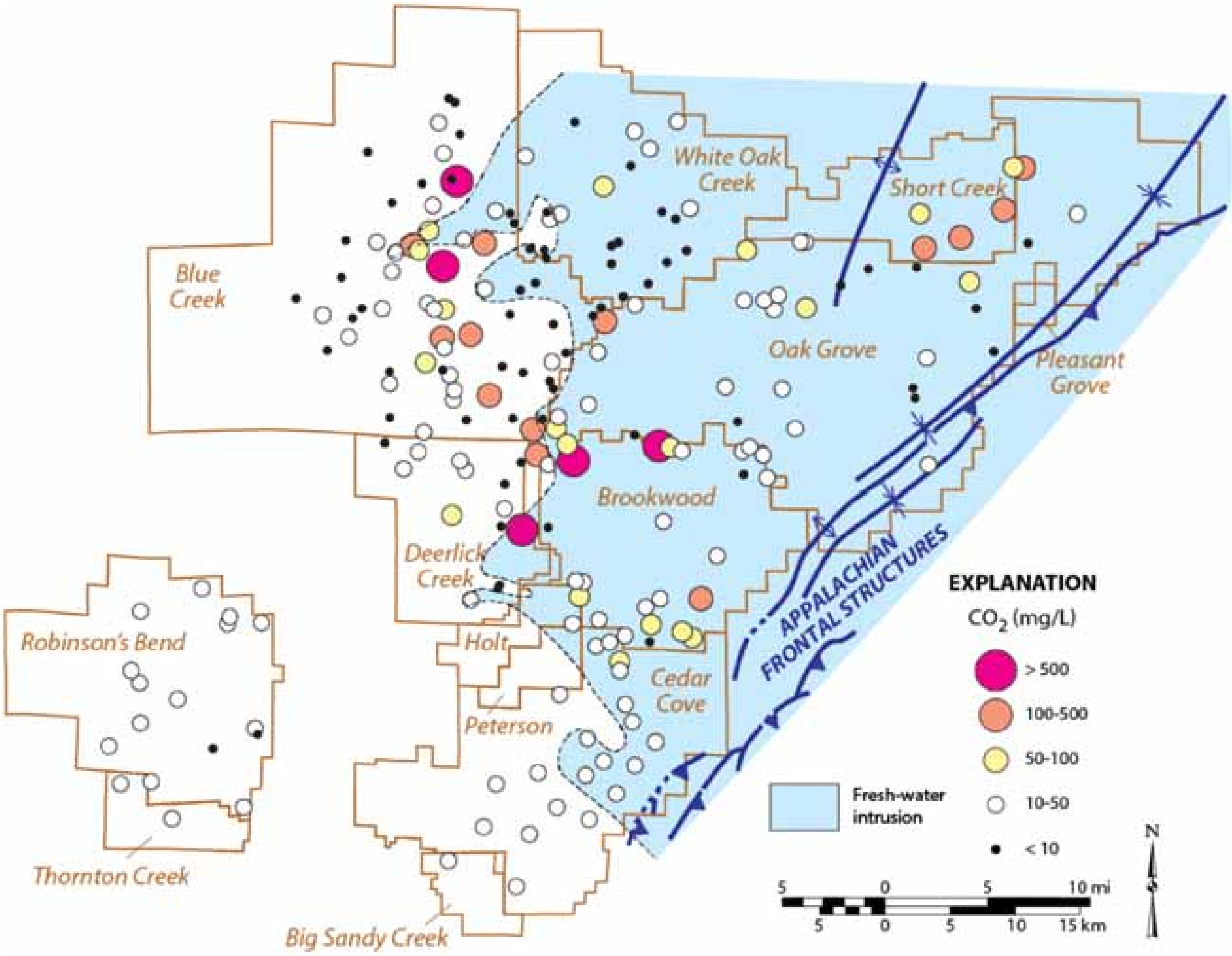


Figure 45.—Map of free CO_2 content of produced water in the active Black Warrior CBM fields.

was the only volatile fatty acid identified, and concentrations are < 1 mg/L. Other fatty acids, including a variety of decanoic and decenoic acids, were detected in the produced water.

The distribution of phenolic compounds has a complex relationship to TDS (figs. 51, 52). The lower limit of detection is 3 μg/L, and samples below the detection limit are from areas where TDS < 22,000 mg/L. Concentrations < 30 μg/L occur at all recorded TDS values, and elevated concentrations of 30 to 103 μg/L form a peak between TDS levels of 6,000 and 13,000 mg/L, which corresponds with the margins of the freshwater plumes. Samples with phenolic constituents exceeding 25 μg/L come primarily from areas where coal is of high volatile A and

Table 4. Summary of selected organic compounds with maximum concentrations greater than 2.00 μg/L from extracts of produced water samples from the Black Warrior basin. Samples analyzed in the geochemical laboratories of the U.S. Geological Survey.

Compound	**Wells with detections (N/65)**	**Estimated concentration range (μg/L)**
Polycyclic aromatic hydrocarbons		
Naphthalene	49	0.01-6.57
methyl-Naphthalene	52	0.01-15.55
dimethyl-Naphthalene	39	0.01-9.51
trimethyl-Naphthalene	23	0.01-4.49
methyl-Biphenyl	18	0.01-2.13
Heterocyclic compounds		
methyl-Quinoline	31	0.03-3.75
Benzothiazole	45	0.01-3.04
Caprolactam	10	0.02-2.39
Phenols		
4-(1,1,3,3-tetramethylbutyl)-Phenol	17	0.01-18.34
2,4-bis(1,1-dimethylethyl)-Phenol	21	0.01-4.94
Other aromatics		
Dioctyl Phthalate	57	0.01-2.30
Non-aromatic compounds		
Triphenyl phosphate	6	0.01-6.77
Tributyl phosphate	23	0.01-2.66
Cyclic octaatomic sulfur	29	0.10-9.63
Dodecanoic acid	30	0.67-2.52
Tetradecanoic acid	53	0.94-5.32
Hexadecanoic acid	50	1.17-3.02
Octadecanoic acid	32	1.62-3.73
Hexadecenoic acid	25	1.13-8.37
Octadecenoic acid	29	1.60-3.40

lower rank and where TDS > 10,000 mg/L (fig. 51). Hence, one possible conclusion is that the hydrocarbons are associated with the catagenesis of coal. Following this line of reasoning, low concentrations in medium volatile bituminous and low volatile bituminous coal, which is in the heart of the thermogenic gas window, could be interpreted as a product of thermal alteration.

Alternatively, the similarity of the extractable hydrocarbons to those identified in thermally submature coal of the Powder River Basin (Orem and others, 2007) suggests that many of these compounds formed either prior to catagenesis or, perhaps preferably, after catagenesis was

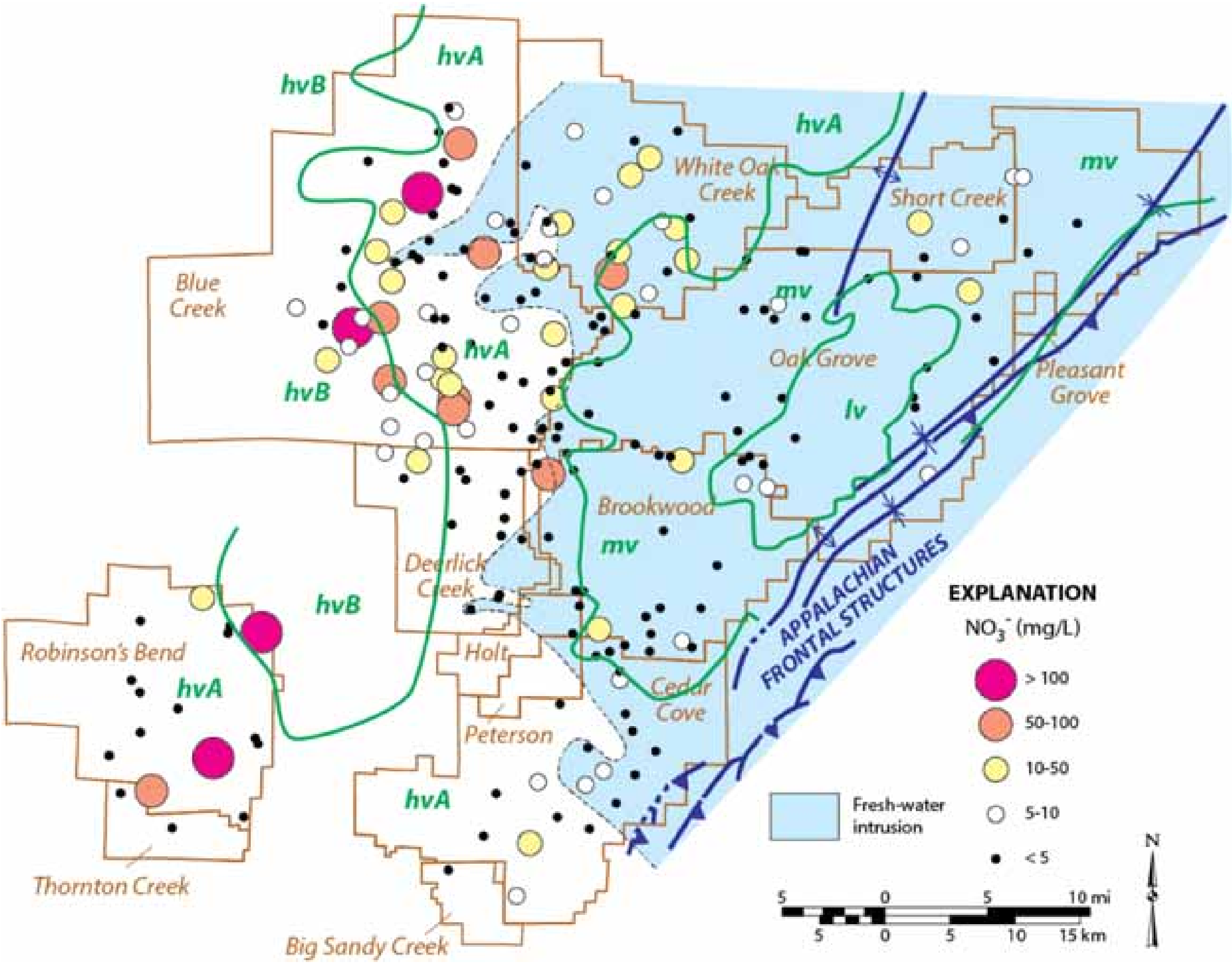


Figure 46.—Map of NO_3 content of produced water in the active Black Warrior CBM fields.

complete. Fatty acids, for example, may be by-products of late-stage microbial activity in the coal seams. Samples with concentrations below detection limits come primarily from Brookwood and White Oak Creek fields, suggesting that the distribution of hydrocarbon compounds reflects not only the regional rank pattern, but may also reflect basinward transport of hydrocarbons during freshwater intrusion. Indeed, the peak of phenolic concentrations between TDS levels of 6,000 and 13,000 mg/L (figs. 51, 52) may indicate accumulation of flushed hydrocarbons in the distal reaches of the plumes.

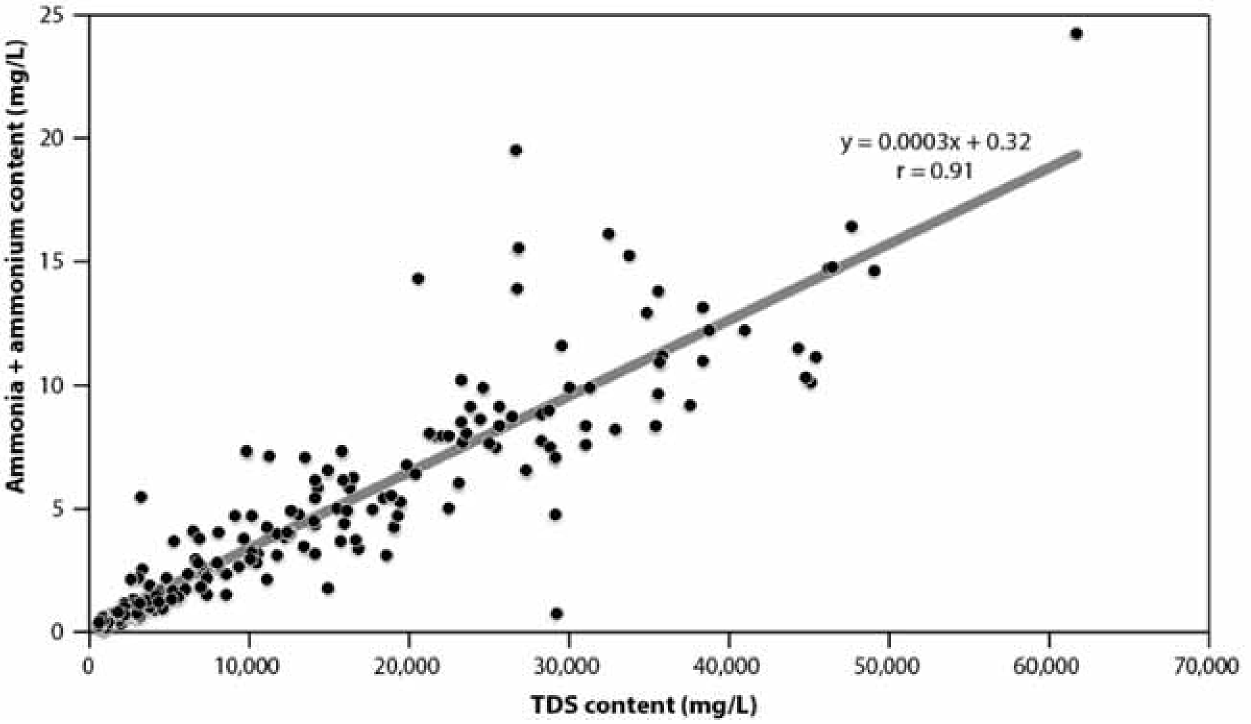


Figure 47.—Plot of ammonia compounds versus TDS in produced water from the active Black Warrior CBM fields.

GAS COMPOSITION

Coalbed methane can be considered a hydrodynamic natural gas play, and so water chemistry and gas chemistry are intimately related (Rice, 1993; Scott, 1993, 2002; Scott and others, 1994; Flores, 2008). Therefore, analyzing gas chemistry has the potential to provide vital insight into the controls on water composition and the prediction and management of water quality. In the following sections, the geochemistry of produced CBM from the Black Warrior Basin is considered in terms of bulk composition and stable isotopes.

Bulk Composition

Wellhead gases produced from the Black Warrior CBM fields are dominated by CH_4 (table 5). Bulk composition is remarkably uniform, and nonhydrocarbon gas content is typically less

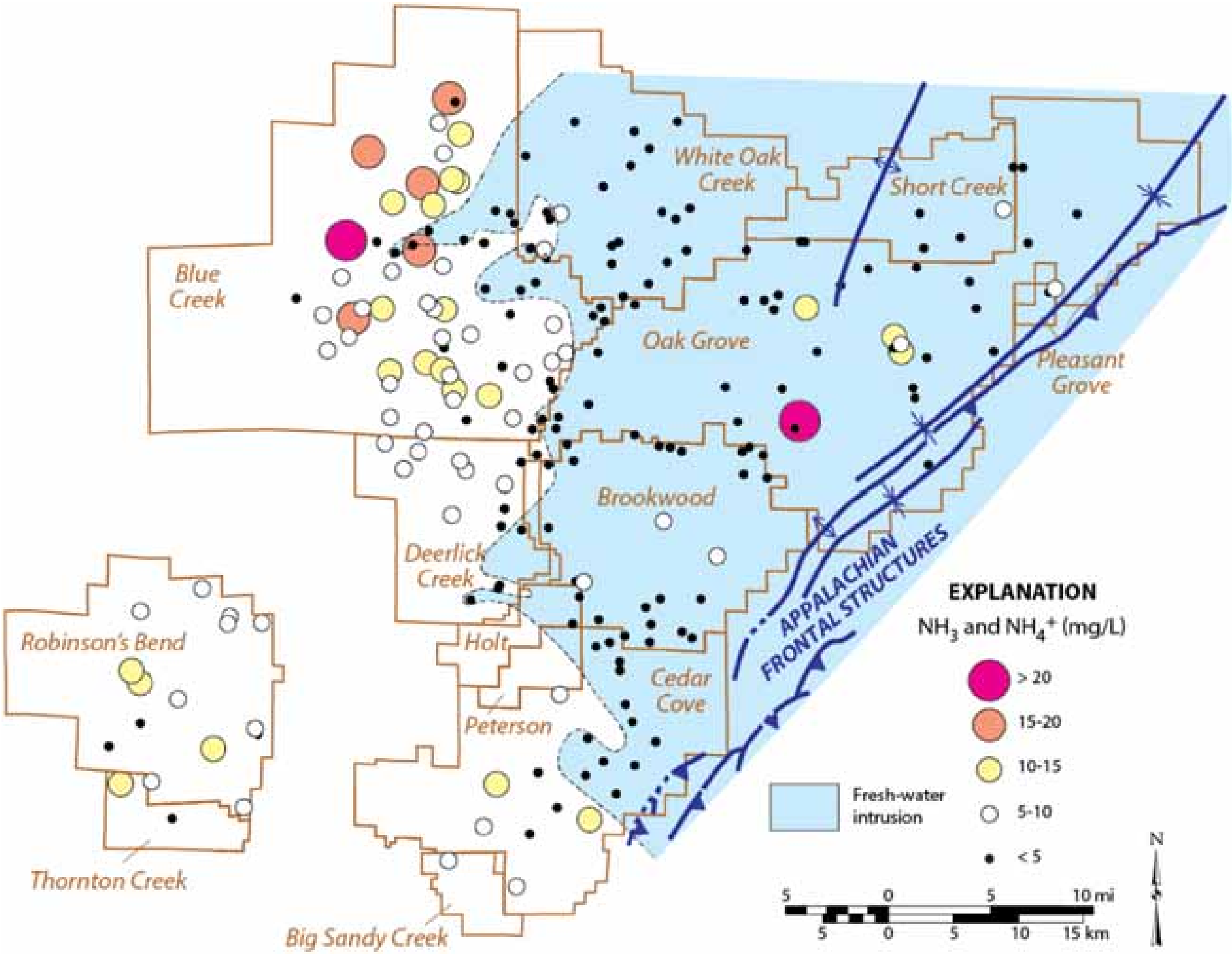


Figure 48.—Map of the concentration of ammonia compounds in produced water in the active Black Warrior CBM fields.

than 1 percent. Carbon dioxide concentrations are lower than 0.70 percent and average only 0.16 percent, which is unusually low for CBM reservoirs (Scott, 1993). Indeed, significant volumes of CO_2 are typically generated thermogenically and biogenically from humic source rocks like coal (Hunt, 1979; Scott and others, 1994, Bates and others, 2011). Note, however, that although little CO_2 is in the produced gas stream, a significant volume of CO_2 is dissolved in the formation water (table 3). Samples with CO_2 content < 0.10 percent are most common in Oak Grove and Brookwood fields, where coal is most thermally mature and is in the heart of the freshwater

Table 5. Summary of geochemical analyses of wellhead gas analyses from coalbed methane wells in the Black Warrior Basin. Analyses performed by Isotech and Weatherford Laboratories.

Variable	**N**	**Minimum**	**Maximum**	**Mean**	**Standard Deviation**
CO_2 (%)	100	0.023	0.692	0.161	0.104
N_2 (%)	100	0.000	5.892	0.584	0.796
CH_4 (%)	100	94.065	99.889	99.161	0.793
C_2H_6 (%)	100	0.000	0.863	0.082	0.117
C_3H_8 (%)	100	0.000	0.321	0.010	0.033
Iso-butane (%)	100	0.000	0.036	0.001	0.004
Butane (%)	100	0.000	0.049	0.001	0.005
Dryness index 100*(C_1/C_{1-5})	100	98.7	100.0	99.9	0.2
$\delta^{13}C_1$ (‰)	100	-60.37	-43.00	-51.43	3.91
δD_{C1} (‰)	100	-206.0	-185.7	-197.7	3.2

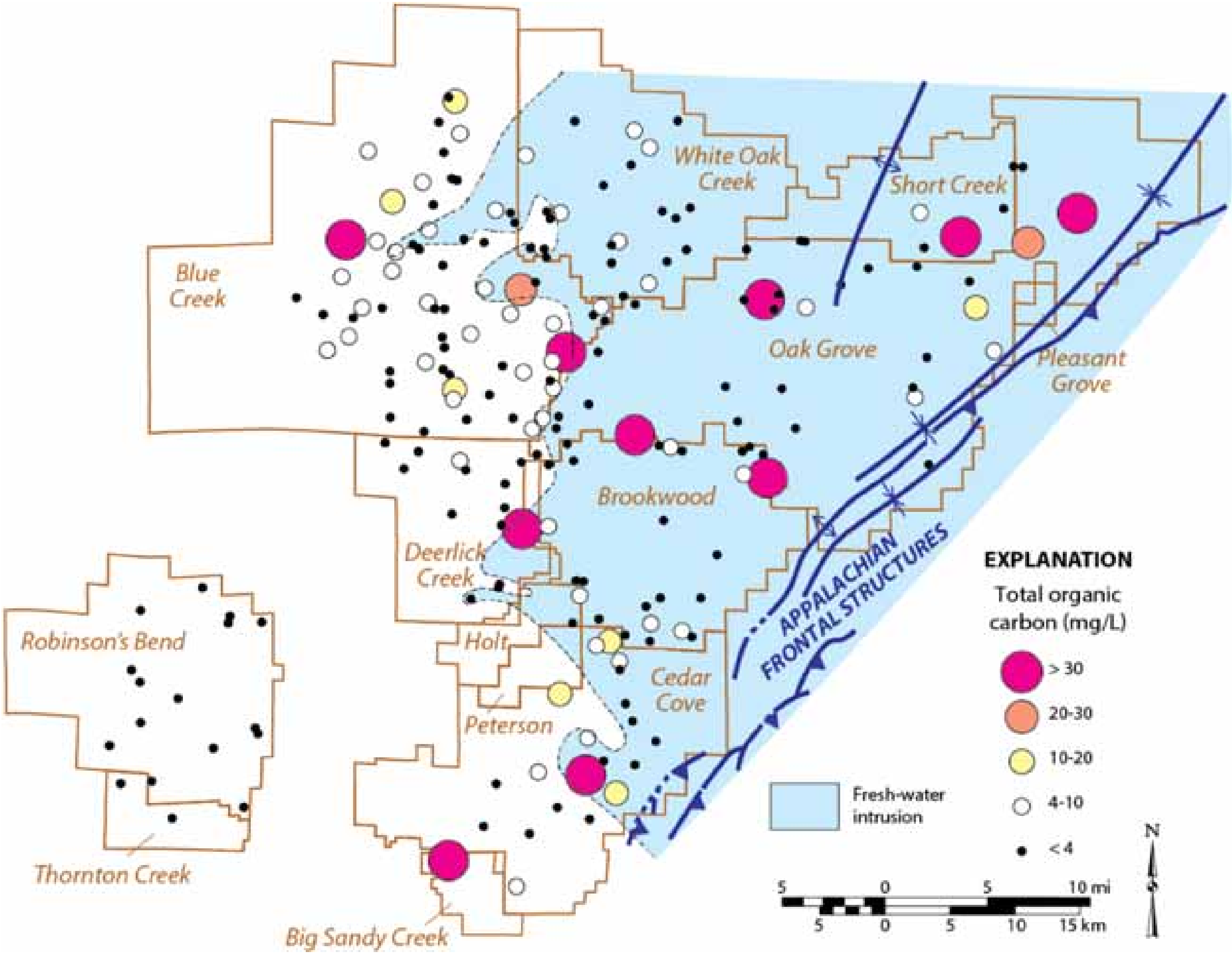


Figure 49.—Map of TOC content of produced water in the active Black Warrior CBM fields.

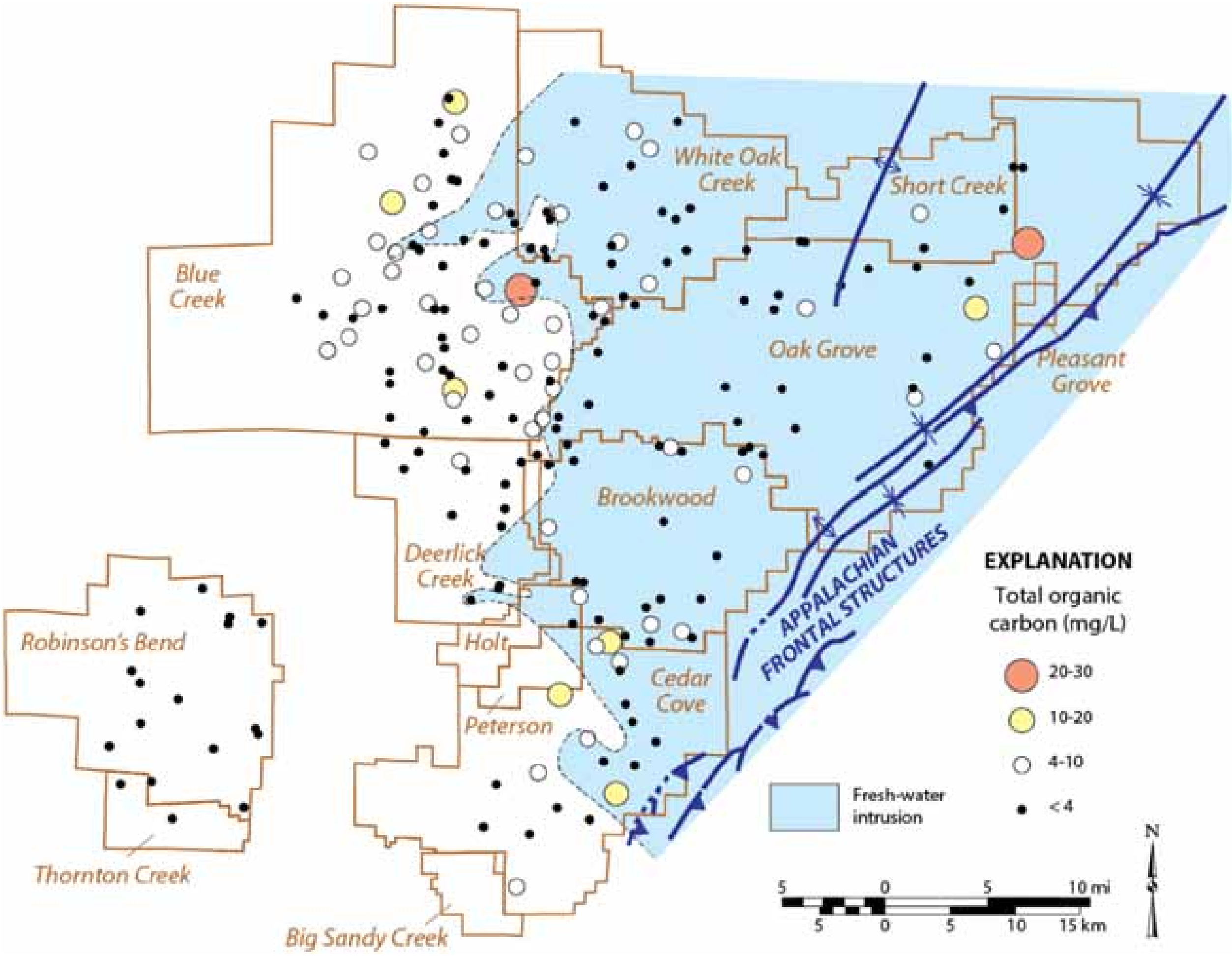


Figure 50.—Map of TOC content of produced water in the active Black Warrior CBM fields with anomalous outlier values removed.

intrusion (fig. 53). Concentrations higher than 0.20 percent are most common along a corridor extending from Blue Creek Field to Cedar Cove Field near the margin of the fresh-water intrusion.

Nitrogen is the most abundant nonhydrocarbon gas, with concentrations locally exceeding 5 percent (table 5). Mean N_2 concentration is only 0.58 percent. Reported N_2 concentrations from the 1980s and 1990s are substantially higher (> 5 percent) (Rice, 1993; Scott, 1993), and most of these samples came from the freshwater plumes. Nitrogen tends to be produced early in the life

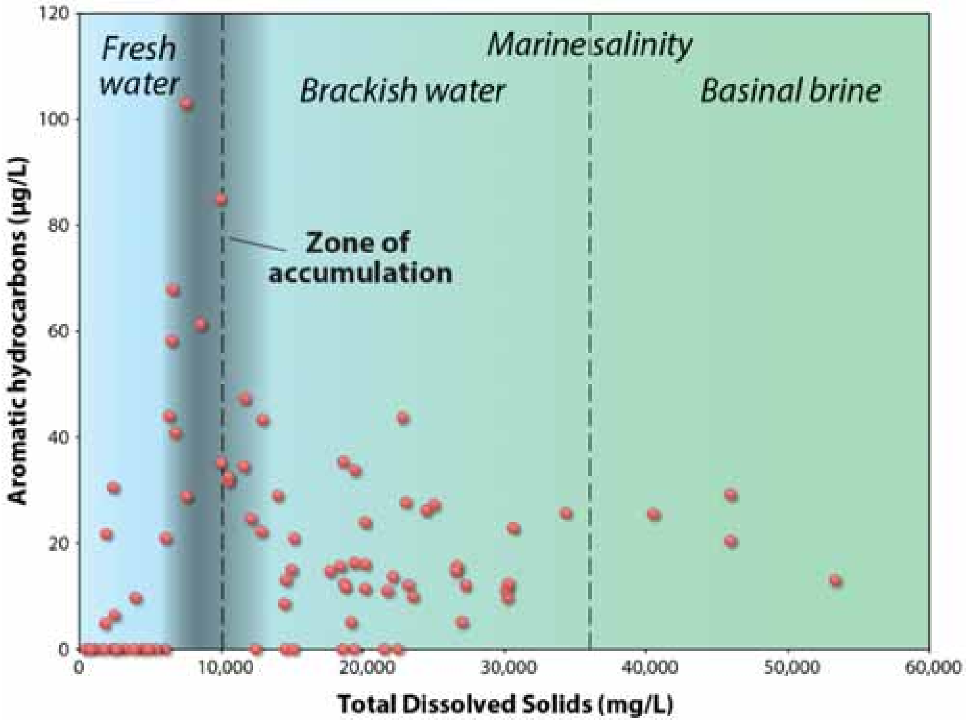


Figure 51.—Crossplot of the concentration of phenolic compounds and TDS content in produced water from the active Black Warrior CBM fields.

of CBM wells because it is a much weaker adsorbate than CO_2 and CH_4 (e.g., Hall and others, 1994). The map of N_2 shows no distinct relationship between N_2 content and the fresh-water intrusion or coal rank (fig. 54). Some of the N_2 may be derived from fixation of atmospheric gas in rain and stream water, as well as from soil gas in the recharge area. Other potential sources include thermal and microbial degradation of organic matter, mineral matter, and formation water, and this possibility is discussed in a later section.

Mean CH_4 content averages more than 99 percent, and the standard deviation is only 1 percent (table 5). The map of CH_4 content indicates that the purest gas is greatest where the TDS of the formation water is < 10,000 mg/L (fig. 55). The total volume of wet hydrocarbon gases (C_2-C_5) is less than 0.1 percent of total gas volume (table 5). Indeed, C_4 hydrocarbons (butane and iso-butane) were detected in only 15 samples, and C_5 hydrocarbons were not detected. The

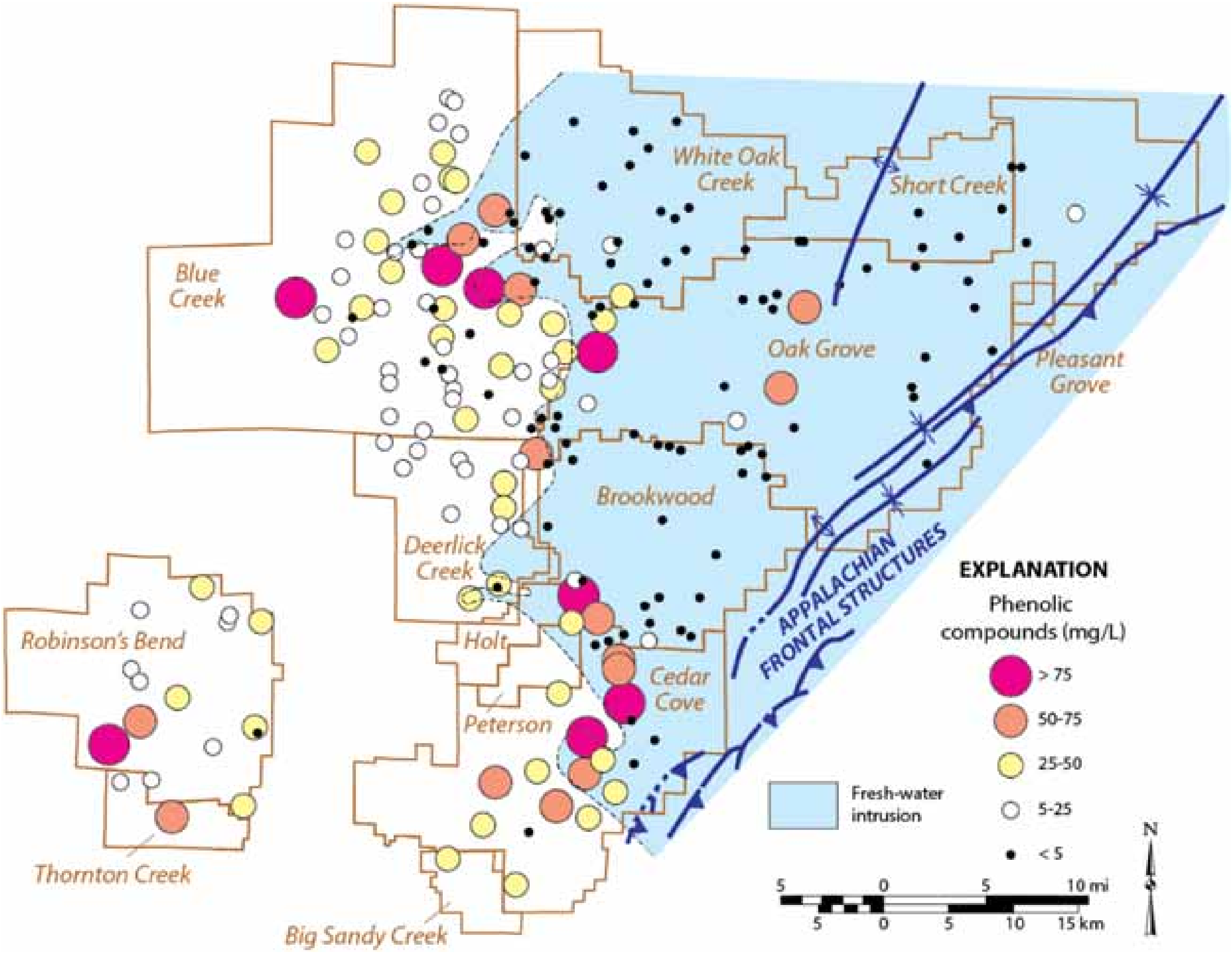


Figure 52.—Map of phenolic content of produced water in the active Black Warrior CBM fields.

produced gas is exceptionally dry, with a mean dryness index of 99.9 and a standard deviation of only 0.2. Mapping indicates that samples with C_2H_6 content > 0.10 percent are most common in the southwestern part of the study area (fig. 56). The consistent gas composition, low concentrations of nonhydrocarbon gases, and absence of H_2S facilitate gas production at pipeline quality. Thus, dehydration and compression constitute all the processing that is required to deliver Black Warrior CBM to market.

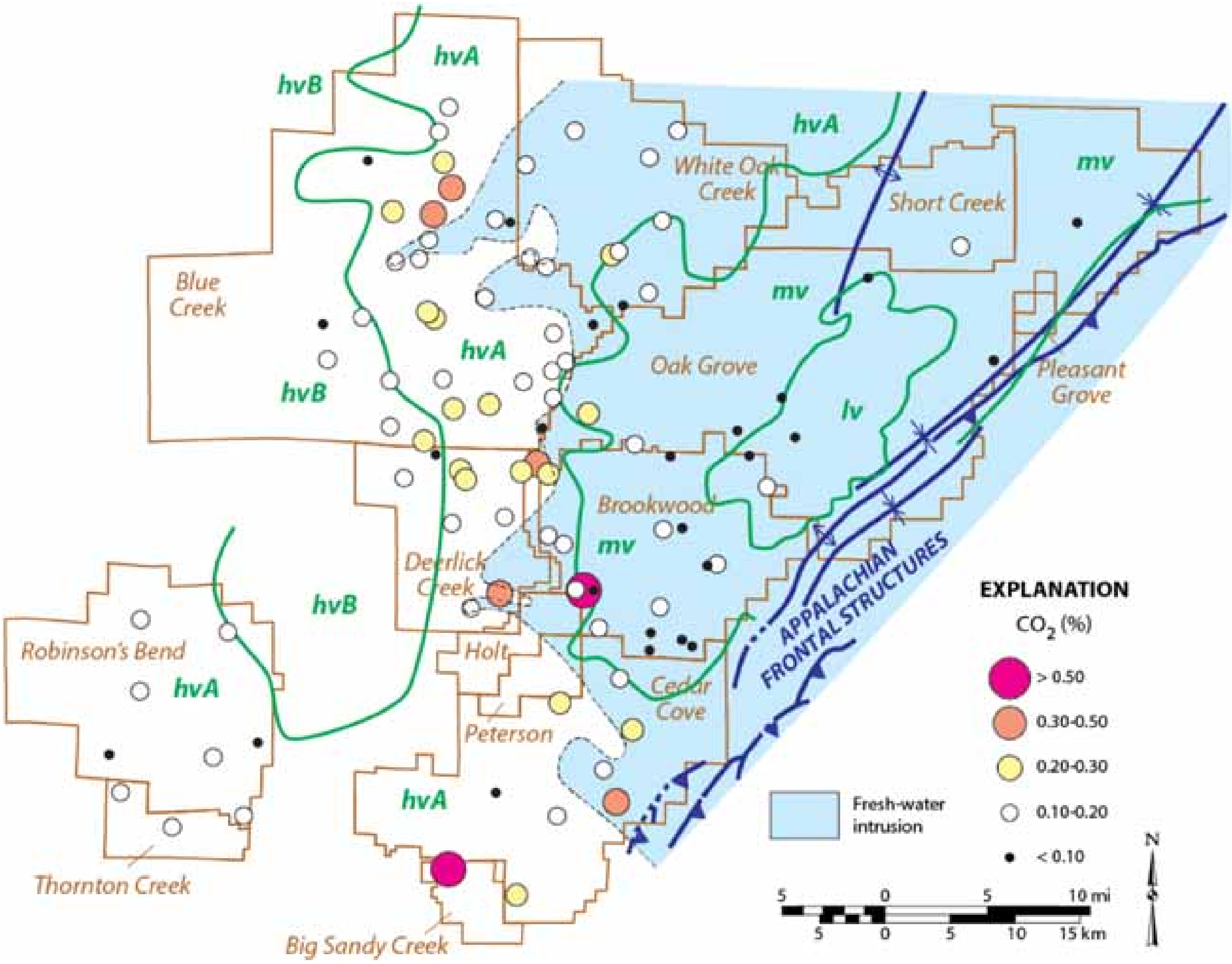


Figure 53.—Map of CO_2 content of produced gas in the active Black Warrior CBM fields. Green lines and text indicate coal rank.

Stable Isotopic Composition

Although bulk gas composition varies little across the study area, stable isotopic composition varies considerably and is of value for characterizing the origin of the gas. Values of $\delta^{13}C_1$ range from -60.37 to -43.00‰ and have a weak central tendency (table 5). By contrast, δD_{C1} values range narrowly from -185.7 to -206.0‰ and have a strong central tendency around a mean value of -197.8‰. Cross-plotting $\delta^{13}C_1$ and δD_{C1} values on the diagram of Whiticar (1996) indicates that the data cluster in the thermogenic and mixed thermogenic-biogenic generation fields (fig.

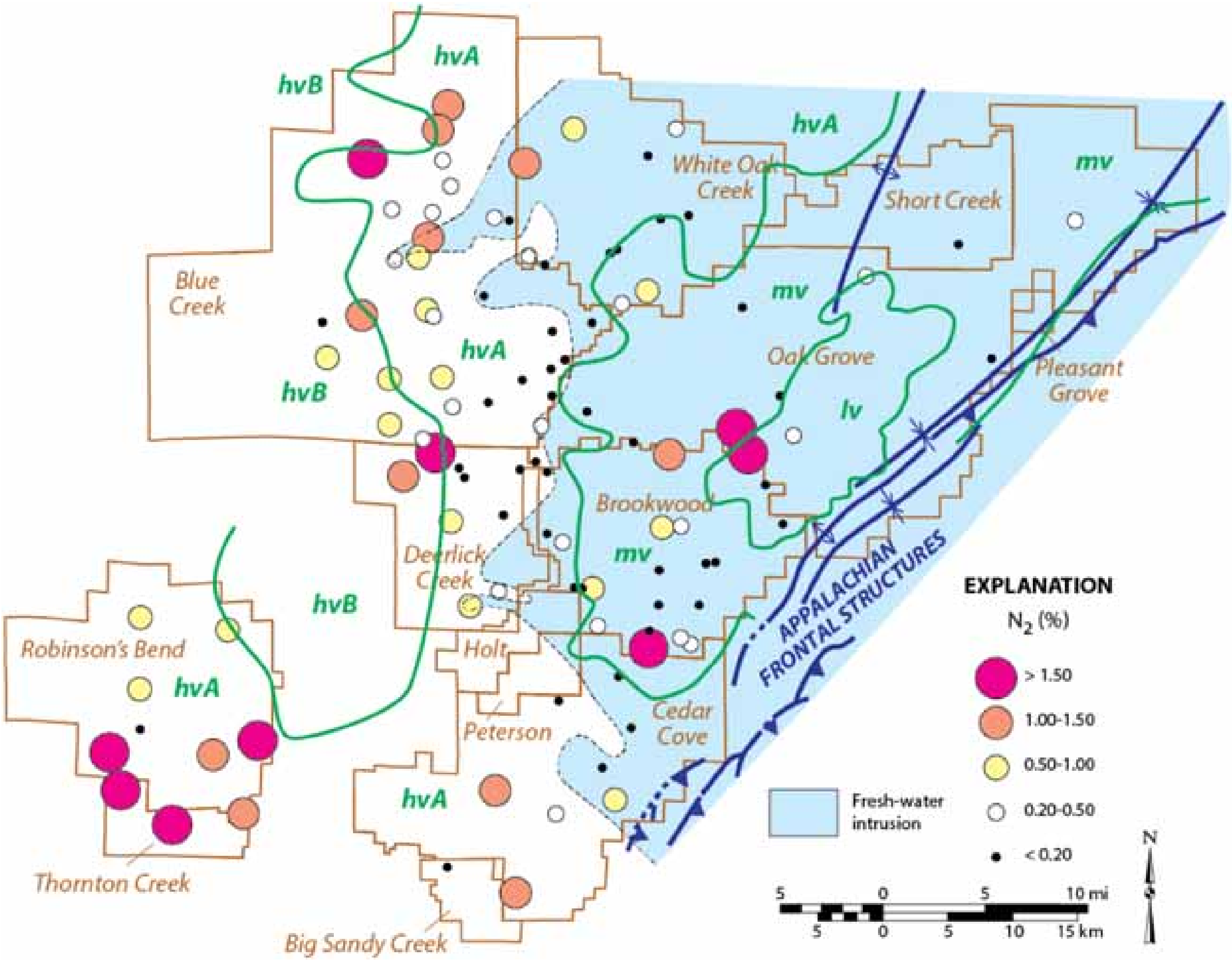


Figure 54.—Map of N_2 content of produced gas in the active Black Warrior CBM fields.

57). The samples that are most depleted in ^{13}C plot at the edge of the biogenic gas field. The δD_{C1} values suggest that microbial CO_2 reduction was the principal metabolic pathway for biogenesis, although this interpretation is made with caution because exchange of H between CH_4 and formation water can result in misleading δD values (Vinson and others, 2012).

Importantly, microbial gas generated by CO_2 reduction can have $\delta^{13}C_1$ values substantially greater than -55.0‰ depending on the source CO_2 (Whiticar, 1999; Martini and others, 2003, 2008; Flores, 2008), and so there is no precise cutoff value that distinguishes mixed gas from pure biogenic gas. As discussed in the section on burial history, basins like the Black Warrior,

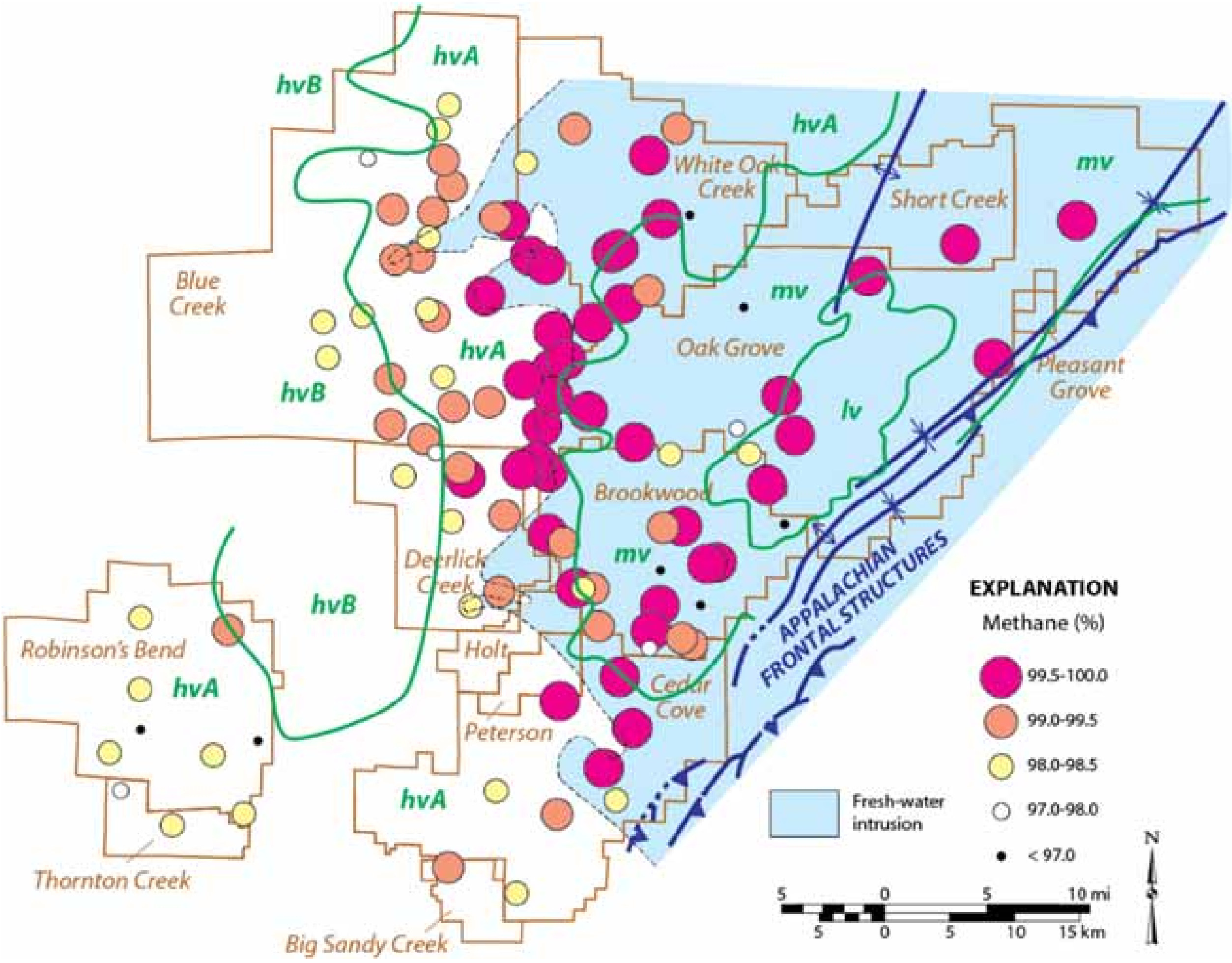


Figure 55.—Map of CH_4 content of produced gas in the active Black Warrior CBM fields.

which have been uplifted and cooled substantially, are predicted to be significantly undersaturated with thermogenic gas (Scott, 2002; Bustin and Bustin, 2008), and so a significant component of microbial gas helps explain the high gas saturation that has been observed in many Pottsville coal seams (Pashin, 2007, 2010b).

Microbial CO_2 reduction involves the conversion of CO_2 to CH_4 in the presence of H_2 (e.g., Whiticar and others, 1986). The basic reaction can be expressed as

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (1).$$

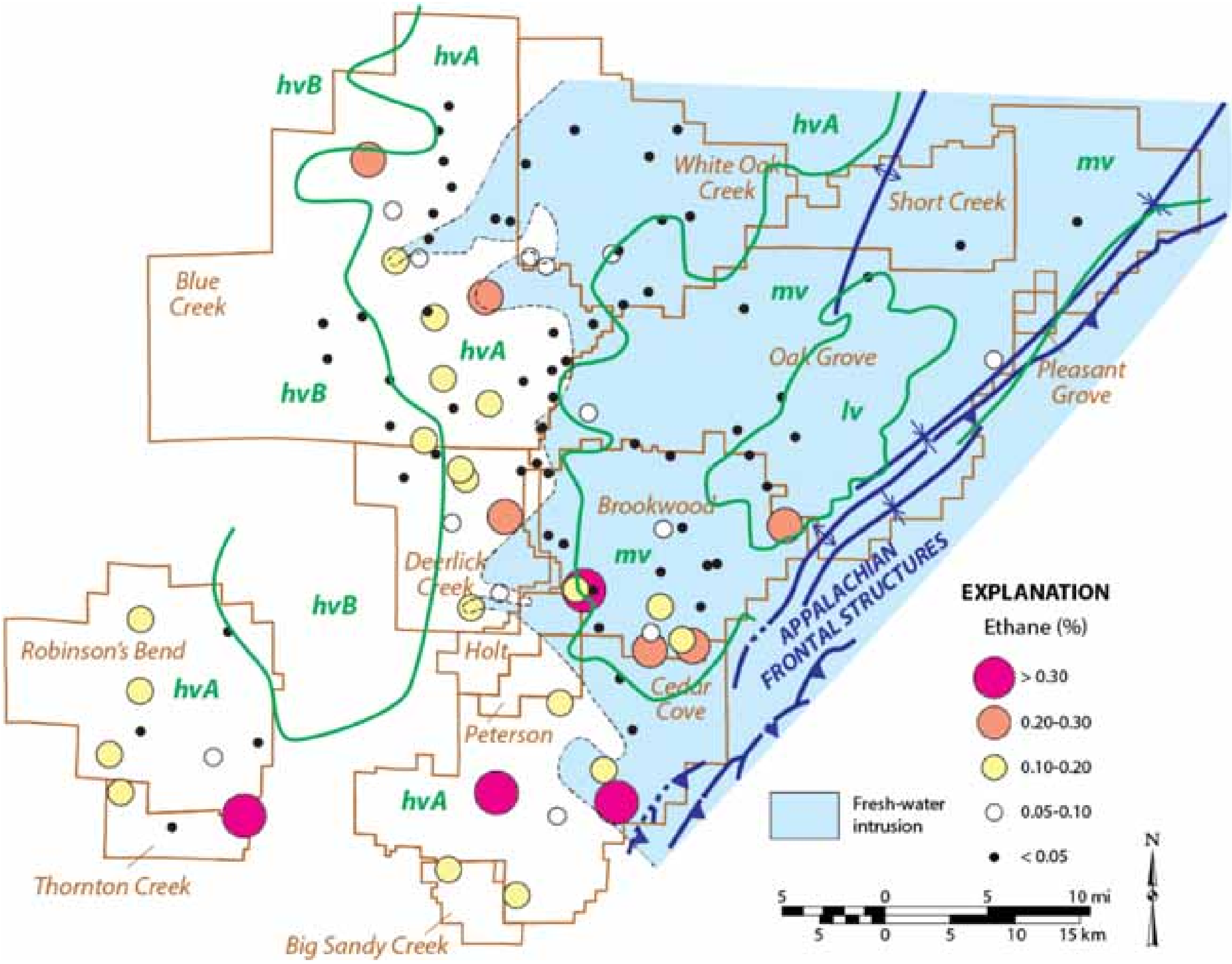


Figure 56.—Map of C_2H_6 content of produced gas in the active Black Warrior CBM fields.

Considering the exceptionally low percentage of CO_2 in the produced gas (table 5), CO_2 dissolved in formation water constitutes the main resource that is available to drive CO_2 reduction (table 3). Obvious sources of H_2 exist in the organic framework of the coal and the organic compounds in the formation fluids, including long-chain fatty acids and phenolic compounds, which have been degraded by microbes in biogenesis experiments (Jones and others, 2010).

Plotting $\delta^{13}C_1$ against vitrinite reflectance of the Mary Lee coal zone demonstrates a significant correlation between thermal maturity and isotopic composition (fig. 58). Comparison

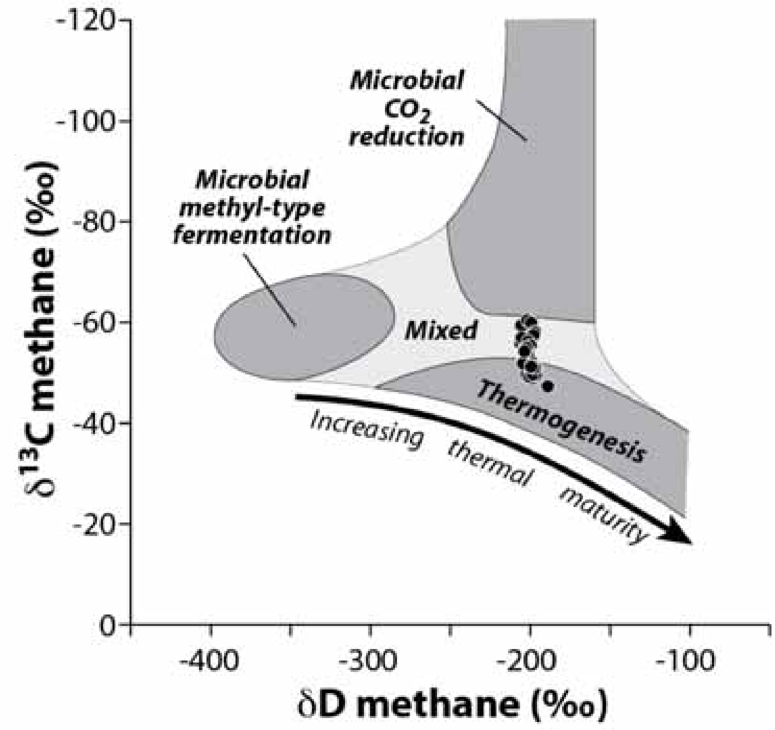


Figure 57.—Crossplot of $\delta^{13}C_1$ and δD isotopes in produced gas from Black Warrior CBM reservoirs. Results indicate mixing of thermogenic and late-stage biogenic gas with biogenesis occurring along a CO_2 reduction metabolic pathway.

of isotopic data with mapped rank patterns further supports covariance of $\delta^{13}C_1$ values and thermal maturity, although there is considerable local variability in ^{13}C enrichment levels (fig. 59). Commingling of gas from multiple coal seams, differences in the intensity of microbially driven isotopic fractionation, and local gas migration help explain these variations.

The lowest $\delta^{13}C_1$ values plot near the high volatile A-B bituminous rank transition, which corresponds to the edge of the thermogenic gas window for coal (Jüntgen and Karweil, 1966; Jüntgen and Klein, 1975) (fig. 59). Pashin (2007) noted that CH_4 produced from coal of medium and low volatile bituminous rank (R_o = 1.1-1.9; Taylor and others, 1998) in the Black Warrior Basin is more depleted in ^{13}C than that produced from coal of similar thermal maturity in other basins. The highest rank coal is in the freshwater plumes close to the recharge area, where

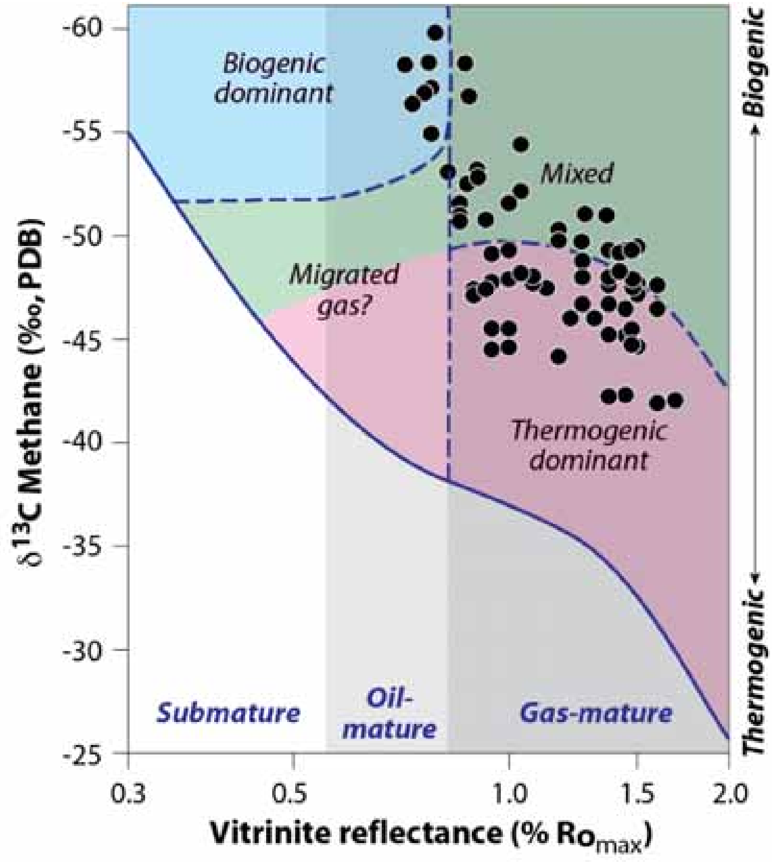


Figure 58.—Crossplot showing relationship of $\delta^{13}C_1$ values to the thermal maturity of coal in the Black Warrior CBM fields.

intense microbial activity would be predicted. In this type of setting, however, intense reduction of CO_2 may actually enrich CH_4 in ^{13}C, as has been observed in the San Juan and Powder River basins (Scott and others, 1994; Bates and others, 2011). Because of this, distinguishing the relative impact of thermogenesis and biogenesis in coal that has entered the gas window and contains freshwater is difficult without additional information on inorganic carbon in CO_2, formation water, or mineral cement, the latter of which is discussed in the petrology section of this report.

Nitrogen compounds, including NH_3, NH_4^+, NO_2^-, and NO_3^-, are important nutrients that are integral parts of the nitrogen cycle (e.g., Karl and Michaels, 2001; Galloway and others, 2004),

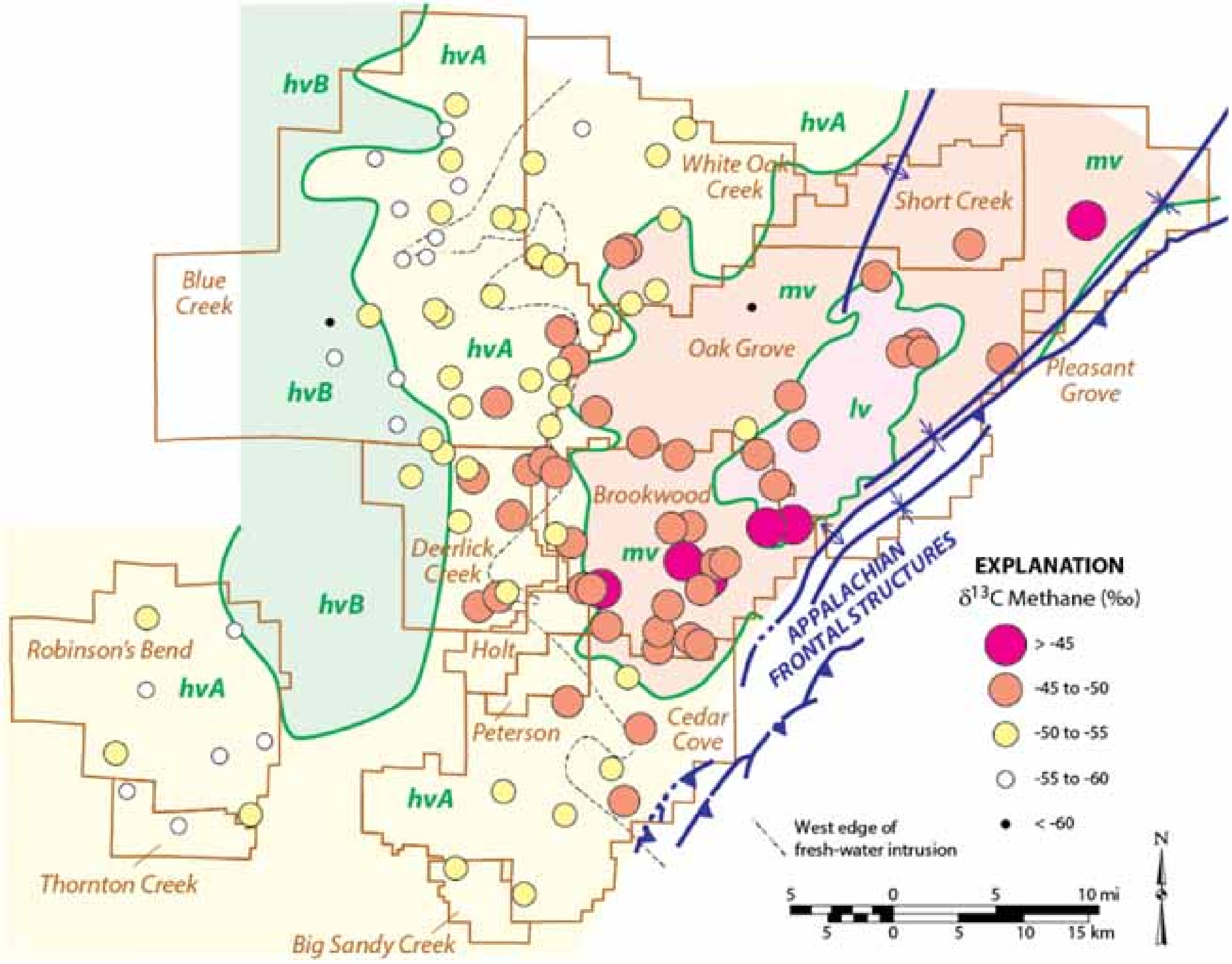


Figure 59.—Map showing relationship of $\delta^{13}C_1$ to coal rank in the Black Warrior CBM fields.

but relatively little is known about the role of these compounds in unconventional reservoirs (Pashin and others, in press). Indeed, the presence of these compounds in Pottsville Formation water raises questions about how these substances may influence subsurface gas composition. For example, deionization of ammonium, expressed as

$$2NH_4^+ \rightarrow 2NH_3 + H_2 \qquad (2),$$

could provide some of the H_2 for microbial CO_2 reduction while simultaneously explaining the NH_3 in the formation water. Low levels of NO_2^-, which is a fouling agent that inhibits biological colonization of subaqueous and subsurface environments, is another factor that probably helped sustain microbial communities. Biologically mediated anaerobic oxidation of NH_4^+, a.k.a. the anammox process (Van de Graaf and others, 1995; Thamdrup and Dalsgaard, 2002), may be a significant natural process in Black Warrior CBM reservoirs. The relevant anammox reaction is:

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \qquad (3).$$

Although this specific process has yet to be substantiated in the deep subsurface, the implications of this type of reaction for late-stage biogenic gas generation in Pottsville CBM reservoirs are twofold. First, this reaction consumes NO_2^-, thereby inhibiting fouling of the reservoir. Second, this and a host of other denitrification-type reactions could account for a significant portion of the N_2 in the coalbed gas.

Assessing the sources of N_2 in the produced gas is difficult because an unknown amount of the parent material may have been consumed. Material balance provides a rudimentary level of constraint and a sense of scale based on the solubility of N_2 in water and the concentration of the remaining nitrogen compounds in the formation water. At 30°C, the solubility of N_2 in water is ~50 mg/L, which equates to 6,850 $sm^3/10^6$ bbl. The remaining nitrogen compounds, by comparison, have equivalent N_2 concentrations on the order of 7 mg/L, which equates to a generative potential of 1,055 $sm^3/10^6$ bbl.

A typical Black Warrior CBM well has cumulative production of about 0.1×10^6 bbl of water and 8.5×10^6 sm^3 of gas (Pashin, 2010a). Of this, N_2 accounts for about 0.7 percent, or 59×10^3

sm^3 of the produced gas. The intrusion of freshwater ~24 km into the basin suggests that > 30 pore volumes of water have swept through a given 16 ha (40-acre) drilling unit over geologic time. If 50 percent of a pore volume has been recovered, the produced water constitutes 1.67 percent of the water that has passed through the reservoir over geologic time. Thus, the N_2 derived from meteoric sources, such as the atmosphere and soil gas, would account for 69 percent of the N_2 in the natural gas, and denitrification of dissolved compounds based on current concentrations would account for 11 percent. By this logic, thermal and microbial degradation of other sources, such as coal and mineral matter, would account for the remaining 20 percent. Of course, geochemical and hydrodynamic variables change greatly across the basin. Accordingly, N_2 derived from meteoric sources is expected to be most abundant near the recharge zone, whereas the proportion of N_2 derived from organic and inorganic compounds is expected to increase toward the interior of the basin. In sum, nitrogen appears to be an important component of the CBM system in the Black Warrior Basin, and the role of nitrogen in unconventional gas systems is a worthwhile topic for further research.

PETROLOGY

The strata from which fluids are produced can contain important clues to the origin of formation water and natural gas, and so petrologic analysis has value for understanding the evolution of sedimentary basins and predicting reservoir quality and the composition of formation water and hydrocarbons. In this section we review the petrology of siliciclastic strata in the upper Pottsville Formation. Following a brief discussion of framework composition, the main emphasis of this section is on epigenetic mineralization in natural fractures, which has proven useful for characterizing paleotemperature and methanogenic processes in CBM reservoirs (Pitman and others, 2003; Pashin and others, in press).

Framework Composition

Sandstone in the upper Pottsville Formation is dominated by litharenite that is texturally and compositionally immature (Mack and others, 1983; Raymond, 1990; Moore, 2012). The sandstone is very fine to coarse-grained and contains quartz, feldspar, and a great variety of rock fragments (fig. 60). Grains are angular to well rounded, and sorting is typically poor. According to the classification of Folk (1974), the sandstone can be classified primarily as arkosic litharenite and includes litharenite, lithic arkose, and sublitharenite (fig. 61).

Quartz constitutes 20 to 50 percent of the sandstone, whereas feldspar content is generally between 5 and 30 percent (fig. 61A). Rock fragments constitute between 10 and 50 percent of the sandstone and include a great variety of sedimentary, igneous, metamorphic, and volcanic lithoclasts (figs. 60-62). Sedimentary rock fragments are dominated by chert, sandstone, shale, and siderite. Low-grade metamorphic rock fragments, mainly phyllite, constitute the bulk of the lithic fraction; schist also is common, as is polycrystalline quartz. Igneous and volcanic rocks include granite, rhyolite, and basalt. Plotting sandstone composition on the classic provenance diagram of Dickinson and Suczek (1979) indicates derivation from recycled orogenic sources (fig. 61B), and examination of the lithic fraction indicates a dominant contribution from metamorphic terranes. Detrital geochronology indicates that most muscovite grains are no more than a few million years older than the host rock, indicating rapid uplift and cooling of the metamorphic core of the ancestral Appalachians, as well as rapid delivery of sediment from the orogen into the foreland basin (Moore, 2012).

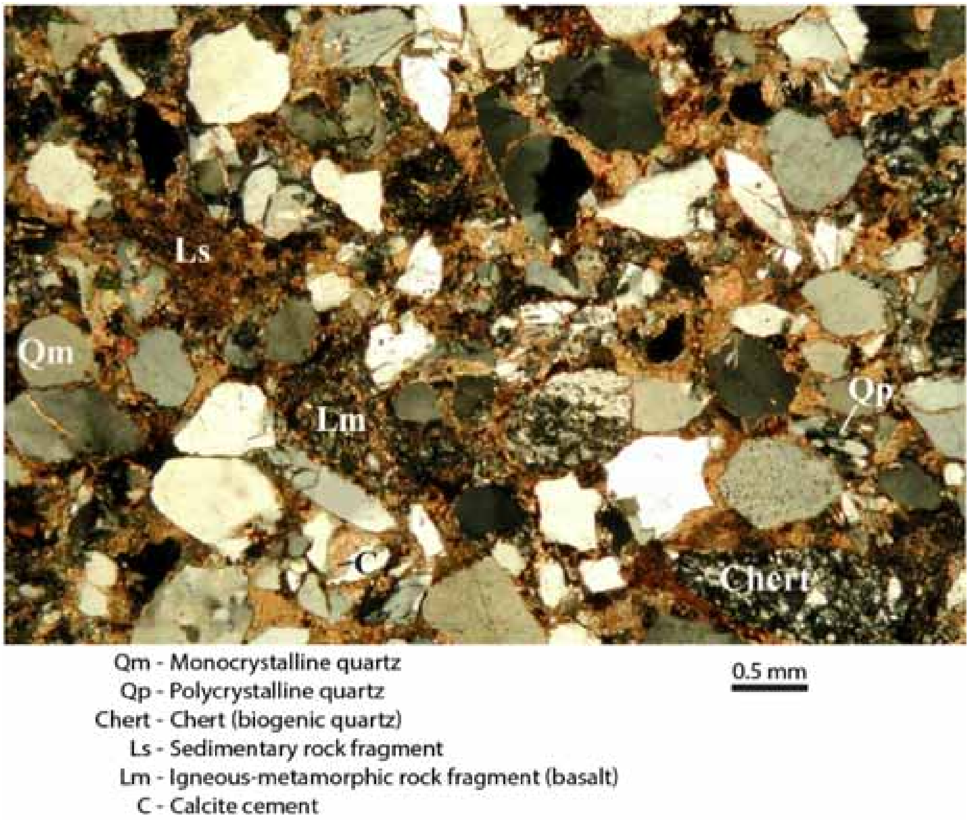


Figure 60.—Photomicrograph of litharenite in the upper Pottsville Formation from the Hendrix core in Moundville Field (modified from Moore, 2012).

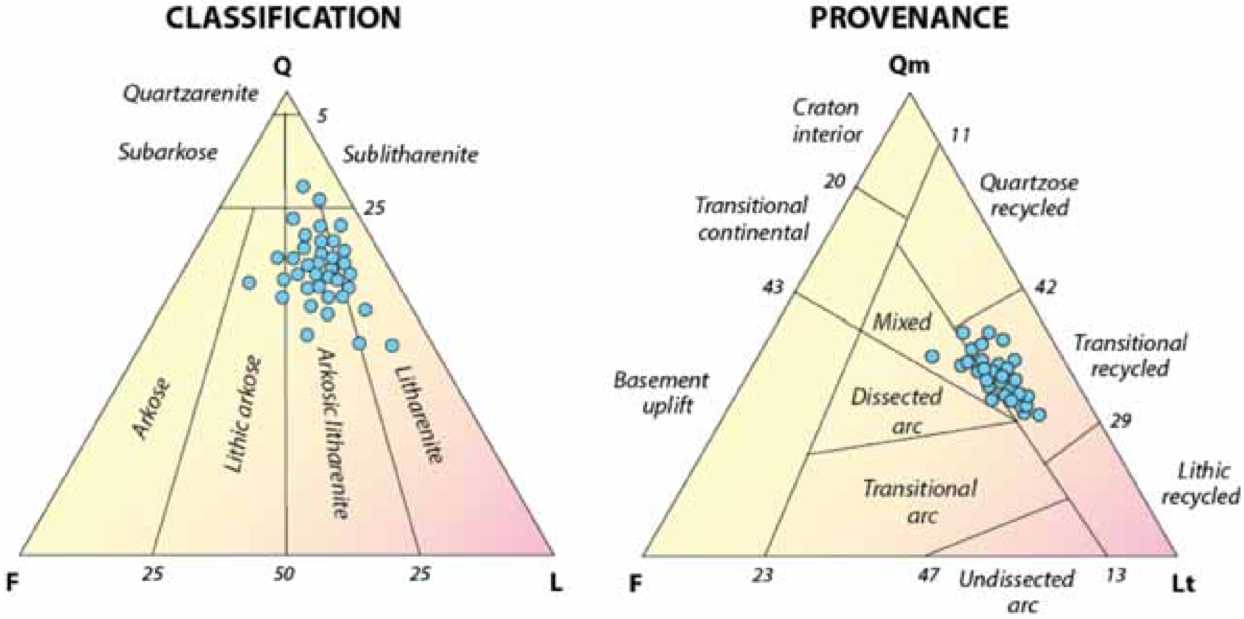


Figure 61.—Ternary diagrams showing (A) framework composition and (B) provenance of lithic sandstone in the Pottsville coal interval.

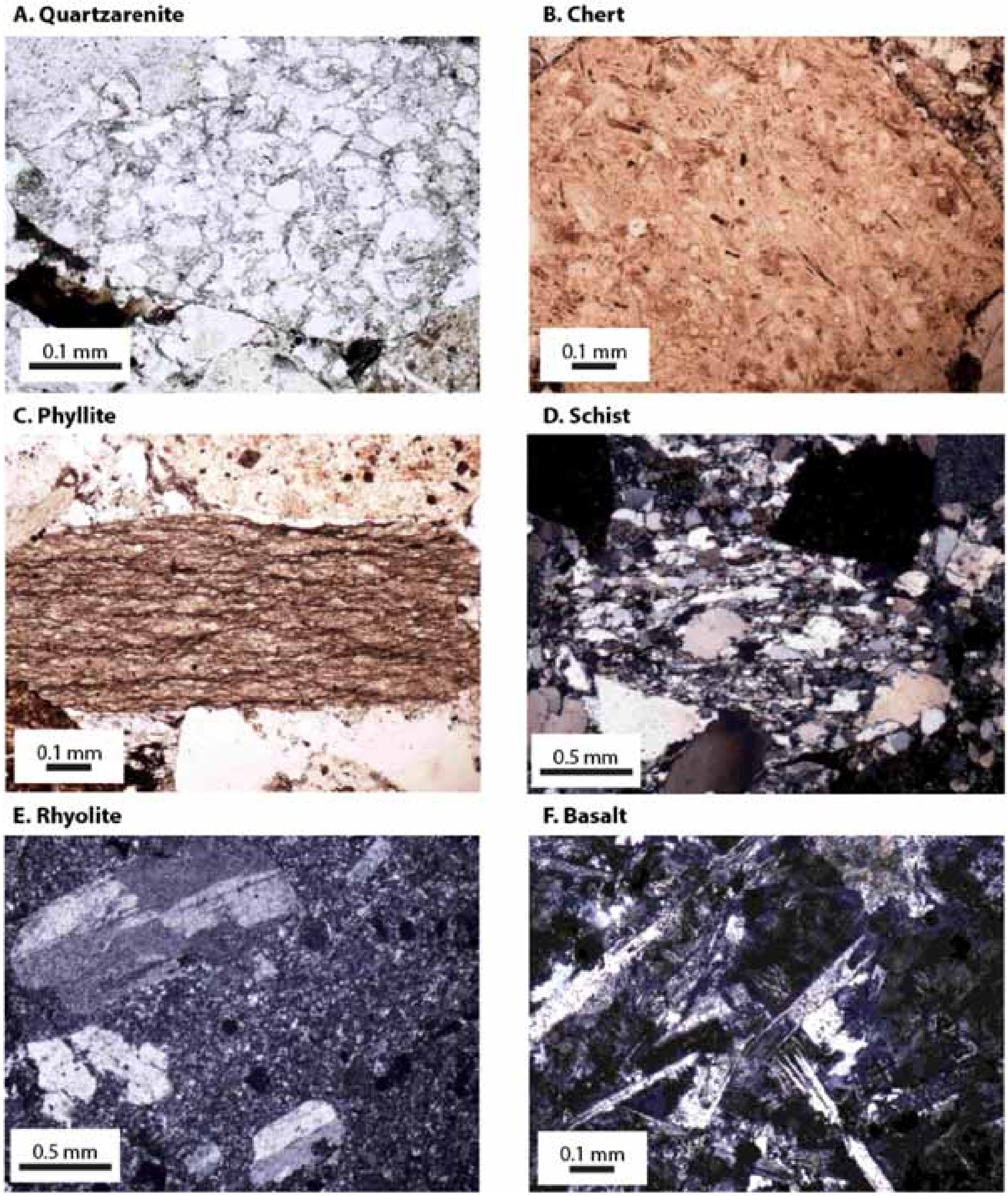


Figure 62.—Photomicrographs of rock fragments in litharenite of the Pottsville Coal Interval, Hendrix core, Moundville Field (modified from Moore, 2012). (A) Quartzarenite clast composed primarily of monocrystalline quartz and chert. (B) Chert containing spicules and filamentous algal structures. (C) Metamorphic rock fragment (phyllite) showing well-developed foliation. (D) Schist fragment displaying foliated quartz and mica with equant quartz inclusions. (E) Rhyolite containing twinned feldspar phenocrysts. (F) Basalt clast containing laths of amphibole.

Pottsville shale samples contain 19 to 69 percent quartz and 9 to 14 percent feldspar (table 6). Carbonate minerals make up no more than 4 percent of the shale. Total clay content is 21 to 59 percent. Illite and mica form the bulk of the clay fraction, and chlorite content is between 9 and 18 percent. Expandable clay constitutes 0 to 2 percent of total clay, and illite-smectite expandability is 25 to 35 percent. TOC is between 0.36 and 0.74 percent, and pyrite constitutes less than 1 percent of the rock. Examination of the shale under SEM shows that the internal fabric is complex. Some samples contain highly layered illite booklets that are folded around quartz grains (fig. 63). Others contain weakly aligned to edgewise illite plates that provide evidence for significant microporosity in the shale (fig. 64). Pyrite forms are diverse and include framboids, pyritohedra, and cubes (fig. 65). Organic matter is widely dispersed in the shale and is in places overgrown by pyrite (fig. 66).

The shale samples exhibit a range of porosity, permeability, and fluid saturation (table 7). Porosity ranges from 1.0 to 4.1 percent. Water saturation is extremely variable, ranging from 1 to 63 percent. Gas saturation ranges from 15 to 98 percent and is inversely correlated to water saturation ($r = -1.00$), indicating that the native fluid system is effectively binary. Some oil, however, is present in the system, and saturations range from 4 to 9 percent. Permeability of the shale parallel to bedding is extremely low, ranging from 0.037 to 0.072 microdarcies.

The compositional immaturity and unstable mineralogy of upper Pottsville litharenite suggests that these strata would be highly reactive with formation fluids. However, the sandstone has negligible porosity. Examination of thin sections of sandstone indicates that compaction of soft sedimentary and metamorphic rock fragments occluded nearly all porosity early in the regional burial history (fig. 60). Some intergranular calcite cement is present in the cores, suggesting that early cementation filled the remainder of the pore space prior to deep burial. The

Table 6. Summary of mineralogy of shale units in the Gorgas #1 borehole, Walker County, Alabama (modified from Clark and others, 2013).

Depth (ft)	Formation	Quartz	K-Feldspar	Plagioclase feldspar	Calcite	Siderite	Ankerite, Fe Dolomite	Dolomite	Pyrite	Fluorapatite	Barite	Magnetite	TOTAL NON-CLAY	Smectite	Illite/Smectite	Illite + Mica	Kaolinite	Chlorite	TOTAL CLAY	Total expandable clay (% of clay fraction)	% Illite/Smectite expandability
1221.0	Pottsville	48	3	10	1	2	0	0	0	1	1	0	**66**	0	4	14	5	12	**35**	1	35
1230.5	Pottsville	55	2	10	0	1	0	0	0	0	2	0	**69**	0	3	13	4	12	**31**	1	35
1241.5	Pottsville	44	3	9	0	2	0	1	0	0	0	1	**60**	0	4	18	7	12	**40**	1	30
1251.0	Pottsville	46	6	8	1	2	0	0	0	0	1	0	**63**	0	5	15	4	14	**37**	1	25
1261.0	Pottsville	34	4	6	4	2	0	0	0	0	2	0	**52**	0	2	27	6	14	**48**	1	35
1264.0	Pottsville	19	9	5	2	3	0	1	1	0	1	0	**41**	0	8	25	9	18	**59**	2	30
1271.0	Pottsville	63	2	7	2	1	3	0	1	1	0	0	**79**	0	1	7	3	10	**21**	0	25
1280.0	Pottsville	50	3	6	1	1	2	0	1	0	2	0	**64**	0	4	17	6	9	**36**	1	35

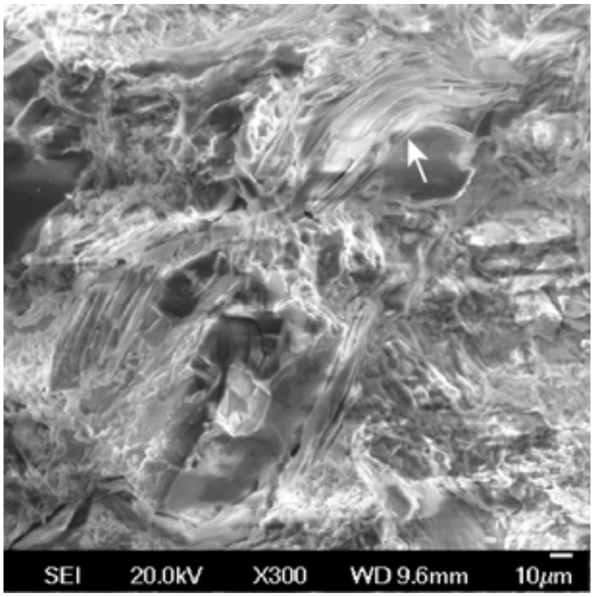


Figure 63.—SEM photomicrograph showing platy illite particles that have been compacted around quartz (arrow).

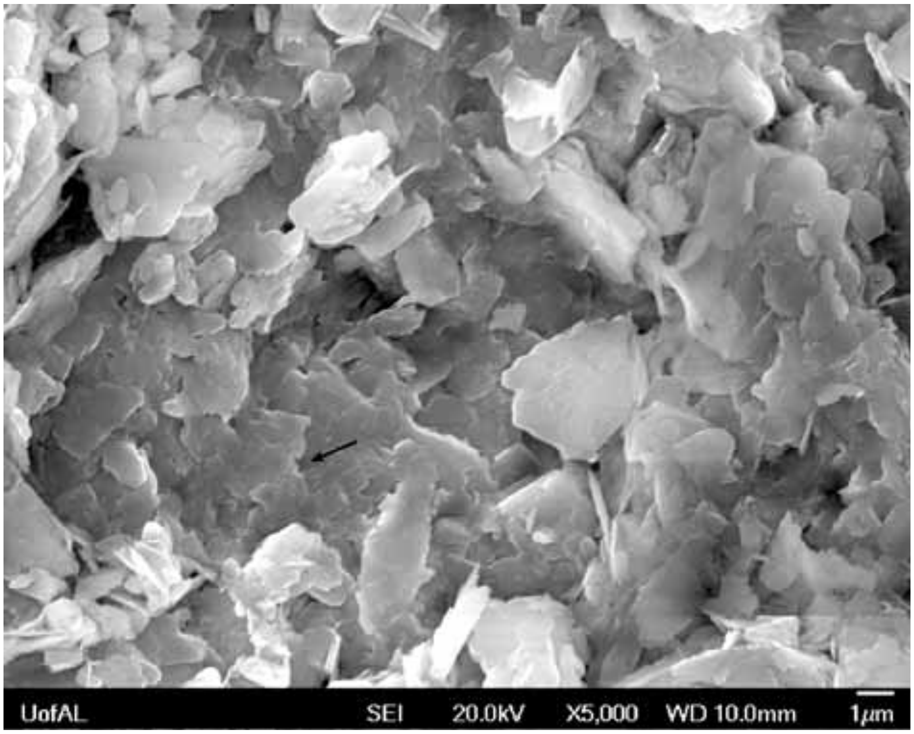


Figure 64.—SEM photomicrograph showing poorly oriented illite flakes in Pottsville shale.

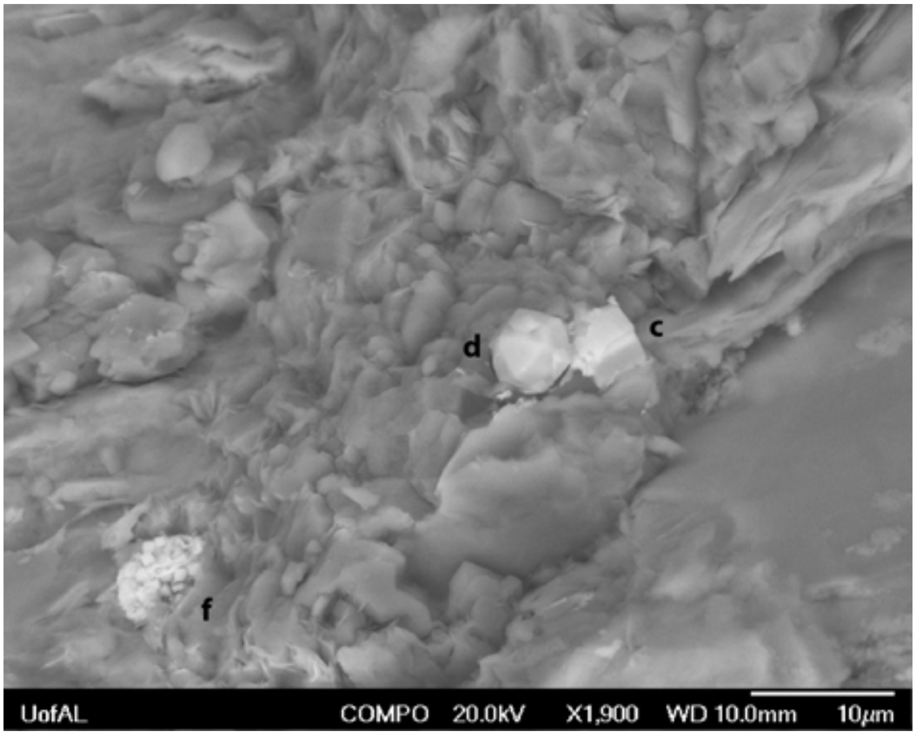


Figure 65.—SEM photomicrograph of disseminated pyrite in Pottsville shale. Pyrite forms include framboids (f), pyritohedra (d), and cubes (c).

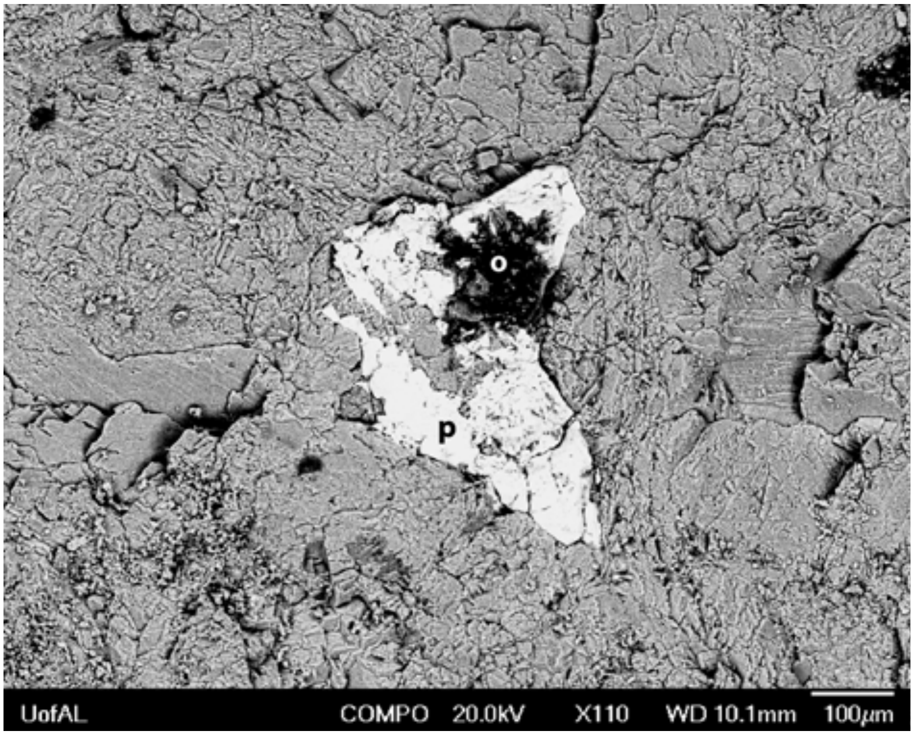


Figure 66.—Backscattered electron image showing pyrite crystals (p) with inclusion of organic matter (o) in clay-rich groundmass (gray).

Table 7. Results of core analysis in Pottsville shale, Gorgas #1 core, Walker County (modified from Clark and others, 2013).

Depth (ft)	Formation	Effective Porosity (%)	Water Saturation (%)	Gas Saturation (%)	Oil Saturation (%)	Pressure-Decay Permeability (μD)
1221.0	Pottsville	2.08	4.27	91.46	4.27	0.037
1230.5	Pottsville	2.00	3.94	91.64	4.43	0.042
1241.5	Pottsville	0.96	9.26	81.49	9.26	0.055
1251.0	Pottsville	1.87	4.74	90.52	4.74	0.062
1261.0	Pottsville	1.49	23.13	70.93	5.95	0.072
1264.0	Pottsville	2.09	63.03	32.73	4.23	0.059
1271.0	Pottsville	4.08	1.17	90.63	8.20	0.053
1280.0	Pottsville	1.70	10.23	84.66	5.11	0.056

mineralogy of shale is chemically more stable than that of sandstone, although this is partly the product illitization during burial and heating. Permeability is negligible in sandstone and shale. Hence, natural fractures formed the only viable conduits for basinal fluid during and after deep burial, and the fluid history of the basin is recorded principally by the epigenetic minerals that fill the fractures.

Epigenetic Cement

Epigenetic cement was observed in 30 percent of the natural fractures studied in numerous long cores of the upper Pottsville Formation in Brookwood and Oak Grove Fields. Calcite is the dominant vein-filling cement in Pottsville joint systems (e.g., Pashin and others, 1999; Pitman and others, 2003) and was identified in 98 percent of the mineralized fractures. Pyrite, clay (kaolinite), and quartz are accessory vein-filling minerals. Cement covers more than 80 percent of fracture surfaces in most mineralized segments of fractures, indicating that mineralization can limit flow through fractures. However, about 40 percent of the mineralized fractures have cement coverage between 1 and 80 percent, indicating that significant porosity exists within many mineralized joint segments. Based on the observations from core, it appears vein fill has a patchy distribution in Pottsville fracture networks. Hence, provided that aperture exists in nonmineralized fracture segments, most fractures have capability to support flow.

Most calcite fracture fills in the Pottsville are simple (fig. 67A) and have been interpreted as the product of a single post-kinematic mineralization event that preserves fracture aperture (Pitman and others, 2003; Pashin and others, 2004). Indeed, the multiple crack-seal textures and fracture-filling breccia that are characteristic of polyphase fracturing and mineralization were observed only in a small percentage of the fault-related shear fractures (fig. 67B).

Stable isotopic analysis of calcite veins in the Pottsville Formation has proven useful for characterizing the evolution of formation fluids and the physical and biotic processes that occurred therein (Pitman and others, 2003; Pashin and others, in press). The veins occur in natural fractures, specifically cleats in coal and joints in shale and sandstone. Carbon isotopic ratios ($\delta^{13}C$) in calcite from coal-bearing strata and organic-rich shale provide information on pore fluid chemistry, specifically the dissolved inorganic carbon in formation water at the time of mineralization, as well as fractionation processes associated with late-stage methanogenesis (Gould and Smith, 1979; Budai and others, 2002; Pitman and others, 2003). Oxygen isotopic ratios ($\delta^{18}O$), by comparison, can be used as paleothermometers, thus providing insight on when diagenesis occurred during the regional burial and unroofing history (Friedman and O’Neil, 1977; Pitman and others, 2003).

Calcite in the cores tends to be enriched in ^{13}C, with $\delta^{13}C$ ratios ranging from about -5 to +25 per mil (‰) (fig. 68). Pitman and others (2003) recognized that calcite is most enriched in ^{13}C adjacent to the recharge area along the southeastern basin margin (fig. 69) and that veins in coal tend to be more enriched than those in shale and sandstone. They interpreted enrichment as the

Figure 67.—Vein fills in cores from the the Black Warrior CBM fields. (A) Simple calcite vein (white) in litharenite with pyrite crystals (dark) lining wall and keel of vein. (B) Complex calcite vein with pyrite nodules in shaly fault breccia.

product of a biotically mediated fractionation process that favored enrichment of the formation fluid and calcite cement in ^{13}C during methanogenesis. A similar process appears to have occurred in the Atlantic Rim region of the greater Green River Basin, where formation water has been enriched in ^{13}C in concert with microbial CO_2 reduction in coal (McLaughlin and others, 2010). Thus, enrichment of the calcite in the freshwater plumes is consistent with the augmentation of thermogenic gas with late-stage microbial gas. The low NO_3^- values coupled

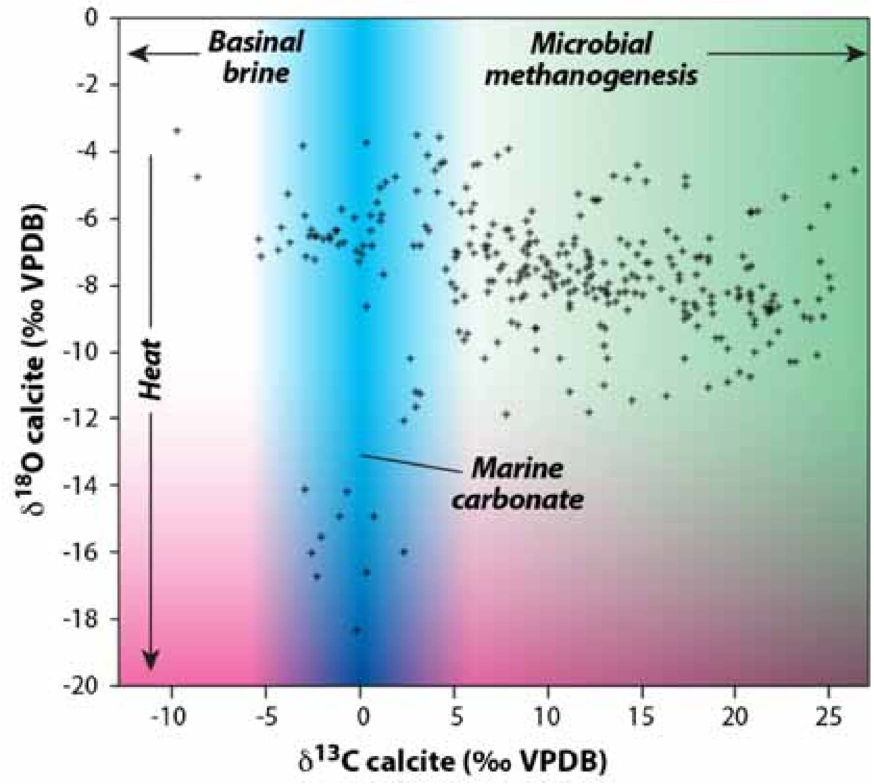


Figure 68.—Crossplot of δ^{13}C and δ^{18}O in calcite veins from the Pottsville Coal Interval.

with elevated HCO_3^- in the freshwater plumes (figs. 46, 48), moreover, may indicate nutrient depletion by intense microbial activity.

The bulk of the δ^{18}O data plot between -12 and -4‰, and no obvious correlation with δ^{13}C ratios is apparent (fig. 68). A secondary cluster of data points plots with δ^{18}O values of -14 to -19‰, and all of these points have δ^{13}C ratios characteristic of normal marine carbonate. Plotting δ^{18}O values against depth reveals some basic relationships (fig. 70). The calcite with δ^{18}O ratios < -14‰ show no relationship to modern burial depth. These calcite samples arguably formed in higher temperatures than the other calcite. One possibility is that it precipitated early in the regional unroofing history, perhaps before the reservoir strata reached the biogenic floor of the basin, which is typically where temperatures approach 80-100°C (Carothers and Kharaka, 1978;

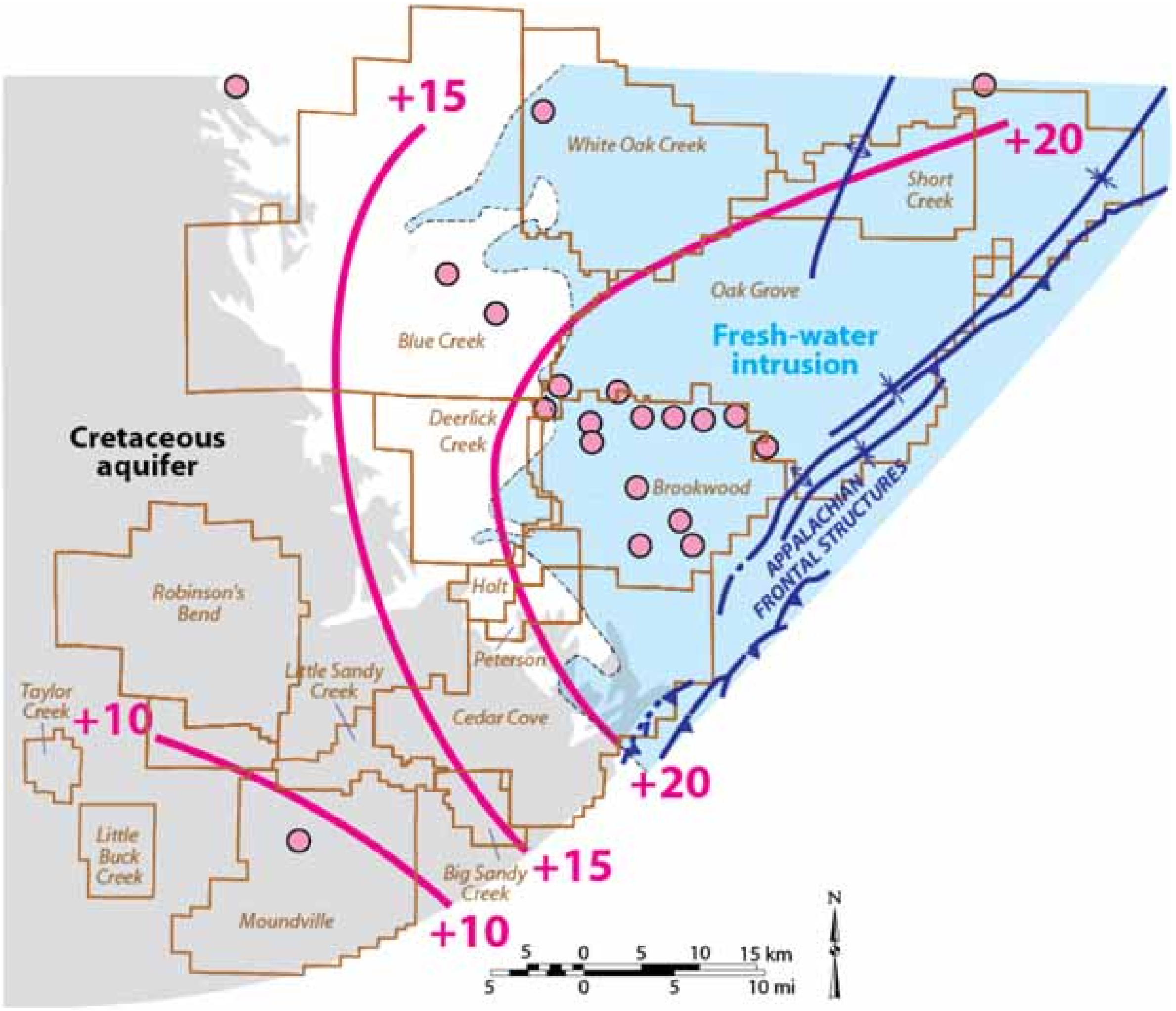


Figure 69.—Map of average δ^{13}C values in calcite veins showing increasing enrichment toward the meteoric recharge area along the Appalachian frontal structures.

Shurr and Ridgley, 2002). The majority of the data have δ^{18}O ratios > -9‰, and maximum values appear to be depth- and hence temperature-limited.

The fractionation equations of Friedman and O'Neil (1977) and Hays and Grossman (1991) suggest that calcite with δ^{18}O ratios of -9 to -4‰ precipitated at temperatures of 20 to 50°C, which is compatible with modern reservoir temperatures in the Pottsville Formation (Pashin and McIntyre, 2003; Pitman and others, 2003). Therefore, major calcite cementation in association

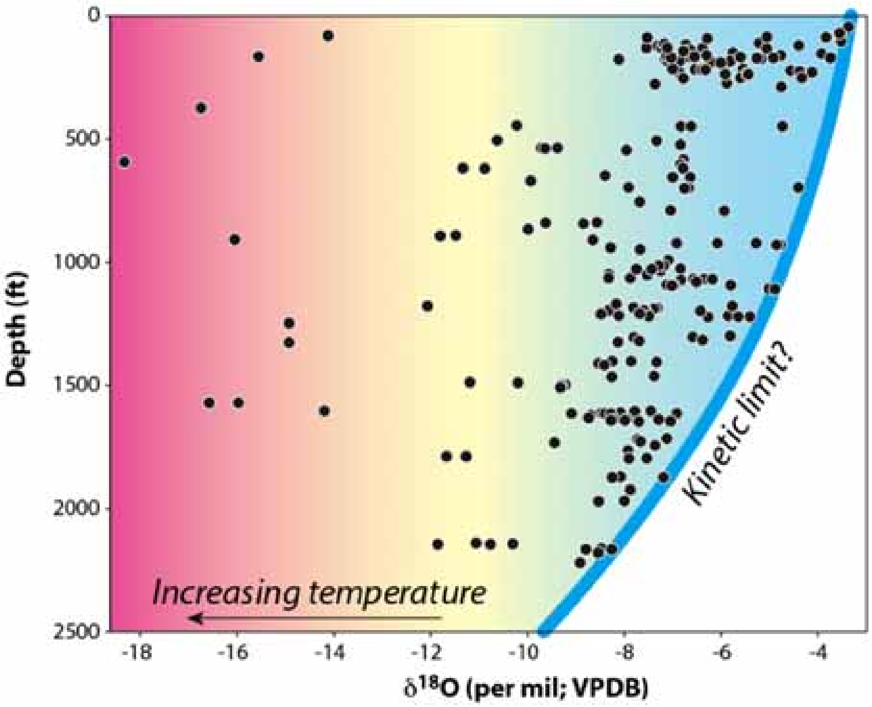


Figure 70.—Plot of $\delta^{18}O$ versus depth in vein calcite from the Black Warrior CBM fields.

with microbial CO_2 reduction apparently occurred late in the regional unroofing history as Pottsville strata approached modern burial depth. Analysis of the regional burial history suggests that calcite precipitation and methanogenesis may have begun during the Mesozoic (~150 Ma) and may continue today (fig. 21).

PRODUCTION ANALYSIS

Understanding the production lifecycle of wells is essential for developing meaningful water management strategies. This section begins with a discussion of the decline characteristics of vertical CBM wells that is intended to show the relationships between the natural gas lifecycle and the water lifecycle. Then the discussion focuses on cumulative and peak production performance, which helps characterize the performance of populations of CBM wells (e.g., Pashin and Hinkle, 1997; Zuber and Boyer, 2001). The final part of this section characterizes annual production trends from the inception of the Black Warrior CBM industry in 1980 to the mature state in 2012, which demonstrates how the industry has evolved and forms a basis for future projections.

Decline Curve Analysis

Analysis of production decline curves is valuable for understanding the relationships between gas and water production in CBM wells and provides a predictive tool that enables valuation of wells and properties (e.g., Hanby, 1991; SPEE, 2011). The decline characteristics of CBM wells are diverse and reflect not only the characteristics of the reservoir, but the maintenance history of the well and interference from nearby wells. Significant differences exist between the decline characteristics of vertical CBM wells and mine-related horizontal and gob wells in the Black Warrior basin (Pashin and Hinkle, 1997). However, no single type of decline curve can be applied universally to the vertical CBM wells in the Black Warrior Basin, although some generalizations can be made based on the relationships among gas saturation, water saturation, and reservoir pressure (Pashin, 2007, 2010a, b).

Exponential decline of gas production accompanied by hyperbolic decline of water production is the most common behavior exhibited by CBM wells in the Black Warrior Basin. An example from Holt Field shows long-term exponential decline of gas production with peak production occurring early in the life of the well (fig. 71). Early peak is typical of wells in reservoirs with high gas saturation, where a large reservoir volume can be depressurized to critical desorption pressure quickly. This example further shows strong hyperbolic decline of water production from 1991 to 2001. During 2001 the pumping rate was adjusted to a lower level

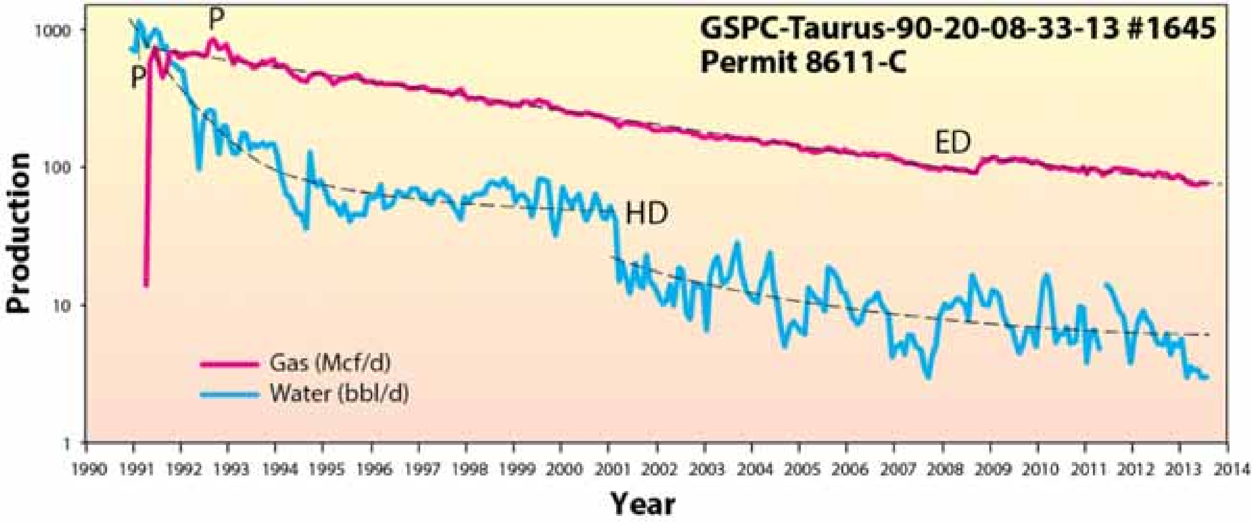


Figure 71.—Decline curves demonstrating exponential decline of gas production and hyperbolic decline of water production in a well from Holt Field.

with no tangible effect on gas decline. Following routine well maintenance in late 2008, gas production increased slightly, and a new exponential decline was established. Maintenance activities that can result in improved production include the removal of scale from perforations and maintenance or replacement of wellhead seals and fittings.

Another example from Holt Field shows long-term exponential decline of gas production and hyperbolic decline of water production (fig. 72). In this case, however, early production showed inclining gas production, and it took nearly four years for the well to achieve peak rate. A long-term incline of gas production is suggestive of reservoirs that are undersaturated with gas. In undersaturated reservoirs, large volumes of water may need to be pumped to build the cone of depression and bring a large part of the drainage area below critical desorption pressure. Exponential decline of gas production has effectively proceeded unabated since late 1994. However, the pumping rate was slowed during 2000, and a secondary hyperbolic decline of water production was established.

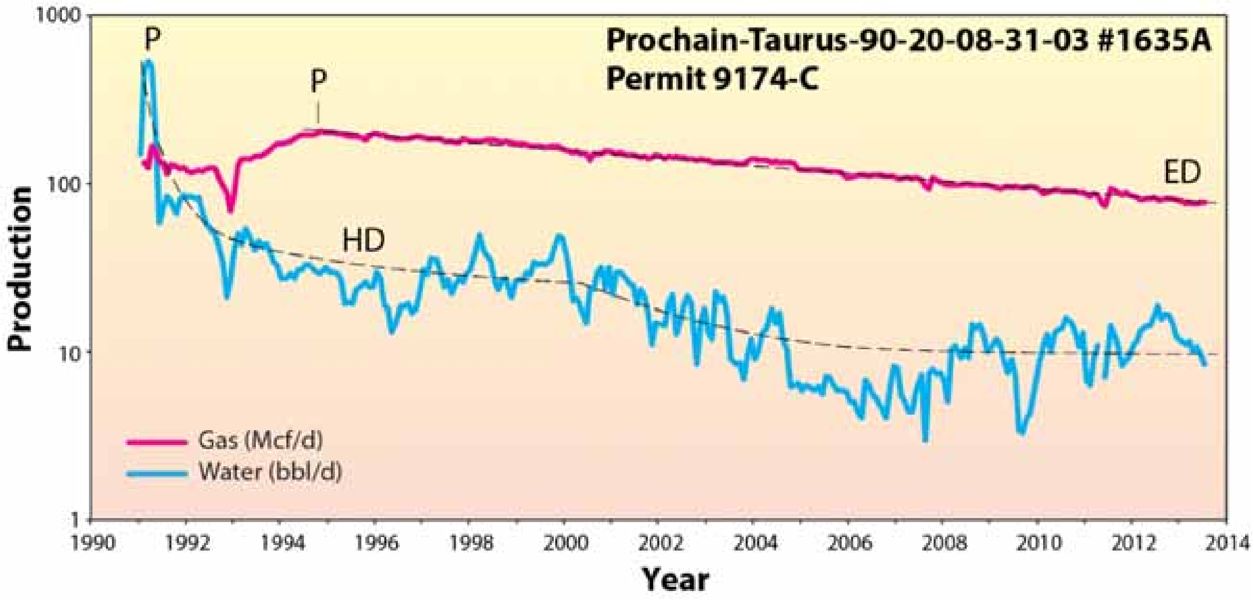


Figure 72.—Production curves showing prolonged incline of gas production prior to peak along with hyperbolic decline of water production in a well from Holt Field.

Decline curves from a well in Deerlick Creek Field demonstrates complexities associated with CBM production (fig. 73). This well is one of two that have produced exceptional amounts of water, and an early spike in production during 1986 established that the pumping potential was 1,585 bbl/d. Water pumping was subsequently managed at less than 500 bbl/d, and variation in the water curve shows several adjustments of pumping strategy over the life of the well. Early pumping established an exponential decline of gas production, and subsequent changes in the water production rate did not have an obvious effect on gas production. Well maintenance in early 1998, however, resulted in increased gas production, whereas similar maintenance in late 2008 had a negligible effect on gas production.

The previous example is typical of wells in areas with high water production rate, and an example from Blue Creek Field shows how some wells perform in areas with minimal water production (fig. 74). Water production was established at 14 bbl/d in 2003 and declined

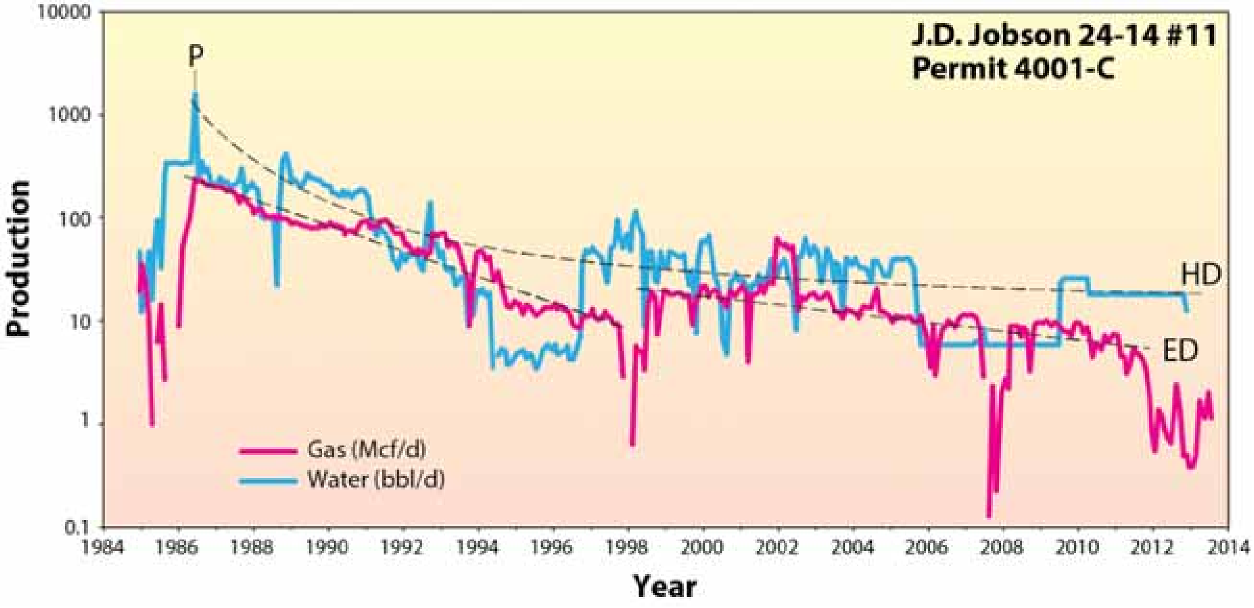


Figure 73.—Production curves showing complex history of gas and water production in a well from Deerlick Creek Field.

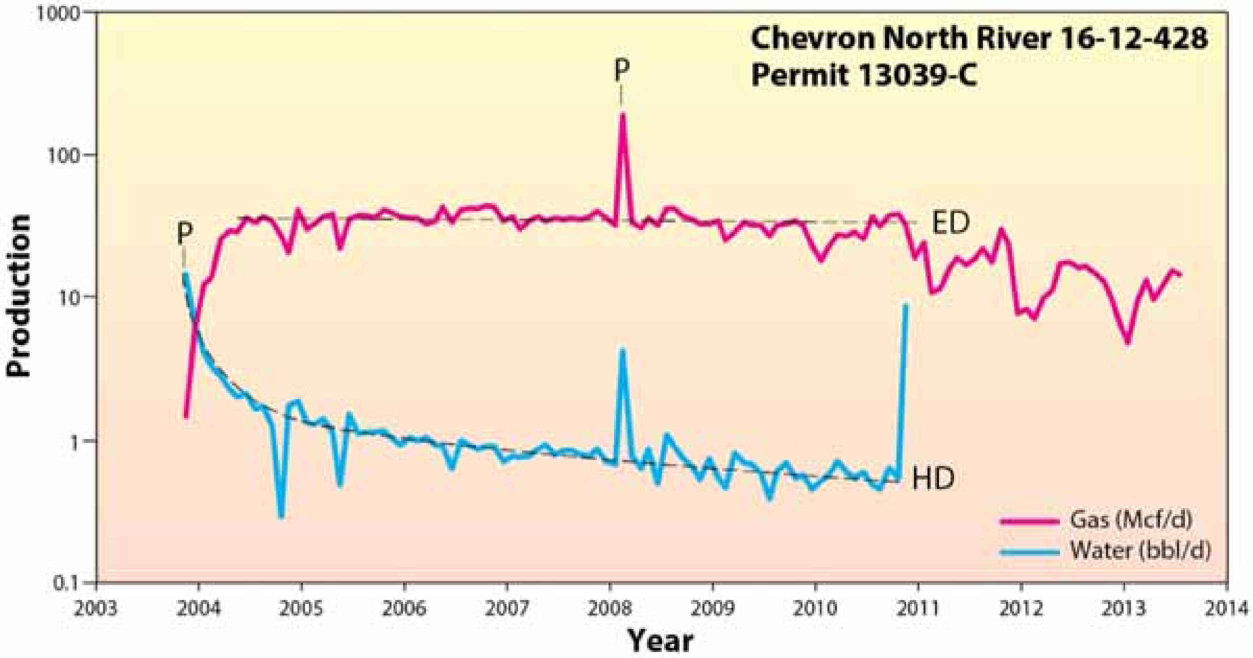


Figure 74.—Long-term stable gas production accompanying hyperbolic decline of water production in the low water yield area of Blue Creek Field.

hyperbolically to about 1 bbl/d from 2005 through 2010. Whereas water declined exponentially, gas flowed steadily at 30 to 40 Mcf/d from 2004 to late 2010 with no sign of exponential decline. Water production has not been reported since 2011, and the well has declined erratically since that time.

Results of decline curve analysis indicate that peak gas production typically occurs during the first four years of the life of a well. Following peak, wells typically exhibit exponential decline, which can persist for decades (figs. 71, 72). However, production performance in many wells can be difficult to predict because of complex maintenance history and interference from nearby wells. Water production declines hyperbolically and is generally more predictable than gas production. However, the production history of many wells, particularly those capable of producing large volumes of water, reflects managed pumping rather than the maximum water production potential of the well (fig. 73). Reduction of the pumping rate late in the life of a well, moreover, may have little effect on gas rate. Hyperbolic decline indicates that managing water volume is of greatest concern early in the life of a well or group of wells. During the later stages of production, the flow of water to the wellbore can be limited, and pumping rate needs to be managed to keep the water level below the perforations so as not to impede the flow of gas to the wellbore. Another advantage of reducing pumping rate late in the life of CBM wells is to avoid overworking pumps and to minimize energy and maintenance expenses associated with pump operation.

Cumulative and Peak Production

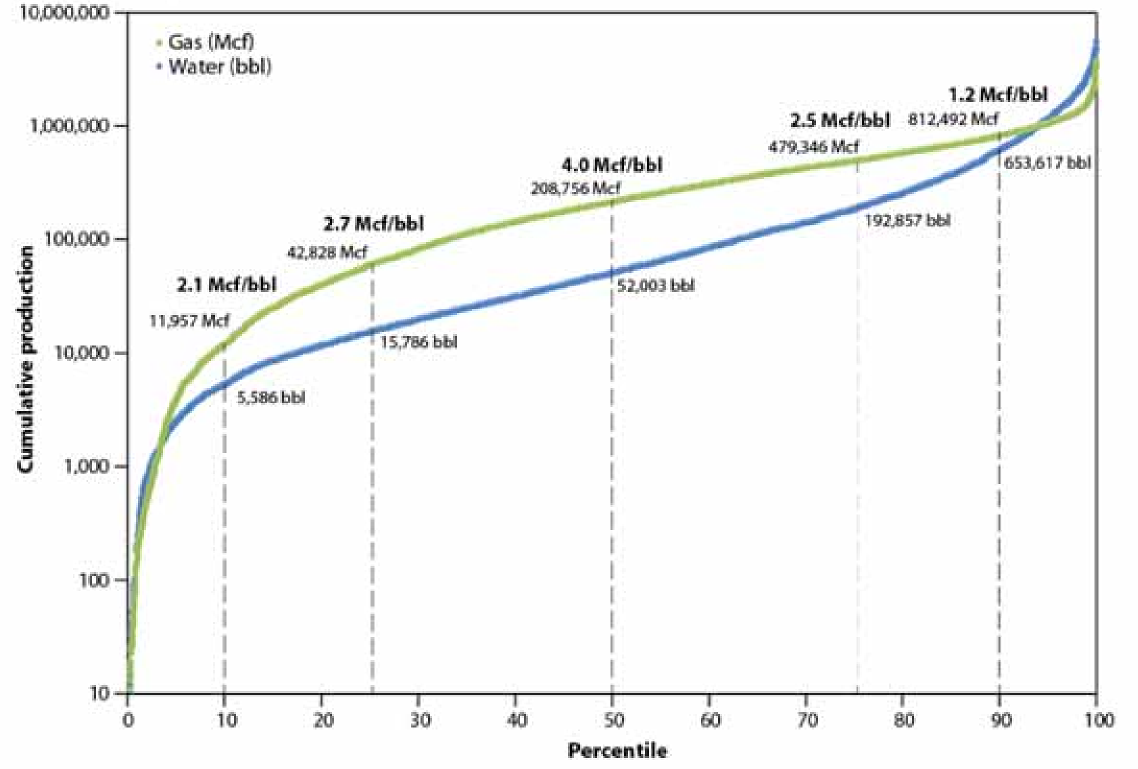
Cumulative production is a long-term metric of well performance, whereas a peak production is a short-term metric that can be used to predict the long-term performance of CBM wells

(Pashin and Hinkle, 1997). Cumulative and peak values range greatly, with the maximum recorded cumulative values being 3.65 billion cubic feet (Bcf) of gas and 11 million bbl of water and the maximum peak values being 4.27 million cubic feet of gas per day and 8,008 bbl of water per day. Percentile plots indicate that 80 percent of the wells have cumulative gas production between 12 and 812 million cubic feet and cumulative water production between 5,586 bbl and 653,617 bbl (fig. 75). Percentile plots of peak production indicate that 80 percent of the wells have peak gas rates between 34 and 507 Mcf/d and peak water rates between 23 and 693 bbl of water per day. At the 50th percentile, cumulative gas and water production are 209 million cubic feet and 52,000 bbl, and peak gas and water production rates are 145 Mcf/d and 106 bbl/d, respectively.

Gas and water production data are log-normally distributed, and peak and cumulative values can thus be correlated using power functions (fig. 76). Peak and cumulative gas production values correlate positively with a coefficient of regression of 0.79, whereas peak and cumulative water production correlate even more strongly with a coefficient of regression of 0.89. However, only order-of-magnitude predictions of long-term performance can be made using peak production values because of the underlying log-normal population distributions. This limits the utility of using peak production values for financial predictions. Regardless, part of the predictive value of these parameters is that they are recorded early in the life of most wells, typically during the first one or two years (Pashin and Hinkle, 1997). Moreover, the basic statistical relationships indicate that meaningful predictions of long-term performance can typically be made with less than 1 percent of cumulative production booked.

The map of cumulative gas production reflects the maturity of the Black Warrior CBM play, with most wells having produced more than 200 million cubic feet of gas (fig. 77). Numerous

A. Cumulative production



B. Peak production

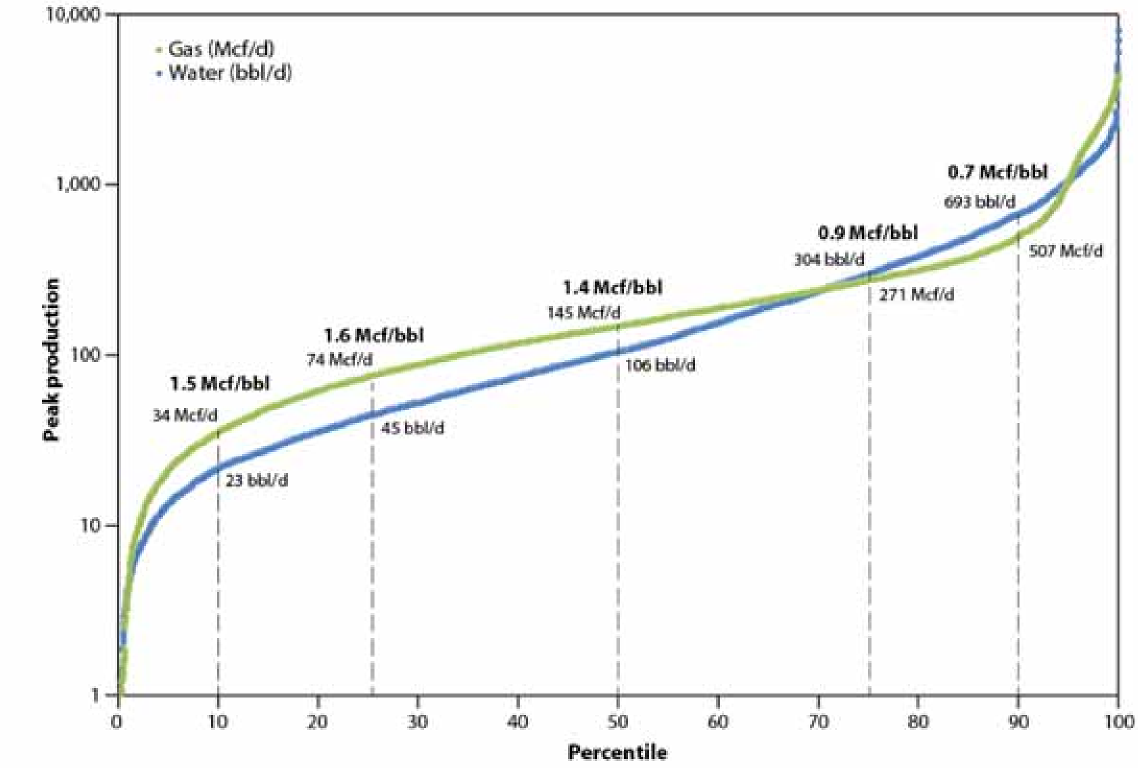
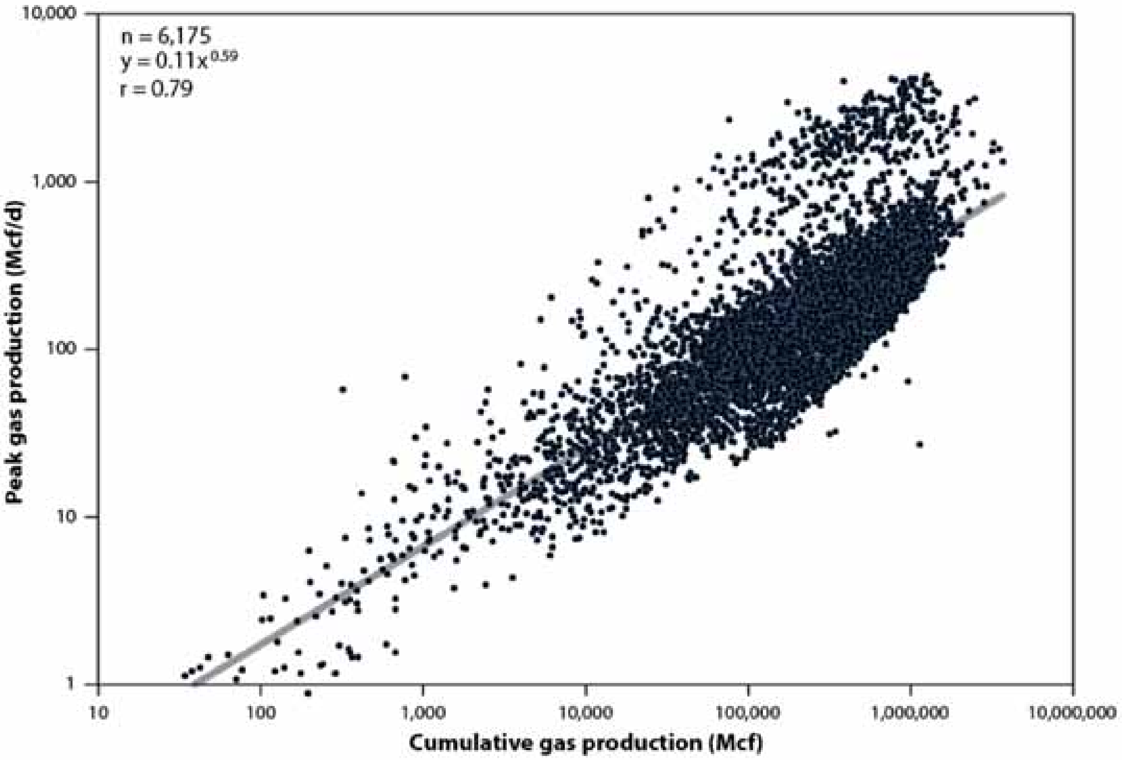


Figure 75.—Percentile plots of cumulative and peak gas and water production based on all production records from the Black Warrior Basin.

A. Gas production



B. Water production

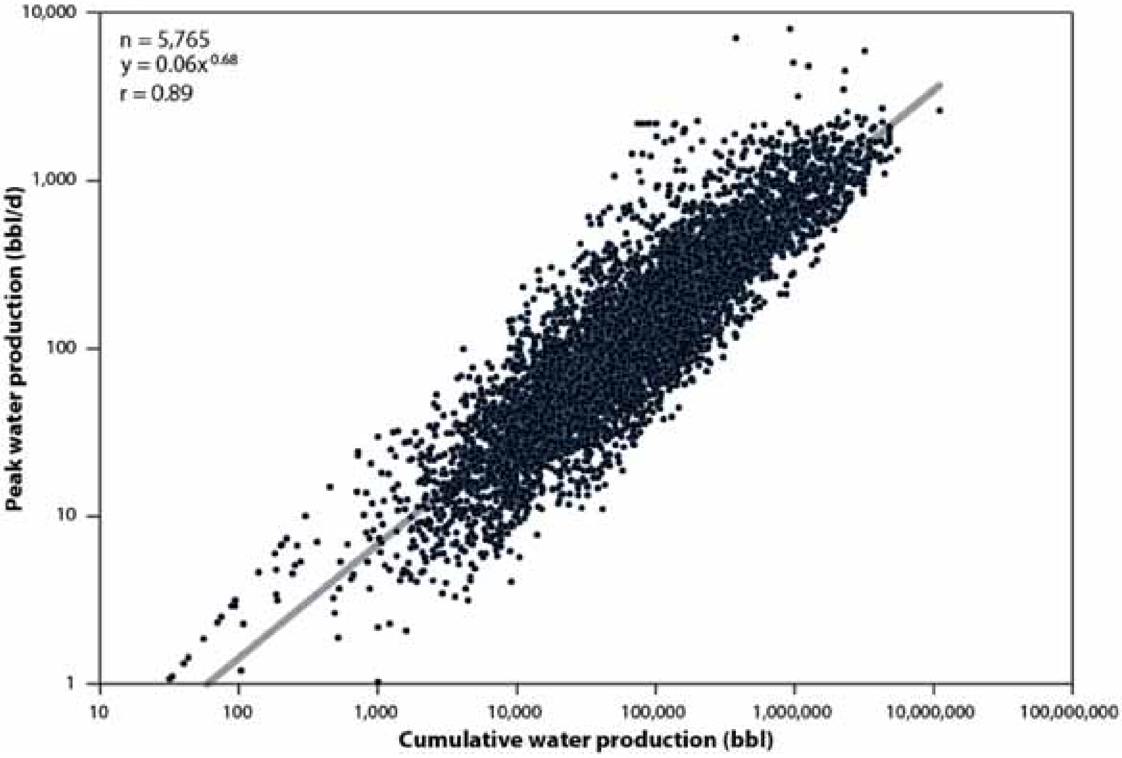


Figure 76.—Scatterplots showing strong correlations between (A) peak and cumulative gas production and (B) peak and cumulative water production.

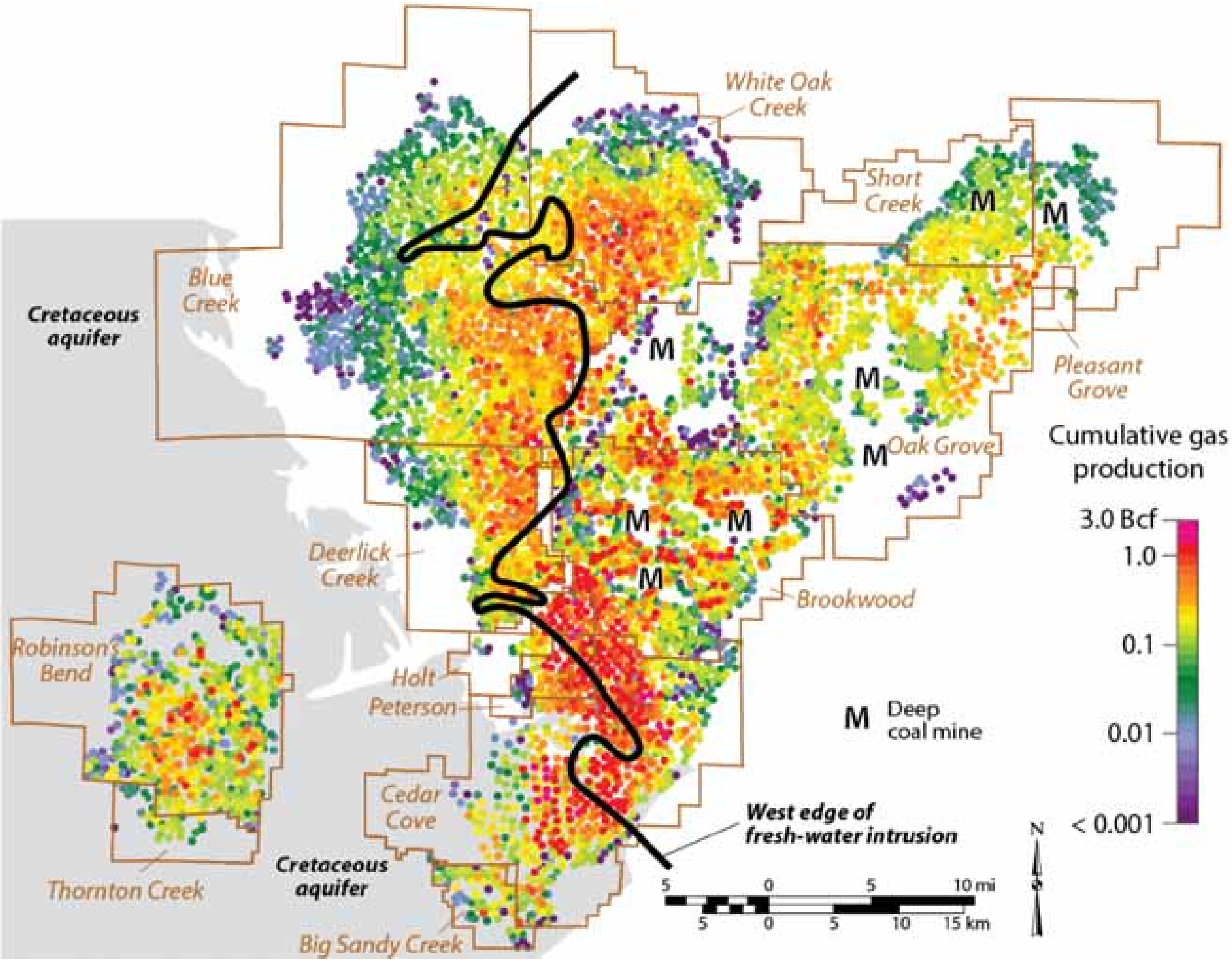


Figure 77.—Map of cumulative gas production in the active Black Warrior CBM fields.

wells in Cedar Cove, Holt, Peterson, and southwestern Brookwood fields have now produced more than 1 Bcf. Regionally, production performance only locally reflects coal thickness or original gas-in-place (Pashin, 2009). Rather, production trends highlight the areas in which coal seams can effectively be depressurized, specifically regions where original reservoir pressure is low and permeability is high (Pashin, 2010a).

Cumulative production is highly variable in Oak Grove and Brookwood fields, where gas resources and reservoir pressure have been impacted by mining. Low gas production in many wells in western Oak Grove Field is in an area that is naturally depleted of methane (Malone and others, 1987). Production is most consistent in an arcuate trend extending from Cedar Cove Field through White Oak Creek Field. The youngest wells in the basin are concentrated along the northern and western fringes of this trend, and the youth of the wells is expressed in low cumulative production numbers. Production is variable in Big Sandy Creek and Robinson’s Bend Fields, which are the only successful fields to be developed below thick Cretaceous cover. In this area coal seams are deep, have reduced permeability, and tend to be undersaturated with methane.

The map of peak gas production (fig. 78) shows a pattern that is similar to cumulative gas production, which is consistent with the high correlation between peak and cumulative values (fig. 76). Peak values are highest in the arcuate trend that extends from Cedar Cove Field to White Oak Creek Field. Most wells west and north of the trend are now past peak, which suggests that ultimate production patterns will resemble the cumulative pattern. Interestingly, the regional pattern of cumulative and peak gas production suggests that the most productive wells tend to be concentrated near the western margin of the freshwater intrusion (figs. 77, 78).

The map of cumulative water production (fig. 79) shows that numerous wells completed within the freshwater intrusion have produced more than 100,000 bbl of water, and many of those wells have produced in excess of 1,000,000 bbl in parts of Oak Grove, Cedar Cove, and Robinson’s Bend fields. Notable exceptions are around the deep coal mines in Brookwood and Oak Grove fields, which form major pressure sinks that limit water production. Most wells west of the intrusion in Blue Creek and Deerlick Creek fields have produced less than 10,000 bbl of water, which helps offset the environmental impact of the elevated salinity. In this area, the coal seams produce large volumes of gas and are naturally underpressured. Underpressuring not only helps limit water lift, but is thought to reflect the presence of free gas in the system (Pashin and

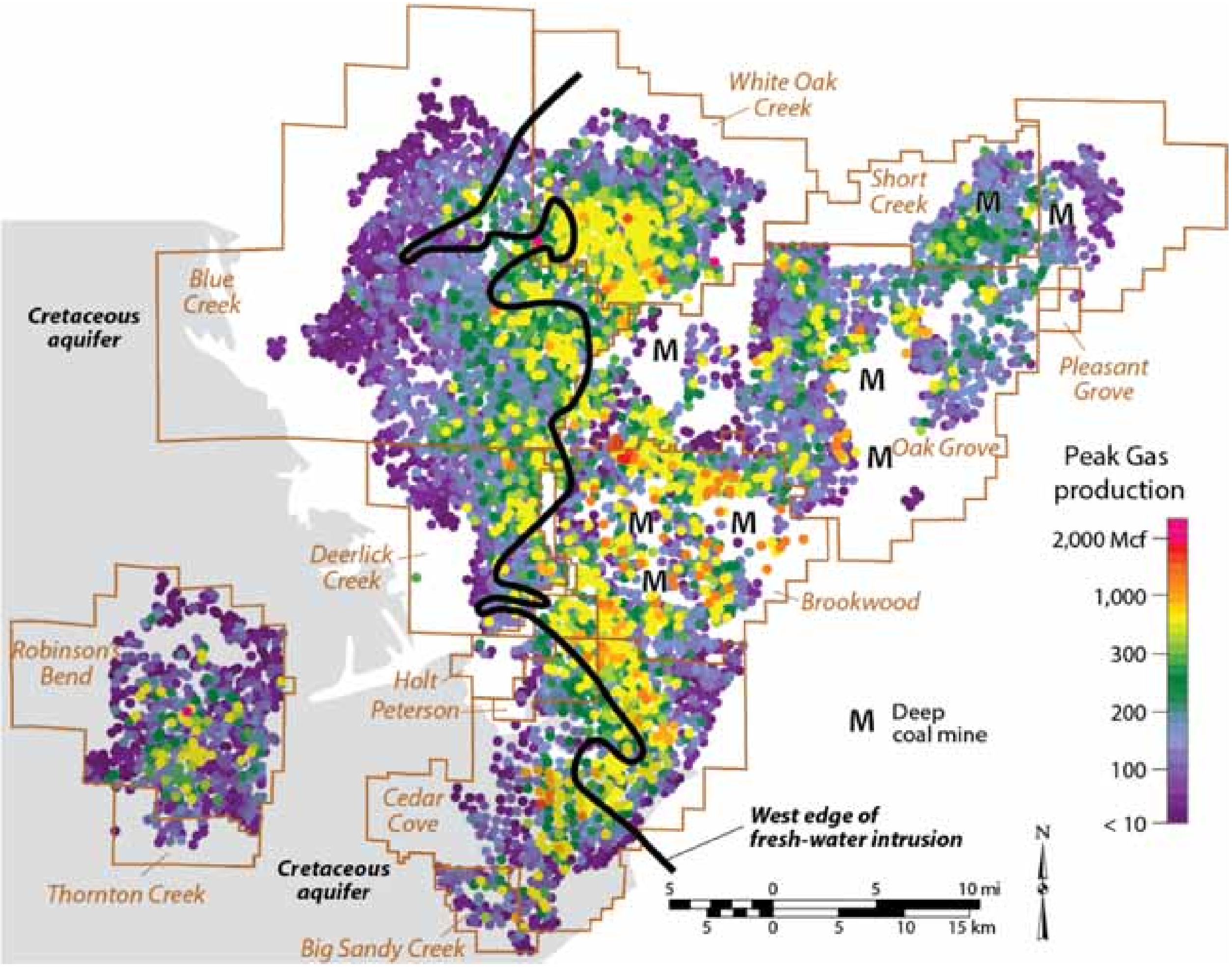


Figure 78.—Map of peak gas production in the active Black Warrior CBM fields.

McIntyre, 2003). A large volume of water has been produced from coal seams below the Cretaceous aquifer in Cedar Cove and Robinson’s Bend fields. The high salinity of most water produced in the Robinson’s Bend area suggests that the coal seams are not well connected to the Cretaceous aquifer, which is a major source of potable water in the region. Rather, the high yield of saline water from Pottsville coal in this area corresponds with normal reservoir pressure and an apparent lack of free gas in the system.

As with gas production, the regional pattern of peak water production resembles that of cumulative water production (fig. 80). Again, the similarity of these maps is consistent with the

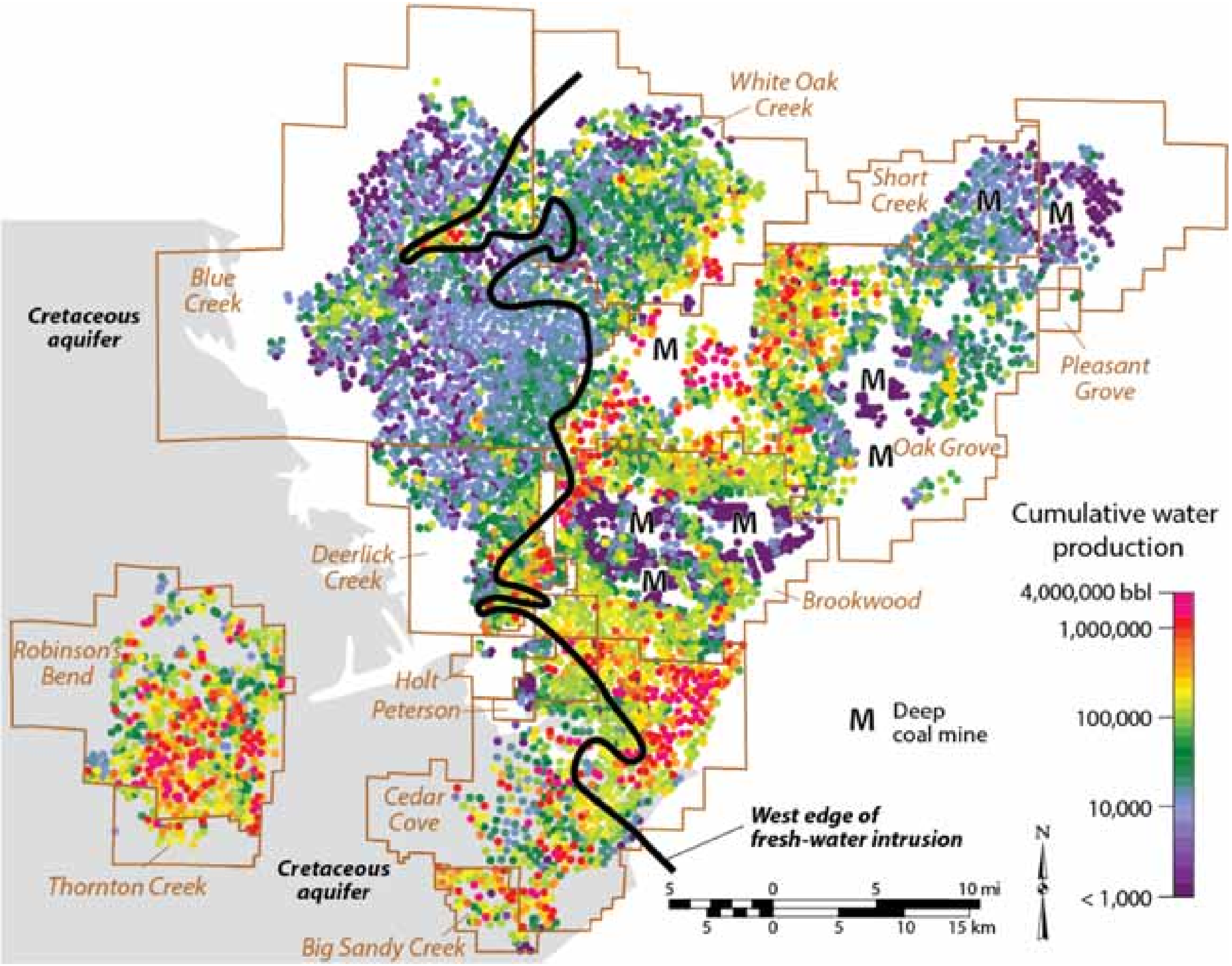


Figure 79.—Map of cumulative water production in the active Black Warrior CBM fields.

strong positive correlation between peak and cumulative water production (fig. 76). Importantly, hyperbolic decline indicates that the peak rate is achieved early in the life of each well. West of the freshwater intrusion in Blue Creek and Deerlick Creek fields, extremely low peak production numbers coupled with the highest TDS values in the CBM fields indicates that the quantity of produced water is less of an issue than the quality.

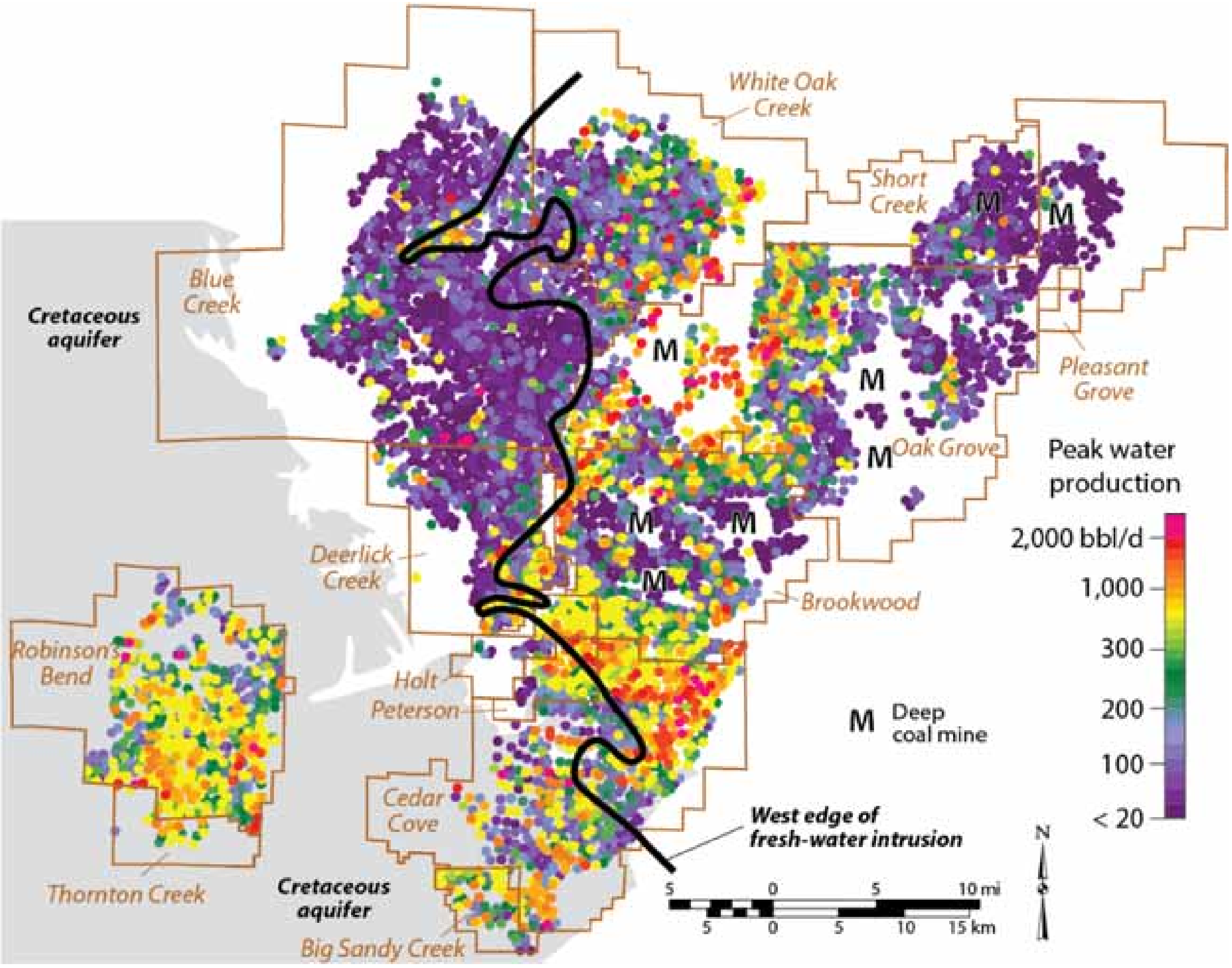


Figure 80.—Map of peak water production in the active Black Warrior CBM fields.

Annual Production

The Black Warrior basin contains the most mature CBM play in the world (fig. 4), and so the basin serves as an example not only of how the CBM industry has evolved, but the types of events that have stimulated that growth. Maps of annual gas and water production are compiled in a pair of QuickTime movies that are bundled with this document as supplemental files. Highlights are summarized herein, and readers can either watch the movies continuously or view them frame by frame to follow the narrative given below.

Although experiments had been conducted in Oak Grove Field since 1974 (Elder and Deul, 1974), the OGB permitted the first commercial production in Pleasant Grove Field in 1980. This was a landmark event that included establishment of the first regulatory structure tailored specifically for CBM, as well as the development of a municipal gas system by the City of Pleasant Grove that produced and utilized CBM independently of coal mining. Oak Grove Field was established in 1981, and so production was formally reported from the wells in the original Oak Grove pattern. Soon thereafter, production was established in western Brookwood Field in 1982 in association with longwall coal mining.

Significant growth of the industry began in 1984 and was marked by a significant expansion of operations in Brookwood Field. Development independent of mining began that year southwest of Brookwood Field, and Cedar Cove, Holt, Peterson, and Deerlick Creek fields were established. A key to CBM development in areas remote to the coal mines was the application of multi-zone completion technology (Graves and others, 1983) In 1989, expansion of CBM development accelerated, and White Oak Creek, Blue Creek, Big Sandy Creek, Little Sandy Creek, and Moundville fields were established. The effects of this acceleration became apparent in 1990, when many new wells were permitted and drilled and Robinson’s Bend Field was established. Key factors driving this acceleration were the success of development in the early fields coupled with the pending expiration of the Section 29 unconventional fuels tax credit, which expired in 1992. Indeed, by the end of 1992, the pattern of wells drilled in the Black Warrior CBM play began resembling that which exists today.

Expansion of drilling and production in White Oak Creek Field during 1995 marked the first significant development following expiration of the Section 29 tax credit. This helped pave the way for continued expansion of CBM development by demonstrating that the resource was competitive with other sources of natural gas without any market incentives. Around this time, however, production in the distant southwestern CBM fields had proven difficult, and so Little Buck Creek and Taylor Creek fields were shut in, and operations in Moundville Field, which contains the thickest coal accumulation in the basin, were scaled back considerably. Natural gas prices increased greatly during 1999. This event sparked a major expansion of operations in Blue Creek and White Oak Creek Fields in 2000 and establishment of Short Creek Field in 2001. With this expansion came significant increases in water production. By 2006, CBM development in Alabama effectively reached its current extent.

By 2009, shale gas had begun glutting domestic natural gas markets, placing economic pressure on the CBM industry. Hence, natural gas prices began collapsing, development slowed, and production began declining because reserves were no longer being replaced. Nevertheless, CBM production in the Black Warrior Basin remains highly active. Indeed, the vast majority of the wells drilled in the Black Warrior Basin remain active today and are expected to remain a vital part of the national gas supply for the foreseeable future.

WATER MANAGEMENT STRATEGIES

Analysis of the geology, hydrodynamics, and geochemistry of the Pottsville Formation indicates a complex interrelationship among water composition, thermogenic hydrocarbon generation, and late-stage microbial methanogenesis. Throughout the study area, gas is produced at pipeline quality and so requires minimal processing prior to commercial distribution. The great variability of water chemistry, in contrast, necessitates that significant attention be paid to water processing and disposal, which must be conducted in an environmentally acceptable manner while controlling operational costs.

Chloride content is the dominant control on water quality in the Black Warrior CBM fields (fig. 34) and is therefore a central concern for developing water management procedures. Most dissolved solids, as well as metallic and nonmetallic substances, correlate positively with TDS and chloride content. Thus, an effective water management strategy will naturally address these substances in concert with the chlorides. Importantly, the metals, nonmetals, and nitrogen compounds in the produced water are generally not constituents of concern from the standpoint of human health and safety (tables 2, 3). Those that are (e.g., As, Hg, Pb, Se, and NH_3) have very low concentrations, save for a few isolated anomalies. An array of organic compounds occurs in the produced water (table 4) and appears to be derived from coal. A number of these compounds, including phenolic substances and PAH, are of environmental concern. Orem and others (2007) pointed out that, at the low concentrations reported in produced water, the risk of acute exposure appears low. The risk of long-term chronic exposure is unclear, but the TDS content of water produced from the Black Warrior Basin precludes direct use for public water supply anyway.

Evaluation of water management strategies included the development of a GIS that assembles the information on geology, production, and infrastructure that is vital for decision making. Options for water management include instream disposal, underground injection, and beneficial use. The discussion of water management begins with a summary of the GIS and continues with a discussion of the various water management options that are available to the Black Warrior CBM industry.

Geographic Information System

The GIS developed during this study was built in Petra software, which integrates many of the geologic and geochemical maps with critical information on infrastructure and reservoir performance. The Petra project is supplied as part of the supplemental data package that is included with this report. Key elements of the GIS are the geographic boundaries of the CBM fields, well locations, basic geologic information, mined areas, geochemical maps, production maps, the NPDES discharge points, salt-water disposal (SWD) wells, and other wells that may be suitable for underground injection. Most of these elements are the geologic, geochemical, and production maps that have been presented elsewhere in this report.

Current water management practice depends strongly on NPDES permits, which are obtained through the Alabama Department of Environmental Management (ADEM). ADEM routinely scans and makes available for download most documents relating to these permits, including the draft and final permits for each issuance and reissuance. The GIS contains the latest NPDES permit areas available for the Alabama CBM fields (fig. 81). The permits not only specify the locations of discharge points along the streams, but also include the catchment areas where water is produced and transmitted to the treatment and discharge facilities that are covered by the permit.

The GIS also includes the locations of streams and lakes within the study area (fig. 82). These data were derived from public sources, such as the National Hydrography Dataset, which is made available by the USGS. The vast majority of the discharge points are on the Black Warrior River, and water processing facilities are typically located near the discharges. Several NPDES discharge points are distributed along Lost Creek in Oak Grove Field, although many of these sites are now inactive. Isolated discharge points occur along other tributaries of the Black Warrior River, including Davis Creek in Brookwood Field and Big Sandy Creek in Big Sandy Creek Field.

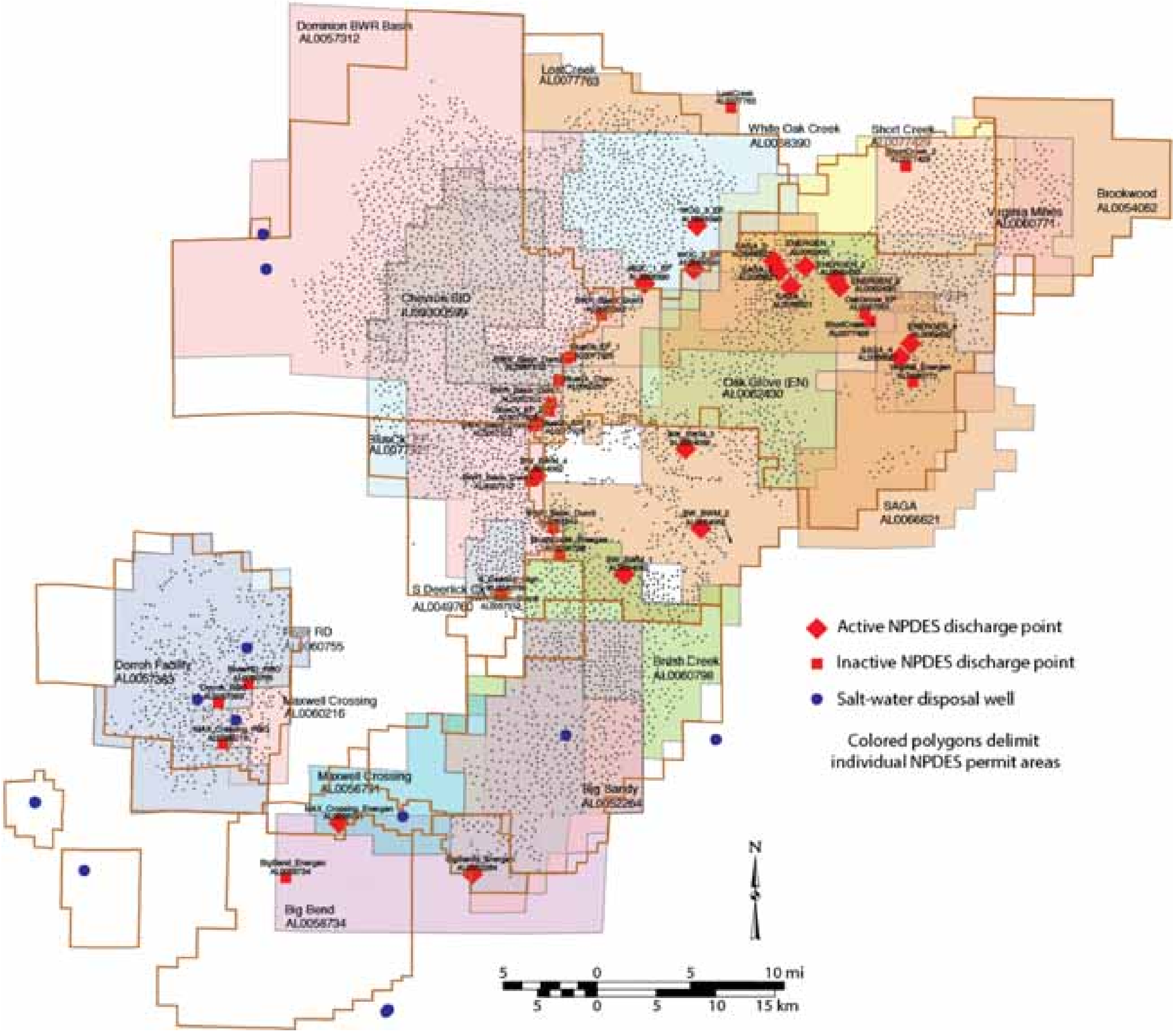


Figure 81.—Map showing NPDES permit areas, discharge points, and SWD wells in the Black Warrior CBM fields.

Field boundaries and the locations of CBM wells and SWD wells were derived from the databases of the OGB (figs. 81, 82). SWD wells are concentrated in and near the southwestern CBM fields, and permits are administered by the OGB as Class II Underground Injection Control (UIC) wells. Most of these wells were drilled in the early 1990s (Raymond, 1991; Ortiz and others, 1993). Only the wells in Robinson's Bend Field are listed as active by the OGB, and the remaining wells have all been plugged and abandoned.

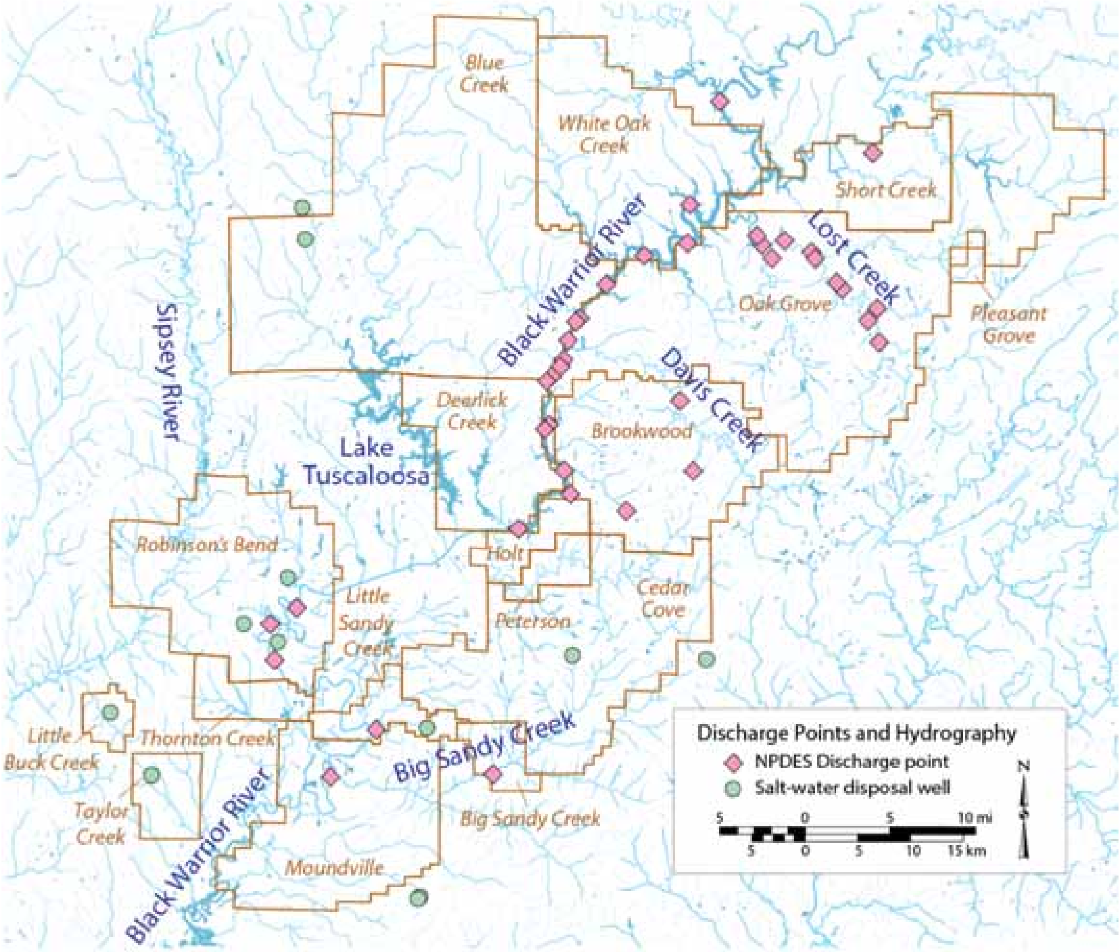


Figure 82.—Map showing relationship of discharge points and SWD wells to hydrography in the Black Warrior CBM fields.

Instream Disposal

Instream discharge to the Black Warrior River is currently the sole means of water disposal employed in the Black Warrior Basin CBM fields, and operators deploy significant facilities for the storage, processing, and disposal of produced water (Pashin, 2010a). A system of storage and treatment ponds is used to manage produced water (figs. 83, 84). Synthetic membrane liners and monitoring wells ensure the integrity of impoundments. Pollutants are removed by suspension settling and aeration, which are crucial for mitigating environmental impact. Settling removes fine particles, such as clay and silt. Aeration enables oxidation and flocculation of metallic

Figure 83.—Lined water treatment impoundments with aerators, which are widely deployed in the Black Warrior CBM fields to prepare produced water for discharge into streams.

compounds and facilitates the evaporation, oxidation, and degradation of organic compounds in the produced water.

During the late 1980s, the membership of the Coalbed Methane Association of Alabama formed the Warrior Basin Environmental Cooperative, Incorporated. The cooperative operated an elaborate monitoring system that extended along 150 miles of the Black Warrior River. Toxicity testing (O'Neil and others, 1989, 1993) was used to determine allowable chloride concentrations in the river. Consequently, discharge permits required that chloride concentrations

Figure 84.—Aerial photograph of two-stage water treatment facility in Robinson’s Bend Field. Aerators and a system of baffles are used to facilitate evaporation of volatile compounds and to facilitate precipitation, flocculation, and suspension settling of particulate matter so that water can be discharged safely into the Black Warrior River.

in the river be < 230 mg/L. Concentrations were < 50 mg/L and never approached the regulatory limit. Accordingly, monitoring requirements were relaxed, and the cooperative was disbanded at the end of 1997.

Where TDS content and produced water volumes are high, water disposal concerns limit the ability to pump CBM wells to capacity (Pashin, 2010b). Reverse osmosis systems are used locally, such as in Robinson’s Bend Field, to process saline formation water, but the economic viability of these systems is currently being challenged by low natural gas prices. Artificial wetlands show promise for removing a broad range of contaminants from produced water, including chlorides, metals, and organic compounds (Rodgers and Castle, 2008; Spacil and others, 2011), and Clemson University and Chevron are conducting a cooperative experimental program to determine the viability of artificial wetlands in the Black Warrior CBM fields. Considering the large volume of low TDS water produced from the CBM fields, artificial wetlands may enable processing of the water for beneficial use in industry and agriculture, as well as human consumption.

Deep Disposal Options

Deep disposal wells were drilled in the southwestern CBM fields during the 1990s as increasing amounts of saline water were produced (Raymond, 1991; Ortiz and others, 1993). Wells were completed in units ranging from the Cambrian-Ordovician carbonate of the Knox Group through the Pennsylvanian-age quartzose sandstone of the lower Pottsville Formation (fig. 85). The two injection wells in the Knox Group were completed at depths of 8,800 feet and 10,000 feet and injected water into up to 1,000 feet of section (table 8). The high rate achieved by the well in Hale County reflects a combination of great reservoir thickness coupled with abundant natural fractures; geophysical well logs indicate that matrix porosity and permeability in Knox strata are very low. The well in Cedar Cove Field supported rates exceeding 3,000 bbl/d with only half of the injectivity that was reported from the Hale County well.

Devonian carbonate and chert units form a southwest-thickening wedge of sedimentary rock in the Black Warrior Basin (Kidd, 1975; Pashin and others, 2011; Clark and others, 2013) (fig.

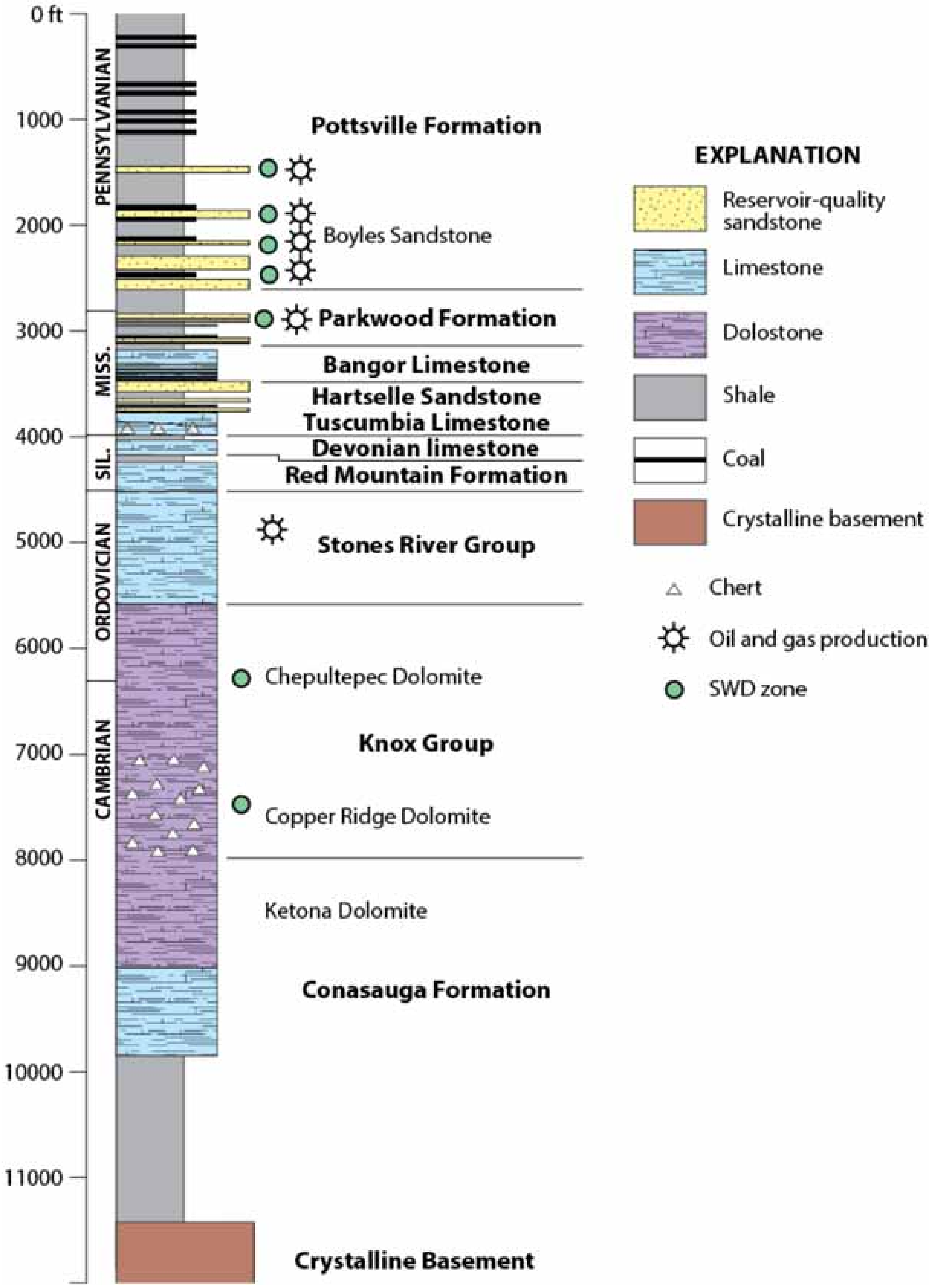


Figure 85.—Stratigraphic column showing subsurface zones used for brine disposal in the Black Warrior CBM fields.

86), and significant porosity is developed in the southwestern CBM fields (Clark and others, 2013). One well in Robinson's Bend was used for disposal of produced water in Devonian chert. Injectivity was only about half of that in the Knox well in Cedar Cove Field.

Two wells completed in Parkwood sandstone were used for brine disposal in southern Fayette County and in Boone Creek Field in northwestern Tuscaloosa County (table 8). These wells were completed at depths of 2,400 and 3,600 feet and had maximum allowable injection rates of 1,350 and 3,600 bbl/d. Significantly higher pressure was required in the Boone Creek well, and this is reflected in injectivity of only 0.8 bbl/d/psig. Injectivity in the Fayette County well was the same as that in the Cedar Cove Knox well.

The highest injectivity was reported from disposal wells in lower Pottsville sandstone (table 4). Depth of the injection zones ranges from 4,500 to 5,150 feet, and wellhead injection pressures were only 350 to 787 psig. Injectivity is between 6.2 and 11.8 bbl/d/psig, reflecting the high reservoir quality of lower Pottsville sandstone relative to all other intervals. Indeed, sandstone in one of the wells supported an injection rate exceeding 9,000 bbl/d, indicating that implementing storage operations in the lower Pottsville Formation holds some promise. However, a concern with all of the deep disposal wells in the Black Warrior Basin is injectivity loss over time coupled with progressive buildup of back-pressure. This not only limits the long-term utility of SWD wells for the disposal of large volumes of fluid, but also points toward risk of induced seismicity, which is a point of increasing public scrutiny.

In addition to the SWD wells in the lower Pottsville, several wells in the Blue Creek area were drilled into the lower Pottsville to explore the production potential of a thick coal seam near the base of the formation (figs. 87, 88). Efforts to produce proved unsuccessful partly because of poor isolation of the coal from the porous lower Pottsville sandstone and conglomerate units. All

Table 8. Injectivity in saltwater disposal wells in the Black Warrior basin.

Permit	Field	Geologic Unit	Depth (ft)	Maximum injection rate (bbl/d)	Injection Pressure (psig)	Injectivity (bbl/d/psig)
2617-A-SWD-89-2	Little Sandy Creek	Pottsville	4,600	4,000	600	6.7
8467-SWD-90-5	Robinson's Bend	Pottsville	4,500	9,325	787	11.8
8376-SWD-90-13	Wildcat	Pottsville	5,150	2,160	350	6.2
3475-A-SWD-90-2	Boone Creek	Parkwood	3,600	1,350	1,700	0.8
4791-A-SWD-88-5	Wildcat	Parkwood	2,400	3,600	1,050	3.4
8864-SWD-90-9	Robinson's Bend	Devonian	7,200	2,435	1,500	1.6
6261-SWD-89-5	Cedar Cove	Knox	10,000	3,350	995	3.4
8940-SWD-90-10	Wildcat	Knox	8,800	10,800	1,750	6.2

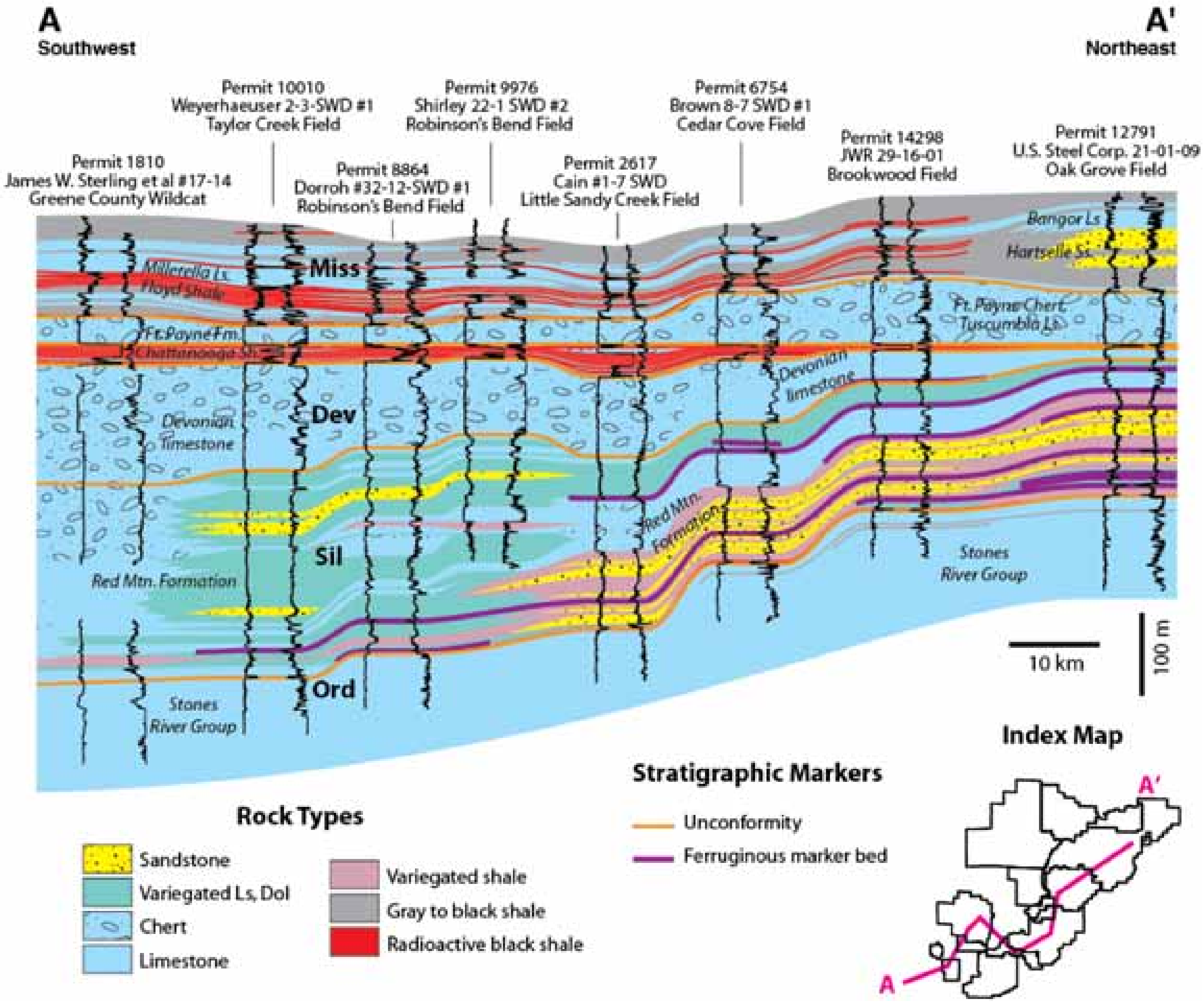


Figure 86.—Stratigraphic cross section showing facies heterogeneity in Silurian-Devonian strata in the area of the Black Warrior CBM fields (modified from Pashin and others, 2011).

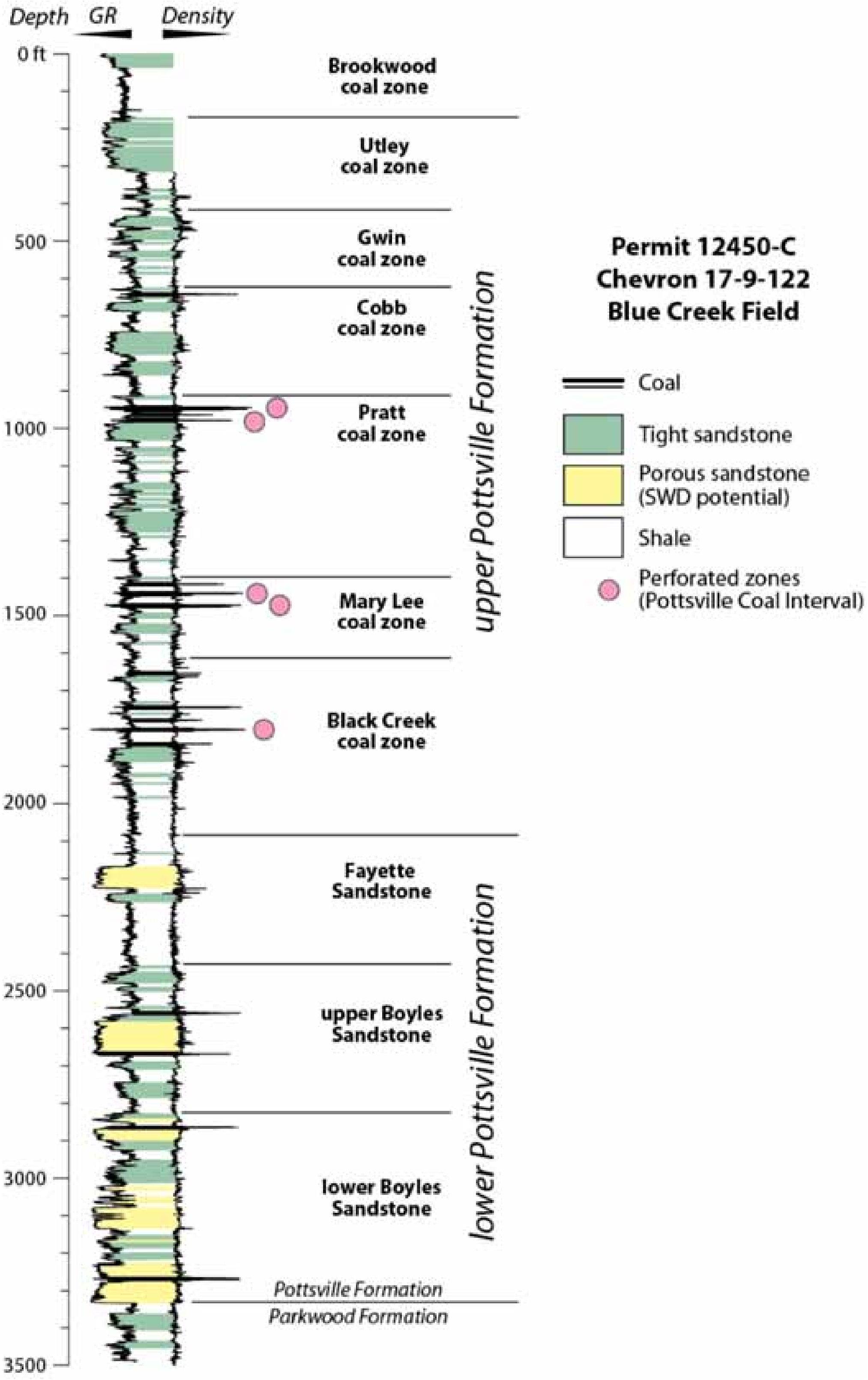


Figure 87.—Geophysical well log of a CBM well from Blue Creek Field that was drilled through lower Pottsville sandstone, which may have significant SWD potential.

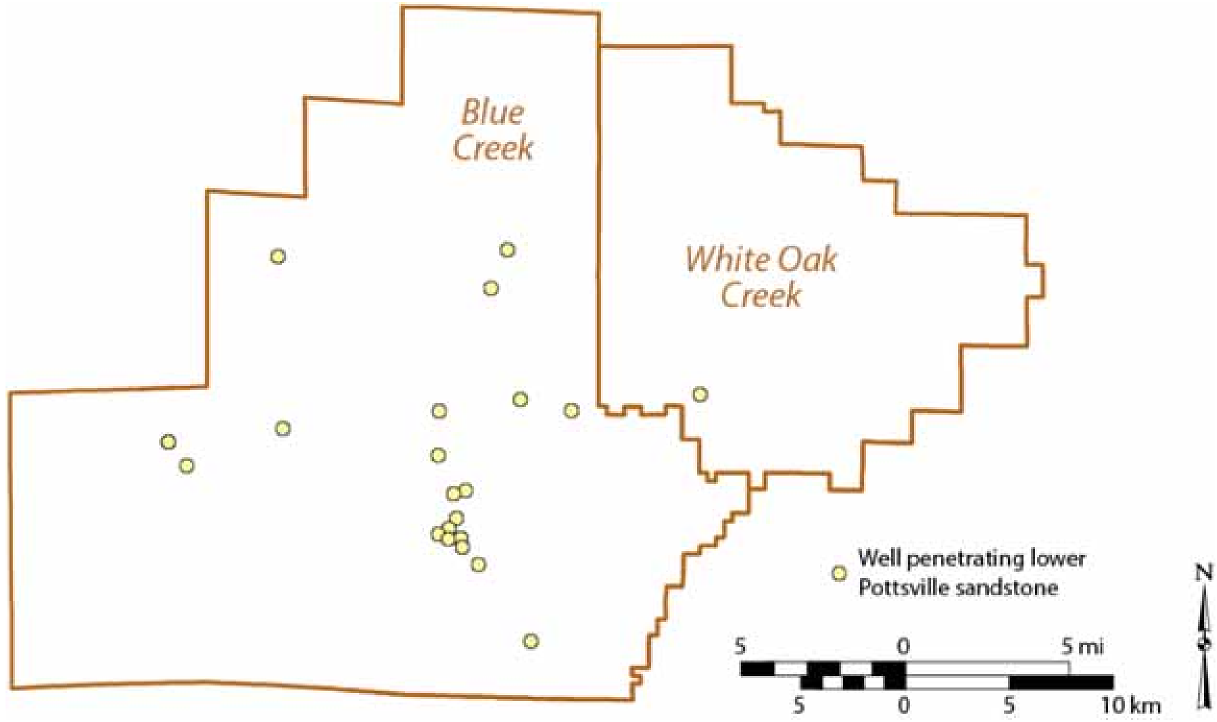


Figure 88.—Map showing locations of wells that have penetrated lower Pottsville sandstone in Blue Creek and White Oak Creek fields.

of these wells were completed in the Black Creek, Mary Lee, and Pratt coal zones (fig. 87). The lower Pottsville sandstone units are severely underpressured and proved to be an effective sink for the formation water from the upper Pottsville coal seams. In well 12450-C, for example, no water passed through the wellhead during the first 8 months of production (Pashin and others, 2010). Water eventually built up in the wellbore, and a bridge plug was set above the Fayette sandstone. Considering the low volume and high TDS content of the produced water in much of Blue Creek Field, disposal of saline water in the lower Pottsville may be a low-risk, low-cost option with some advantages over transportation to processing facilities and instream disposal.

Beneficial Use Options

Beneficial uses for produced water include public water supply, agricultural application, and industrial application (fig. 4). The CBM fields are an integral part of the Birmingham-Tuscaloosa economic corridor, which hosts a population of more than 1.3 million people. The Birmingham area has periodically been impacted by major drought that has severely stressed water supply. Drought was particularly acute during the summer of 2007, when rainfall fell 25 inches short of the annual average of 54 inches. As a result, the level of Lake Purdy fell to critically low levels, posing a serious threat to the southern suburbs. At the time, a significant part of the problem was that the primary water sources in the area were not interconnected, which left some areas more prone to water shortages than others. Considering the large volume of low TDS water that had been produced from the CBM fields at that time, the water could have been processed by deploying any number of reverse osmosis and membrane technologies and used to reduce stress on the municipal water supply. Fortunately, major improvements have been made to the municipal water system in the Birmingham area, and major sources like the Black Warrior River and Lake Tuscaloosa have proven resistant to major drought. Even so, assessing the utility of the produced water would be worthwhile from the standpoints of emergency management and prioritizing sources of water for a range of municipal and industrial applications.

The TDS content of the produced water precludes most agricultural uses without significant processing. However, a brackish-water shrimp farming industry has been active in Tuscaloosa and Greene Counties since the 1990s (Teichert-Coddington, 2002; Whitis, 2007) (fig. 89), and brackish-water catfish farming has been a staple of the local economy for many decades that produces annual farm gate receipts exceeding 60 million dollars. Interestingly, several of these farms are in and near Robinson’s Bend and Thornton Creek fields. Catfish benefit from saline

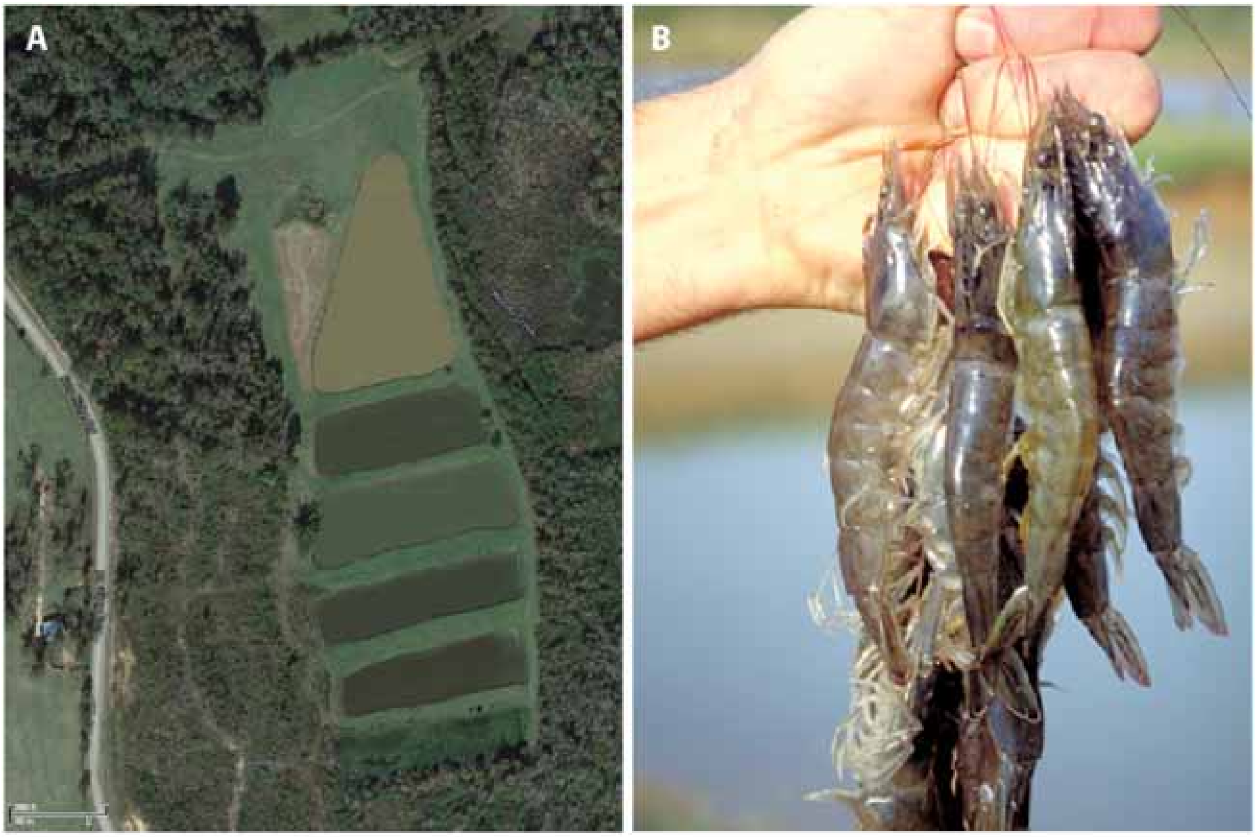


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Figure 89.—Aquaculture in and near the study area includes catfish and shrimp farming. (A) Aquaculture ponds near Robinson's Bend Field. (B) Pacific white shrimp (*Litopenaeus vannamei*) grown near the study area. (C) Advertisement published in the Tuscaloosa News for inland shrimp grown in west-central Alabama.

water with TDS content of about 5,000 mg/L, which is similar to much of the water produced from the CBM fields. The shrimp variety that is farmed is the pacific white shrimp (*Litopenaeus vannamei*), which need to be acclimated to the strongly brackish conditions in the ponds. One possibility is to use some of the produced water from the area to increase the salinity, which may help mitigate difficulty acclimating the shrimp, thereby increasing the productivity of the shrimp farms. A problem with the water that is currently used for shrimp farming is deficiency in Mg, and concentrations exceeding 200 mg/L in some of the saline brine from the Pottsville Formation may be of assistance.

Produced water can be used for any number of industrial purposes, especially those that do not require potable water but nevertheless draw on municipal water sources. Candidate industries in the region include oil refining, automotive manufacturing, and steel milling. The principal challenges for industrial reuse of produced water are removal of dissolved solids, suspended solids, metals, and dissolved organic compounds (e.g., Ahmadun and others, 2009; SPE, 2011). Technologies that assist in achieving these goals include flocculation, filtration, reverse osmosis, membrane separation, and artificial wetlands. Many of these technologies, including flocculation, reverse osmosis, and artificial wetlands, are already deployed by the CBM industry in Alabama at pilot to commercial scale.

Perhaps the most obvious industrial application for the produced water is reuse by the CBM industry. Reuse of water used in hydraulic fracturing is becoming common practice in the shale gas industry (e.g., Blauch, 2010; Gregory and others, 2011). Currently, the Alabama CBM industry is not using formation fluid for hydraulic fracturing. About a decade ago, a legal case related to concerns about contamination of domestic water supplies resulted in hydraulic fracturing being regulated as a Class II UIC process. A consequence of this action was the CBM industry relying exclusively on municipal water supplies for drilling and completion fluid. Hydraulic fracturing was excluded from regulation under the UIC program by the Energy Policy Act of 2005, but the industry continues using municipal water supplies, which can stress water systems during episodes of high usage and drought. Filtration of suspended solids is probably the only processing step that is needed to use produced water for hydraulic fracturing, and the water could easily be drawn from the retaining ponds at existing water treatment facilities.

TECHNOLOGY TRANSFER

The project team has conducted a vigorous technology transfer program throughout this project. Project results have been presented at several technical meetings and workshops and have been disseminated through technical publications. An essential part of this research was the support and cooperation of the CBM industry, and the Coalbed Methane Association of Alabama played a vital role in this effort. All producers in the basin participated in the program, which not only facilitated well access, but provided valuable information and feedback that guided the project and helped ensure the dissemination of results. A project web site has been developed to highlight the project and to make publications and other materials available for download. The URL for the website is:

http://www.gsa.state.al.us/gsa/cbm/Coalbed%20Methane%20Research.htm.

This final report, including supporting data and the GIS product will be made available through this website upon final approval and successful closeout of the project. A listing of the presentations and publications developed during this project is given below.

Presentations

October 2013, Dynamics of Thermogenic and Late-Stage Biogenic Gas Generation: Examples from Black Warrior Basin Coalbed Methane Reservoirs (keynote lecture): State College, Pennsylvania, International Conference on Coal Science and Technology.

August 2013, Basin Hydrology and Water Management in Coalbed Methane Reservoirs of the Black Warrior Basin: Innovative Water Management (short course), Applied Technology Workshop sponsored by Petroleum Technology Transfer Council, Morgantown West Virginia.

August 2013, Unconventional Resources Technology Conference (coalbed methane session), Denver, Colorado.

June 2013, Water Risks and Mitigation Strategies in Unconventional Development, American Association of Petroleum Geologists Annual Conference and Exposition, Pittsburgh, Pennsylvania.

November 2012, Appalachian-Ouachita-Marathon Fold-Thrust Belts and Foreland Basins: Their Stratigraphy, Sedimentology, Structural Evolution, and Economic Significance (theme session): Charlotte, North Carolina, Geological Society of America Annual Meeting.

November 2011, The Astronomical Pottsville: From Milankovitch Cycles to Rolling Tides (lecture): Birmingham, Alabama Paleontological Society Monthly Meeting.

October 2011, Structural Geology and Tectonics of Foreland Basins (theme session): Minneapolis, Minnesota, Geological Society of America Annual Meeting.

October 2011, Coal Systems: Sedimentation, Petrology, Natural Resources, and Environmental Sustainability (theme session): Minneapolis, Minnesota, Geological Society of America Annual Meeting.

September 2011, Coalbed Methane: The Unrealised Potential: Kolkata, West Bengal, India, Society of Petroleum Engineers Applied Technology Workshop.

August 2010, Environmental technologies for environmental and resource management for shale gas and coalbed methane plays (technical session): San Antonio, Texas, 17th International Petroleum and Biofuels Environmental Conference, sponsored by U.S. Department of Energy and Petroleum Technology Transfer Council.

May 2010, International Coalbed & Shale Gas Symposium, University of Alabama, Tuscaloosa, Alabama.

April 2010, Geology of unconventional gas plays in the southern Appalachian thrust belt (field trip), American Association of Petroleum Geologists Annual Conference and Exposition, New Orleans, Louisiana.

March 2010, Energy resources in the eastern United States and environmental effects (theme session): Baltimore, Maryland, Geological Society of America Combined Northeastern and Southeastern Section Meeting.

October 2009, Unconventional energy resources: making the unconventional conventional: 29th Annual Gulf Coast Section SEPM Foundation Bob. F. Perkins Research Conference, Houston, Texas.

September 2009, Unconventional gas research at the Geological Survey of Alabama: Tuscaloosa, Alabama, University of Alabama College of Continuing Studies, 2009 Alabama Mining Institute.

Publications

Pashin, J. C., McIntyre, M. R., Mann, S. D., Kopaska-Merkel, D. C., Varonka, M., and Orem, W., in press, Relationships between Water and Gas Chemistry in Mature Coalbed Methane Reservoirs of the Black Warrior Basin: International Journal of Coal Geology, http://dx.doi.org/10.1016/j.coal.2013.10.002.

Pashin, J. C., in press, Geology of North American coalbed methane reservoirs, in Thakur, P., Aminian, K., and Schatzel, S. A., eds., Coalbed Methane: From Prospect to Pipeline: Amsterdam, Elsevier.

Pashin, J. C., in press, Unconventional energy resources: 2013 review—Coalbed methane: Natural Resources Research, http://dx.doi.org/10.1007/s11053-013-9224-6.

McIntyre-Redden, M. R., Mann, S. M., and Pashin, J. C., 2013, Produced water variability and water management strategies in the coalbed methane play of the Black Warrior Basin, Alabama: Geological Society of America Abstracts with Programs, v. 45, no. 7, p. 175.

Pashin, J. C., 2013, Dynamics of thermogenic and late-stage biogenic gas generation in coalbed methane reservoirs of the Black Warrior basin: Denver, Unconventional Resources Technology Conference Proceedings, paper 1580306, 9 p.

Pashin, J. C., 2013, Dynamics of thermogenic and late-stage biogenic gas generation: example from Black Warrior Basin coalbed methane reservoirs: State College, Penn State University, International Conference on Coal Science and Technology Proceedings, unpaginated CD-ROM.

Orem, W. H., Tatu, C. A., Varonka, M., Pashin, J. C., and Engle, M., 2013, Organic substances in produced and formation water from natural gas production in coal and shale: American Association of Petroleum Geologists Annual Conference and Exposition Proceedings, unpaginated CD-ROM.

Moore, M. F., Hames, W. E., Pashin, J. C., and Uddin, Ashraf, 2012, Competing depositional systems: ^{40}Ar/^{39}Ar detrital muscovite age and sandstone compositional analysis in

determining paleodrainage patterns and provenance of the Pottsville Formation in the greater Black Warrior basin Geological Society of America Abstracts with Programs, v. 44, no. 7, p. 539.

Hames, W. E., Uddin, Ashraf, Pashin, J. C., Eriksson, K. A., and Moore, M. F., 2011, From source to sink: a comparison of muscovite ages from the southern Appalachian bedrock and Carboniferous basin: Geological Society of America Abstracts with Programs, v. 43, no. 5, p. 44.

Moore, M. F., Hames, W., Uddin, A., and Pashin, J. C., 2011, Voices from the deep: the sedimentology and detrital mineral geochronology of the Black Warrior basin depocenter: Geological Society of America Abstracts with Programs, v. 43, no. 5, p. 315.

Moore, M. F., Hames, W., Uddin, A., and Pashin, J. C., 2011, ^{40}Ar/^{39}Ar dating of detrital muscovite from the Pottsville Formation in the greater Black Warrior basin and implications for Appalachian tectonics: Geological Society of America Abstracts with Programs, v. 43, no. 2, p. 10.

Moore, M. F., Hames, W., Uddin, A., Pashin, J. C., and Priester, Catherine, 2011, Petrology and detrital geochronology of the Carboniferous sedimentary Appalachians, southeastern USA: Geological Society of America Abstracts with Programs, v. 43, no. 5, p. 432.

Pashin, J. C., and Groshong, R. H., Jr., 2011, Structural chronology of the Black Warrior foreland basin: Geological Society of America Abstracts with Programs, v. 43, no. 5, p. 315.

Pashin, J. C., 2011, Unconventional energy resources: 2011 review—Coalbed methane: Natural Resources Research, v. 20, p. 282-286.

Pashin, J. C., McKinney, G. M., Mann, S. D., Kopaska-Merkel, D. C., and McIntyre, M. R., 2011, Developing produced water management strategies for coalbed methane operations in the Black Warrior basin: Geological Society of America Abstracts with Programs, v. 43, no. 5, p. 498.

Pashin, J. C., 2010, Variable gas saturation in coalbed methane reservoirs of the Black Warrior basin: implications for exploration and production: International Journal of Coal Geology, v. 82, p. 135-146, doi:10.1016/j.coal.2009.10.017.

Pashin, J. C., 2010, Mature coalbed natural gas reservoirs and operations in the Black Warrior basin of Alabama, *in* Reddy, K. J., ed., Coalbed Natural Gas: Energy and Environment: Haupage, New York, Nova Science Publishers, p. 31-57.

Pashin, J. C., Carroll, R. E., McIntyre, M. R., and Grace, R. L. B., 2010, Geology of unconventional gas plays in the southern Appalachian thrust belt: Society for Sedimentary Geology (SEPM) Guidebook, Field Trip 7, American Association of Petroleum Geologists Annual Conference and Exposition, New Orleans, Louisiana, 86 p.

Pashin, J. C., McIntyre, M. R., McKinney, G. M, III, Kopaska-Merkel, D. C., and Mann, S. D., 2010, Developing produced water management strategies for coalbed methane operations in the Black Warrior basin: Tuscaloosa, Alabama, University of Alabama, College of Continuing Studies, 2010 International Coalbed & Shale Gas Symposium Proceedings, paper 1017, 6 p.

Uddin, Ashraf, Hames, W. E., Peavy, Tara, and Pashin, J. C., 2010, Stratigraphic and detrital source constraints for Lower Pennsylvanian Pottsville Formation of Alabama and Mississippi: Geological Society of America Abstracts with Programs, v. 42, no. 5, p. 196.

Al-Jubori, A., Johnston, S., Boyer, C., Lambert, S. W., Bustos, O. A., Pashin, J. C., and Wray, A., 2009, Coalbed methane: clean energy for the world: Oilfield Review, v. 21, no. 2, p. 4-13.

Pashin, J. C., 2009, Implications of variable gas saturation in coalbed methane reservoirs of the Black Warrior basin, *in* Carr, T., D'Agostino, T., Ambrose, W. A., Pashin, J. C., and Rosen, N. C., eds., Unconventional energy resources: making the unconventional conventional: 29th Annual Gulf Coast Section SEPM Foundation Bob. F. Perkins Research Conference Proceedings, p. 329-352.

Groshong, R. H., Jr., Pashin, J. C., McIntyre, M. R., 2009, Structural controls on fractured coal reservoirs in the southern Appalachian Black Warrior foreland basin: Journal of Structural Geology, v. 31, p. 874-886, doi:10.1016/j.jsg.2008.02.017.

FUTURE RESEARCH DIRECTIONS

This project has made significant progress in understanding the controls on the composition of formation water in Black Warrior CBM reservoirs and the possibilities for disposal and utilization of the produced water. Along the way, a number of research issues were identified that can benefit industry and contribute to a fundamental understanding of the characteristics and behavior of unconventional gas reservoirs. These issues include treatment efficiency, the origin of nitrogen compounds, organic geochemistry, biogenic gas generation, flow modeling, and computer simulation.

Besides chlorides, organic and nitrogen compounds are the principal constituents of concern in produced water from the Black Warrior CBM fields. Regulatory limitations on instream disposal are based principally on conductivity, which is a proxy for TDS and chloride content. Although the water processing technologies employed by the CBM industry are expected to minimize the concentration of organic and nitrogen compounds through aeration, evaporation, and flocculation, the precise fate of these and other compounds is currently unknown. Thus, one possibility for future research is to analyze water composition at a series of processing steps in a range of processing facilities so that the changes in composition can be quantified and understood. Analyzing the effectiveness of different processing technologies, moreover, will inform the decision process for selecting instream disposal, underground disposal, reverse osmosis, artificial wetland, and beneficial use options, such as those involving the inland shrimping industry.

From the perspective of basic science, one of the most important contributions of this research is the realization of the importance of nitrogen compounds in unconventional reservoirs, particularly those that support methanogenic microbial communities. The nitrogen cycle is well understood in marine, lacustrine, and soil environments, but relatively little is known about how the nitrogen cycle applies to the deep subsurface. Avenues for future research include additional characterization of nitrogen compounds and associated chemical processes in produced water, developing a fundamental understanding of nitrogen isotope fractionation processes in CBM reservoirs, and development of a nitrogen cycle model for the subsurface.

Organic compounds in the produced water are varied and complex, and these compounds are of interest from the standpoints of human health and safety. Indeed, understanding the potential impacts of organic compounds is essential for beneficial use of the produced water beyond industrial applications in the CBM industry. The organic compounds, moreover, play an important role in the formation of the coalbed gas reservoirs and are the product of a complex interplay among burial diagenesis, thermal maturation, and biogenesis. Accordingly, continued research is necessary to develop a more robust knowledge of the varieties of organic compounds that are present in unconventional gas reservoirs and how they relate to the thermal, geochemical, and biotic history of sedimentary basins.

Recent geochemical research (e.g., Vinson and others, 2012) indicates that the geochemical pathways for microbial methanogenesis may proceed along different lines than is commonly assumed. Because of this, established isotopic fractionation equations for biogenic gas systems commonly do not apply to organic-rich strata like coal and shale. Hence, continued analysis of basic water chemistry and organic compounds should be coupled with analysis of stable isotopes in organic-rich strata to develop new geochemical models that can aid in exploration and development of unconventional reservoirs.

Freshwater intrusions have long been understood to control the development of biogenic gas systems in coal and shale (e.g., Pashin and others, 1991; Ayers and Kaiser, 1994), but relatively little is known about the rates of plume development and the attendant geochemical processes that result in commercial hydrocarbon accumulations. Evidence from the Pottsville Coal Interval indicates that hydraulic properties of coal-bearing strata are strongly stratified, giving each coal zone different properties that affect the recoverability of natural gas. A major impediment for the development of realistic flow models simulating plume formation and drainage in CBM reservoirs is difficulty in model dual porosity systems containing large populations of natural fractures. This difficulty arises from computational inefficiency when simulating flow in discrete fractures along with flow in porous or microporous rock matrix. Recent research at the GSA on combining discrete network and continuum modeling techniques made significant progress toward solving this difficulty (Clark and others, 2013) and can form the basis of next-generation reservoir simulators and basin models for unconventional gas reservoirs.

SUMMARY AND CONCLUSIONS

The Black Warrior Basin of Alabama is the cradle of the modern coalbed methane industry and has produced more than 2.6 trillion cubic feet of gas and 1.6 billion barrels of water since 1980. The coalbed gas industry in this area is dependent on instream disposal of co-produced water, which ranges from nearly potable sodium-bicarbonate water to hypersaline sodium-chloride water. This report summarizes a four-year effort that was directed at characterizing the geology and geochemistry of the produced fluids and evaluating water management strategies in the basin. Options for produced water management include instream disposal, underground injection, and beneficial use for water supply, agriculture, and industry.

This study employed diverse analytical methods. A range of subsurface and surface methods that utilized geophysical well logs and geological databases were employed to refine the stratigraphic, structural, and hydrodynamic framework of the basin. Wellhead water samples from 206 coalbed methane wells were analyzed for a broad range of geochemical parameters, including physical and aggregate properties, major ionic compounds, metallic and nonmetallic substances, organic compounds, and nitrogen compounds. Wellhead gas samples were taken from 103 sites and analyzed for bulk composition and stable isotopes, specifically carbon and deuterium. Petrologic techniques were applied to determine the framework composition of sandstone and shale and to analyze carbon and oxygen isotopes in calcite veins. Production data were compiled to evaluate the decline characteristics of coalbed methane wells. Cumulative, peak, and annual production data were analyzed statistically and mapped. A geographic information system was developed that assembles the broad range of data collected during this project. This system was used to evaluate historical and current water management practice and to inform the identification of new practices that may be of value to the coalbed methane industry.

Integrated geological and geochemical analysis of produced water and gas reveals strong interrelationships among regional geology, water chemistry, and gas chemistry. Coalbed methane is produced from multiple coal seams in Pennsylvanian-age strata of the Pottsville Coal Interval, which constitutes a thick succession of shale, sandstone, and coal. Water chemistry in the Pottsville Coal Interval is influenced by a structurally controlled meteoric recharge area along the southeastern margin of the basin, and the most promising opportunities for beneficial use are near the recharge zone. Salinity increases with distance from the recharge zone, and the inability to pump wells to capacity where salinity is highest helps determine the economic viability of gas production. The most important constituents of concern in the produced water include chlorides, ammonia compounds, and organic substances. Regional mapping and statistical analysis indicate that the concentrations of most ionic compounds, metallic substances, and nonmetallic substances correlate with total dissolved solids and chlorides.

Bulk chemistry of the produced gas is nearly invariant, whereas the stable isotopic composition of the gas varies regionally. The produced gas is enriched in ^{13}C in medium-volatile and low-volatile bituminous coal, suggesting a significant thermogenic component of gas generation. However, regional unroofing and cooling indicates that the coal would have been greatly undersaturated with CH_4 without additional gas generated by late-stage microbial methanogenesis. The gas becomes depleted in ^{13}C as coal rank decreases to high volatile B bituminous away from the recharge area. Stable isotopic analysis of produced gas and calcite cement indicates that widespread late-stage microbial methanogenesis occurred primarily along a CO_2 reduction metabolic pathway.

Significant concentrations of organic compounds in the produced water appear to have helped sustain microbial communities. Ammonia and ammonium levels increase with total dissolved solids content and appear to have played a role in late-stage microbial methanogenesis and the generation of N_2. Indeed, a range of reactions involving, organic matter, minerals, and formation water, may have contributed some N_2, which is the only significant nonhydrocarbon impurity in the produced gas. Biotic degradation of organic compounds may have been augmented by deionization of NH_4^+ thus providing multiple sources of H_2 for microbial CO_2 reduction.

Petrologic analysis indicates that sandstone in the Pottsville Coal Interval is principally litharenite with minimal matrix porosity and permeability. Flow of water occurs mainly in natural fractures, and closely spaced cleats give the coal seams the ability to support commercial flow rates. Fractures are commonly filled with calcite, and carbon and oxygen isotopes are valuable recorders of ancient thermal and geochemical conditions. Carbon isotopic data confirm that microbial methanogenesis was an important process in the Pottsville Coal Interval. Oxygen isotopes, moreover, suggest that mineralization and microbial methanogenesis occurred at or near modern burial depth.

Analysis of production data indicates that gas production tends to decline exponentially, whereas water production tends to decline hyperbolically. Hyperbolic decline of water production indicates that managing water volume is of primary concern early in the life of a coalbed methane project and that wells tend to produce at steady rate later in the life cycle. Peak production correlates strongly with cumulative production and is thus a valuable early indicator of long-term well performance. Regional mapping indicates that gas production is controlled primarily by the ability to depressurize permeable coal seams that are natively within the steep part of the adsorption isotherm. Water production is greatest in areas with near normal hydrostatic reservoir pressure within the freshwater intrusion and below thick Cretaceous cover strata. By comparison, water production is least in areas of induced underpressure associated with coal mining and in areas of natural underpressure basinward of the freshwater intrusion.

Water management strategies include instream disposal, which can be applied effectively in most parts of the basin. Deep disposal may be applicable locally, particularly where high salinity limits the ability to dispose into streams. Artificial wetlands show promise for the management of saline water, especially where the reservoir yield is limited. Beneficial use options include municipal water supply, agricultural use, and industrial use. The water may be of use to an inland shrimp farming industry, which is active around the southwestern coalbed methane fields. The best opportunities for beneficial use are reuse of water by the coalbed methane industry for drilling and hydraulic fracturing. This research has further highlighted opportunities for additional research on treatment efficiency, the origin of nitrogen compounds, organic geochemistry, biogenic gas generation, flow modeling, and computer simulation. Results of this study are being disseminated through a vigorous technology transfer program that includes web resources, numerous presentations to stakeholders, and a variety of technical publications.

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REFERENCES CITED

Ahmadun, F. L., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S. and Abidin, Z. Z., 2009, Review of technologies for oil and gas produced water treatment: Journal of Hazardous Materials, v. 170, p. 530-551.

Ayers, W. B., Jr., and Kaiser, W. A. (eds.), 1994, Coalbed methane in the Upper Cretaceous Fruitland Formation, San Juan Basin, Colorado and New Mexico: Texas Bureau of Economic Geology Report of Investigations 218, 216 p.

Barker, D. S., 1964, Ammonium in alkali feldspars: American Mineralogist, v. 49, p. 851–854.

Bates, B. L., McIntosh, J. C., Lohse, K. A., and Brooks, P. D., 2011, Influence of groundwater flowpaths, residence times, and nutrients on the extent of microbial methanogenesis in coal beds: Powder River Basin, USA: Chemical Geology, v. 284, p. 45-61.

Blauch, M. E., 2010, Developing effective and environmentally suitable fracturing fluids using hydraulic fracturing flowback waters: Society of Petroleum Engineers paper, doi: 10.2118/131784-MS, 12 p.

Bradley, J. S., 1975, Abnormal formation pressure: American Association of Petroleum Geologists Bulletin, v. 59, p. 957-973.

Bradley, J. S., and Powley, D. E., 1994, Pressure compartments in sedimentary basins: a review: American Association of Petroleum Geologists Memoir 61, p. 3-26.

Budai, J. M., Martini, A. M., Walter, L. M., and Ku, T. C. W., 2002, Fracture-fill calcite as a record of microbial methanogenesis and fluid migration: a case study from the Devonian Antrim Shale, Michigan Basin: Geofluids, v. 2, p. 163–183.

Bustin, R. M., 1997, Importance of fabric and composition on the stress sensitivity of permeability in some coals, northern Sydney basin, Australia: relevance to coalbed methane exploitation: American Association of Petroleum Geologists Bulletin, v. 81, p. 1894-1908.

Bustin, A. M. M., and Bustin, R. M., 2008, Coal reservoir saturation: impact of temperature and pressure: American Association of Petroleum Geologists Bulletin, v. 92, p. 77–86.

Butts, Charles, 1910, Description of the Birmingham Quadrangle, Alabama: U.S. Geological Survey Geologic Atlas, Folio 175, 24 p.

___1926, The Paleozoic rocks, *in* Adams, G. I., Butts, Charles, Stephenson, L. W., and Cooke, C. W., Geology of Alabama: Alabama Geological Survey Special Report 14, p. 41-230.

___1927, Bessemer-Vandiver folio: U.S. Geological Survey Geologic Atlas, Folio 221, 22 p.

Carlston, C. W., 1944, Ground-water resources of the Cretaceous area of Alabama: Alabama Geological Survey Special Report 18, 203 p.

Carothers, W. W., and Kharaka, Y. K., 1978, Aliphatic acid anions in oil-field waters—implications for the origin of natural gas: American Association of Petroleum Geologists Bulletin, v. 62, p. 2441-2453.

Carroll, R. E., Pashin, J. C., and Kugler, R. L., 1995, Burial history and source-rock characteristics of Upper Devonian through Pennsylvanian strata, Black Warrior basin, Alabama: Alabama Geological Survey Circular 187, 29 p.

Cates, L. M., and Groshong, R. H., Jr., 1999, Confirmation of regional thin-skinned extension in the eastern Black Warrior basin, Alabama, *in* Pashin J. C., and Carroll, R. E., eds., 1999, Geology of the Cahaba coalfield: Alabama Geological Society 36th Annual Field Trip Guidebook, p. 49-57.

Clark, P. E., Pashin, J. C., Carlson, E., Goodliffe, A. M., and Thompson, Mason, 2013, Site characterization for CO_2 storage from coal-fired power facilities in the Black Warrior Basin of Alabama: U.S. Department of Energy, National Energy Technology Laboratory, Final Report, contract DE-FE0001910, 219 p.

Clayton, J. L., Leventhal, J. S., Rice, D. D., Pashin, J. C., Mosher, Byard, and Czepiel, Peter, 1994, Atmospheric methane flux from coals—preliminary investigation of coal mines and geologic structures in the Black Warrior basin, Alabama, *in* Howell, D. G., ed., The Future of Energy Gases: U.S. Geological Survey Professional Paper 1570, p. 471-492.

Culbertson, W. C., 1964, Geology and coal resources of the coal-bearing rocks of Alabama. U.S. Geological Survey Bulletin 1182-B, 79 p.

Debajyoti, P. and Skrzypek, G., 2007, Assessment of carbonate-phosphoric acid analytical technique performed using GasBench II in continuous flow isotope ratio mass spectrometry: International Journal of Mass Spectrometry, v. 262, p. 180-186.

Demko T. M., and Gastaldo R. A., 1996, Eustatic and autocyclic influences on deposition of the lower Pennsylvanian Mary Lee coal zone, Warrior Basin, Alabama: International Journal of Coal Geology, v. 31, p. 3-19.

Dickinson, W. R., and Suczek, C. A., 1979, Plate tectonics and sandstone compositions: AAPG Bulletin, v. 63, p. 2164-2182.

Duit, W., Jansen, J. B. H., van Breemen, A., and Bos, A., 1986, Ammonium micas in metamorphic rocks as exemplified by Dome de L'Agout (France): American Journal of Science, v. 286, p. 702-732.

Eble, C. F., 1990, A palynological transect, swamp interior to swamp margin, in the Mary Lee coal bed, Warrior basin, Alabama, *in* Gastaldo, R. A., Demko, T. M., and Liu, Y. eds., Carboniferous coastal environments of the Mary Lee coal zone, Marion and Walker

Counties, Alabama: Geological Society of America Southeastern Section Guidebook, Field Trip 5, Alabama Geological Survey Guidebook Series 3-VI, p. 65-81.

Ellard, J. S., Roark, R. P., and Ayers, W. B., Jr., 1992, Geologic controls on coalbed methane production: an example from the Pottsville Formation (Pennsylvanian Age), Black Warrior basin, Alabama, U.S.A., in Beamish, B. B., and Gamson, P. D., eds., Symposium on coalbed methane research and development in Australia: Townsville, Australia, James Cook University of North Queensland, p. 45-61.

Elder, C. H., and Deul, Maurice, 1974, Degasification of the Mary Lee coalbed near Oak Grove, Jefferson County, Alabama, by vertical borehole in advance of mining: U.S. Bureau of Mines Report of Investigations 7968, 21 p.

Eugster, H. P., and Munoz, J., 1966, Ammonium micas: Possible sources of atmospheric ammonia and nitrogen: Science, v. 151, p. 683–686.

Ferm, J. C., Ehrlich, Robert, and Neathery, T. L., 1967, A field guide to Carboniferous detrital rocks in northern Alabama: Geological Society of America 1967 Coal Division Field Trip Guidebook, 101 p.

Ferm, J. C., and Weisenfluh, G. A., 1989, Evolution of some depositional models in Late Carboniferous rocks of the Appalachian coal fields: International Journal of Coal Geology, v. 12, p. 259-292.

Flores, R. M., ed., 2008, Microbes, methanogenesis, and microbial gas in coal: International Journal of Coal Geology, v. 76, 186 p.

Folk, R. L., 1974, Petrology of sedimentaty rocks: Hemphill, 182 p.

Friedman, I., and O’Neil, J. R., 1977, Compilation of stable isotope fractionation factors of geochemical interest, *in* Fleischer, M. (ed.), Data of Geochemistry, 6th edition, U.S. Geological Survey Professional Paper 440-KK, 12 p.

Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., Asner, G. P., Cleveland, C. C., Green, P. A., Holland, E. A., Karl, D. M., Michaels, A. F., Porter, J. H., Townsend, A. R., and Vörösmarty, C. J., 2004, Nitrogen cylces: Past, present, and future: Biogeochemistry, v. 70, p. 153-226.

Galloway, W.E., 1989, Genetic stratigraphic sequences in basin analysis I: architecture and genesis of flooding-surface bounded depositional units: American Association of Petroleum Geologists Bulletin, v. 73, p. 125-142.

Gamson, P. D., Beamish, B. B., and Johnson, D. P., 1993, Coal microstructure and micropermeability and their effects on natural gas recovery: Fuel, v. 72, p. 87-99.

Gastaldo, R. A., Demko, T. M., and Liu, Y., 1993, Application of sequence and genetic stratigraphic concepts to Carboniferous coal-bearing strata: An example from the Black Warrior Basin, USA: Geologische Rundschau, v. 82, p. 212-226.

Goldhaber, M. B., Lee, R. C., Hatch, J. R., Pashin, J. C., and Treworgy, J., 2003, The role of large-scale fluid flow in subsurface arsenic enrichment, *in* Welch, A. H. and Stollenwerk, K. G., eds., Arsenic in Ground Water: Geochemistry and Occurrence: Dordrecht, Kluwer Academic Press, p. 127-164.

Gould, K. W., Smith, J. W., 1979, The genesis and isotopic composition of carbonates associated with some Permian Australian coals: Chemical Geology, v. 24, p. 137-150.

Graves, S. L., Patton, A. F., and Beavers, W. M., 1983, Multiple zone coal degasification potential in the Warrior coal field of Alabama: Gulf Coast Association of Geological Societies Transactions, v. 33, p. 275-280.

Gregory, K. B., Vidic, R., and Dzombak, D. A., 2011, Water management challenges associated with the production of shale gas by hydraulic fracturing: Elements, v. 7, p. 181-186.

Groshong, R. H., Jr., Pashin, J. C., McIntyre, M. R., 2009, Structural controls on fractured coal reservoirs in the southern Appalachian Black Warrior foreland basin: Journal of Structural Geology, v. 31, p. 874-886, doi:10.1016/j.jsg.2008.02.017.

Groshong, R. H., Jr., Hawkins, W. B, Jr., Pashin, J. C., and Harry, D. L., 2010, Extensional structures of the Alabama promontory and Black Warrior foreland basin: Styles and relationship to the Appalachian fold-thrust belt, *in* Tollo, R.P., Bartholomew, M.J., Hibbard, J. P., and Karabinos, P. M., eds., From Rodinia to Pangea: The Lithotectonic Record of the Appalachian Region: Geological Society of America Memoir 206, p. 579-605.

Hall, F. E., Zhou, C., Gasem, K. A. M., Robinson, R. L., and Yee, D., 1994, Adsorption of pure methane, nitrogen, and carbon dioxide and their binary mixtures on wet Fruitland coal: Society of Petroleum Engineers, paper 29194.

Hanby, K. P., 1991, The use of production profiles for coalbed methane valuations: Tuscaloosa, Alabama, University of Alabama, 1991 Coalbed Methane Symposium Proceedings, p. 443-452.

Harpalani, S., and Ouyang, S., 1999: A new laboratory technique to estimate gas diffusion characteristics of coal: Tuscaloosa, University of Alabama, 1999 International Coalbed Methane Symposium Proceedings, p. 141-152.

Harpalani, S., and Schraufnagel, R. A., 1990, Shrinkage of coal matrix with release of gas and its impact on permeability of coal: Fuel, v. 69, p. 551-556.

Hatch, J. R., and Pawlewicz, M. J., 2007, Petroleum assessment of the Pottsville coal total petroleum system, Black Warrior basin, Alabama and Mississippi: U.S. Geological Survey Digital Data Series 69-1, Chapter 4, 28 p.

Hays, P. D., and Grossman, E. L., 1991, Oxygen isotopes in meteoric calcite cements as indicators of continental paleoclimate: Geology, v. 19, p. 441-444.

Hewitt, J. L., 1984, Geologic overview, coal, and coalbed methane resources of the Warrior basin—Alabama and Mississippi, *in* Rightmire, C. T., Eddy, G. E., and Kirr, J. N., eds., Coalbed methane resources of the United States: American Association of Petroleum Geologists Studies in Geology 17, p. 73-104.

Hobday, D. K., 1974, Beach and barrier island facies in the Upper Carboniferous of northern Alabama: Geological Society of America Special Paper 148, p. 209-224.

Horsey, C. A., 1981, Depositional environments of the Pennsylvanian Pottsville Formation in the Black Warrior basin of Alabama: Journal of Sedimentary Petrology, v. 51, p. 799-806.

Hunt, J. M., 1979, Petroleum Geochemistry and Geology: San Francisco, Freeman, 617 p.

Jones, E. P., Voytek, M.A., Corum, M. D., and Orem, W. H., 2010, Stimulation of methane generation from nonproductive coal by addition of nutrients or a microbial consortium: Applied Environmetal Microbiology, v. 7, p. 7013-7022.

Jüntgen, H., and Karweil, J., 1966, Gasbildung und Gasspeicherung in Steinkohlenflözen, Teilen 1 und 2: Erdol und Kohle-Erdgas-Petrochemie, v. 19, p. 339-344.

Jüntgen, H., and Klein, J., 1975, Entstehung von erdgas gos kohligen sedimenten: Erdöl und Köhle Petrochemistrie , v.1, p. 52-69.

Juster, T. C., Brown, P. E., and Bailey, S. W., 1987, NH_3-bearing illite in very low-grade metamorphic rocks associated with coal, northeastern Pennsylvania: American Mineralogist, v. 72, p. 555–565.

Kaiser, W. R., 1993, Abnormal pressure in coal basins of the western United States: Tuscaloosa, Alabama, University of Alabama, 1993 International Coalbed Methane Symposium Proceedings, v. 1, p. 173-186.

Karl, D. M., and Michaels, A. F., 2001, Nitrogen cycle, *in* Steele, J. H., Turekian, K. K., and Thorpe, S. (eds.), Encyclopedia of Ocean Sciences: New York, Academic Press, v. 4, p. 1876-1884.

Kidd, J. T., 1975, Pre-Mississippian stratigraphy of the Warrior Basin: Gulf Coast Association of Geological Societies Transactions, v. 25, p. 20-39.

___1976, Configuration of the top of the Pottsville Formation in west-central Alabama: Alabama State Oil and Gas Board Oil and Gas Map 1.

Koenig, R. A., 1989, Hydrologic characterization of coal seams for optimal dewatering and methane drainage: Quarterly Review of Methane from Coal Seams Technology, v. 7, p. 30–31.

Kreitler, C. W., 1989, Hydrogeology of sedimentary basins: Journal of Hydrology, v. 106, p. 29-53.

Kroos, B. M., van Bergen, F., Gensterblum, Y., Siemons, N, Pagnier, H. J. M., and David, P., 2001, High-pressure methane and carbon dioxide sorption on dry and moisture-equilibrated Pennsylvanian coals: International Journal of Coal Geology, v. 51, p. 69-92.

Lee, R. W., 1985, Geochemistry of ground water in Cretaceous sediments of the Southeastern Coastal Plain of eastern Mississippi and western Alabama: Water Resources Research, v. 21, p. 1545-1556.

Levine, J. R., 1996, Model study of the influence of matrix shrinkage on the absolute permeability of coal bed reservoirs: Geological Society of London Special Publication 109, p. 197-212.

Levine, J. R., and Telle, W. R., 1989, A coalbed methane resource evaluation in southern Tuscaloosa County, Alabama: School of Mines and Energy Development Research Report, 89-1, University of Alabama, 90 p.

Liu, Y., and Gastaldo, R. A., 1992, Characteristics of a Pennsylvanian ravinement surface: Sedimentary Geology, v. 77, p. 197-213.

Mack, G. H., Thomas, W. A., and Horsey, C. A., 1983, Composition of Carboniferous sandstones and tectonic framework of southern Appalachian-Ouachita orogen: Journal of Sedimentary Petrology, v. 54, p. 1444-1456.

Malone, P. G., Briscoe, F. H., Camp, B. S., and Boyer, C. M., II, 1987a, Discovery and explanation of low gas contents encountered in coalbeds at the GRI/USSC Big Indian Creek Site, Warrior basin, Alabama: Tuscaloosa, Alabama, University of Alabama, 1987 Coalbed Methane Symposium Proceedings, p. 63-72.

Martini, A. M., Walter, L. M., Ku, T. C. W., Budai, J. M., McIntosh, J. C., and Schoell., M., 2003, Microbial production and modification of gases in sedimentary basins: A geochemical case study from a Devonian shale gas play, Michigan basin: American Association of Petroleum Geologists Bulletin, v. 87, p. 1355-1375.

Martini, A. M., Walter., L. M., and McIntosh, J. C., 2008, Identification of microbial and thermogenic gas components from Upper Devonian black shale cores, Illinois and Michigan basins: American Association of Petroleum Geologists Bulletin, v. 92, p. 327-339.

McCalley, Henry, 1900, Report on the Warrior coal basin: Alabama Geological Survey Special Report 10, 327 p.

McFall, K. S., Wicks, D. E., and Kuuskraa, V. A., 1986, A geological assessment of natural gas from coal seams in the Warrior basin, Alabama - topical report (September 1985-September 1986): Washington, D. C., Lewin and Associates, Inc., Gas Research Institute contract no. 5084-214-1066, 80 p.

McKee, C. R., Bumb, A. C., and Koenig, R. A., 1988, Stress-dependent permeability and porosity of coal and other geologic formations: Society of Petroleum Engineers Formation Evaluation, March, 1988, p. 81-91.

McLaughlin, J. F., Frost, C. D., and Sharma, S. S., 2010, Geochemical analysis of Atlantic Rim water, Carbon County, Wyoming: New applications for characterizing coalbed natural gas reservoirs: American Association of Petroleum Geologists Bulletin, v. 95, p. 191-217.

Metzger, W. J, 1965, Pennsylvanian stratigraphy of the Warrior basin, Alabama: Alabama Geological Survey Circular 30, 80 p.

Mingram, B., Hoth, P., Lüders, V., and Harlov, D., 2005, The significance of fixed ammonium in Palaeozoic sediments for the generation of nitrogen-rich natural gases in the North German Basin: International Journal of Earth Sciences, v. 94, p. 1010-1022.

Moore, M. F., 2012, ^{40}Ar/^{39}Ar dating of detrital muscovite and sediment composition analysis from the southern Carboniferous Appalachian basin in Alabama: Implications for Tectonics and Sedimentation: unpublished M.S. thesis, Auburn University, 101 p.

Oh, M. S., Taylor, R. W., Coburn, T. T., Crawford, R. W., 1988, Ammonia evolution during oil shale pyrolysis: Energy Fuels, v. 2, p. 100-105.

O'Neil, P. E., Harris, S. C., Drottar, K. R., Mount, D. R., Fillo, J. P., and Mettee, M. F., 1989, Biomonitoring of a produced water discharge from the Cedar Cove degasification field, Alabama: Alabama Geological Survey Bulletin 135, 195 p.

O'Neil, P. E., Harris, S. C., Mettee, M. F., Shepard, T. E., and McGregor, S. W., 1993, Surface discharge of wastewaters from the production of methane from coal seams in Alabama, the Cedar Cove model: Alabama Geological Survey Bulletin 155, 259 p.

Orem W. H., Tatu C. A., Lerch H. E., Rice C. A., Bartos T. T., Bates A. L., Tewalt S., and Corum M. D., 2007, Organic compounds in produced waters from coalbed natural gas wells in the Powder River Basin, Wyoming, USA: Applied Geochemistry, v. 22, p. 2240-2256.

Ortiz, I., Weller, T. F., Anthony, R. V., Frank, J., Linz, D., and Nakles, D., 1993, Disposal of produced waters: underground injection option in the Black Warrior basin: Tuscaloosa, Alabama, University of Alabama, 1993 International Coalbed Methane Symposium Proceedings, p. 339-364.

Osborne, W. E., Szabo, M. W., Copeland, C. W., Jr., and Neathery, T. L., 1989, Geologic map of Alabama: Alabama Geological Survey Special Map 221, scale 1:500,000.

Pashin, J. C., 1994a, Flexurally influenced eustatic cycles in the Pottsville Formation (Lower Pennsylvanian), Black Warrior basin, Alabama, *in* Dennison, J. M., and Ettensohn, F. R. eds., Tectonic and Eustatic Controls on Sedimentary Cycles: Society of Economic Paleontologists and Mineralogists Concepts in Sedimentology and Paleontology, v. 4, p. 89-105.

___1994b, Cycles and stacking patterns in Carboniferous rocks of the Black Warrior foreland basin: Gulf Coast Association of Geological Societies Transactions, v. 44, p. 555-563.

___1994c, Coal-body geometry and synsedimentary detachment folding in Oak Grove coalbed-methane field, Black Warrior basin, Alabama: American Association of Petroleum Geologists Bulletin, v. 78, p. 960-980.

___1998, Stratigraphy and structure of coalbed methane reservoirs in the United States: an overview: International Journal of Coal Geology, v. 35, p. 207-238.

___2004, Cyclothems of the Black Warrior basin in Alabama: eustatic snapshots of foreland basin tectonism, *in* Pashin, J. C. and Gastaldo, R. A., eds., Sequence stratigraphy, paleoclimate, and tectonics of coal-bearing strata: American Association of Petroleum Geologists Studies in Geology 51, p. 199-217.

___2007, Hydrodynamics of coalbed methane reservoirs in the Black Warrior Basin: key to understanding reservoir performance and environmental issues: Applied Geochemistry, v. 22, p. 2257-2272.

___2008, Coal as a petroleum source rock and reservoir rock, *in* Ruiz, I. S., and Crelling, J. C., eds., Applied Coal Petrology—The Role of Petrology in Coal Utilization: Amsterdam, Elsevier, p. 227-262.

___2009, Implications of variable gas saturation in coalbed methane reservoirs of the Black Warrior basin, *in* Carr, T., D'Agostino, T., Ambrose, W. A., Pashin, J. C., and Rosen, N. C., eds., Unconventional energy resources: making the unconventional conventional: 29th Annual Gulf Coast Section SEPM Foundation Bob. F. Perkins Research Conference Proceedings, p. 329-352.

___2010a, Variable gas saturation in coalbed methane reservoirs of the Black Warrior basin: implications for exploration and production: International Journal of Coal Geology, v. 82, p. 135-146, doi:10.1016/j.coal.2009.10.017.

___2010b, Mature coalbed natural gas reservoirs and operations in the Black Warrior basin of Alabama, in Reddy, K. J., ed., Coalbed Natural Gas: Energy and Environment: Haupage, New York, Nova Science Publishers, p. 31-57.

Pashin, J. C., Carroll, R. E., Hatch, J. R., and Goldhaber, M. B., 1999, Mechanical and thermal control of cleating and shearing in coal: examples from the Alabama coalbed methane fields, USA, in Mastalerz, M., Glikson, M., and Golding, S., eds., Coalbed Methane: Scientific, Environmental and Economic Evaluation: Dordrecht, Netherlands, Kluwer Academic Publishers, p. 305-327.

Pashin, J. C., and Groshong, R. H., Jr., 1998, Structural control of coalbed methane production in Alabama: International Journal of Coal Geology, v. 38, p. 89-113.

Pashin, J. C., Guohai Jin, and Payton, J. W., 2004, Three-dimensional computer models of natural and induced fractures in coalbed methane reservoirs of the Black Warrior basin: Alabama Geological Survey Bulletin 174, 62 p.

Pashin, J. C., Guohai Jin, Chunmiao Zheng, Song Chen, and McIntyre, M. R., 2008, Discrete fracture networks for Risk Assessment of Carbon Sequestration in Coal: Final Technical Report, U.S. Department of Energy, National Energy Technology Laboratory, Award DE-FC26-05NT42435, 118 p.

Pashin, J. C., and Hinkle, Frank, 1997, Coalbed methane in Alabama: Alabama Geological Survey Circular 192, 71 p.

Pashin, J. C., Kopaska-Merkel, D. C., Arnold, A. C., and McIntyre, M. R.*, 2011, Geological foundation for production of natural gas from diverse shale formations: Research Partnership to Secure Energy for America (RPSEA) Final Report 07122.17.01, 156 p.

Pashin, J. C., and McIntyre, M. R., 2003, Temperature-pressure conditions in coalbed methane reservoirs of the Black Warrior basin, Alabama, U.S.A: implications for carbon sequestration and enhanced coalbed methane recovery: International Journal of Coal Geology, v. 54, p. 167-183.

Pashin, J. C., McIntyre, M. R., Carroll, R. E., Groshong, R. H., Jr., and Bustin, R. M., 2009, Carbon sequestration and enhanced recovery potential of mature coalbed methane reservoirs in the Black Warrior basin, *in* Grobe, M., Pashin, J. C., and Dodge, R. L., eds., Carbon dioxide sequestration in geological media: State of the science: American Association of Petroleum Geologists Studies in Geology 59, p. 125-147.

Pashin, J. C., McIntyre, M. R., Clark, P. E., and Esposito, R. A., 2010, Final report, Southeastern Regional Carbon Sequestration Partnership (SECARB) Phase II, SECARB Black Warrior Test Site, Blue Creek Field, Tuscaloosa County, Alabama: Virginia Tech Subaward Agreement CR-19655-415227 under U.S. Department of Energy Prime Award DE-FC26-05NT42590, 101 p.

Pashin, J. C., McIntyre, M. R., Mann, S. D., Kopaska-Merkel, D. C., Varonka, M., and Orem, W., in press, Relationships between water and gas chemistry in mature coalbed methane reservoirs of the Black Warrior Basin: International Journal of Coal Geology, http://dx.doi.org/10.1016/j.coal.2013.10.002.

Pashin, J. C., and Raymond, D. E., 2004, Glacial-eustatic control of coalbed methane reservoir distribution (Pottsville Formation; Lower Pennsylvanian) in the Black Warrior basin of Alabama: Tuscaloosa, Alabama, University of Alabama College of Continuing Studies, 2004 International Coalbed Methane Symposium Proceedings, Paper 0413, 15 p.

Pashin, J. C., Ward, W. E., II, Winston, R. B., Chandler, R. V., Bolin, D. E., Richter, K. E., Osborne, W. E., and Sarnecki, J. C., 1991, Regional analysis of the Black Creek-Cobb coalbed-methane target interval, Black Warrior basin, Alabama: Alabama Geological Survey Bulletin 145, 127 p.

Pitman, J. K., Pashin, J. C., Hatch, J. R., and Goldhaber, M. B., 2003, Origin of minerals in joint and cleat systems of the Pottsville Formation, Black Warrior basin, Alabama: implications for coalbed methane generation and production: American Association of Petroleum Geologists Bulletin, v. 87, p. 713-731.

Raymond, D. E., 1990, Petrography of sandstones of the Pottsville Formation in the Jasper Quadrangle, Black Warrior basin, Alabama: Alabama Geological Survey Circular 144, 48 p.

Raymond, R. N., 1991, Regulatory aspects of permitting and operating a class II salt water disposal (SWD) well in the coalbed methane production areas of Alabama: Tuscaloosa, Alabama, University of Alabama, 1991 Coalbed Methane Symposium Proceedings, p. 69-73.

Reddy, K. J., ed., 2010, Coalbed Natural Gas: Energy and Environment: Haupage, New York, Nova Science Publishers, p. 533 p.

Rheams, L. J., and Benson, D. J., 1982, Depositional setting of the Pottsville Formation in the Black Warrior basin: Alabama Geological Society 19th Annual Field Trip Guidebook, 94 p.

Rice, C. A., 2003, Production waters associatedwith the Ferron coalbed methane fields, central Utah: chemical and isotopic composition and volumes: International Journal of Coal Geology, v. 56, p. 141–169.

Rice, C. A., Ellis, M. S., and Bullock J. H., Jr., 2000, Water co-produced with coalbed methane in the Powder River Basin, Wyoming: preliminary compositional data: U.S. Geological Survey Open File-Report 00-372, unpaginated.

Rice, D. D., 1993, Composition and origins of coalbed gas: American Association of Petroleum Geologists Studies in Geology 38, p. 159-184.

Rodgers J. H., Jr., and Castle, J. W., 2008, Constructed wetland treatment systems for efficient and effective treatment of contaminated waters for reuse: Environmental Geosciences, v. 15, p. 1-8.

Scott, A. R., 1993, Composition and origin of coalbed gases from selected basins in the United States: Tuscaloosa, Alabama, University of Alabama, 1993 International Coalbed Methane Symposium Proceedings, p. 207-222.

___2002, Hydrogeologic factors affecting gas content distribution in coal beds: International Journal of Coal Geology, v. 50, p. 363-387.

Scott, A. R., Kaiser, W. R., and Ayers, W. B., Jr., 1994, Thermogenic and secondary biogenic gases, San Juan basin, Colorado and New Mexico—Implications for coalbed gas producibility: American Association of Petroleum Geologists Bulletin, v. 78, p. 1186-1209.

Seidle, John, 2011, Fundamentals of Coalbed Methane Reservoir Engineering: Tulsa, PennWell Corporation, 470 p.

Semmes, D. R., 1929, Oil and gas in Alabama: Alabama Geological Survey Special Report 15, 408 p.

Shurr, G. W., and Ridgley, J. L., 2002, Unconventional shallow biogenic gas systems: AAPG Bulletin, v. 86, p. 1939-1969.

Smith, J. K., 1995, Normal faults in Holt and Peterson coalbed methane fields, Black Warrior basin, Tuscaloosa County, Alabama: Tuscaloosa, University of Alabama, unpublished Master's thesis, 76 p.

Spacil, M. M., Rodgers, J. H., Jr., Castle, J. W., and Chao, W. Y., 2011, Performance of a pilot-scale constructed wetland treatment system for selenium, arsenic, and low molecular weight organics in simulated fresh produced water: Environmental Geosciences, v. 18, p. 145-156.

SPE, 2011, Challenges in reusing produced water: Society of Petroleum Engineers White Paper, 6 p.

SPEE, 2011, Guidelines for the practical evaluation of undeveloped reserves in resource plays: Society of Petroleum Evaluation Engineers Monograph 3.

Taylor, G. H., Teichmüller, M., Davis, A., Diessel, C. F. K., Littke, R., and Robert, P., 1998, Organic Petrology: Berlin, Gebrüder Borntraeger, 704 p.

Teichert-Coddington, D., 2002, Inland saltwater shrimp production in Alabama: Reality and potential: Alabama Cooperative Extension System Report, 4 p.

Telle, W. R., and Thompson, D. A., 1987, Preliminary characterization of the coalbed methane potential of the Cahaba coal field, central Alabama: Tuscaloosa, Alabama, University of Alabama, 1987 Coalbed Methane Symposium Proceedings, p. 141-151.

Thamdrup, B., and Dalsgaard, T., 2002, Production of N_2 through anaerobic ammonium oxidation coupled to nitrate reduction in marine sediments: Applied Environmental Microbiology, v. 68, p. 1312–1318.

Thomas, W. A, 1985a, The Appalachian-Ouachita connection: Paleozoic orogenic belt at the southern margin of North America: Annual Review of Earth and Planetary Sciences, v. 13, p. 175-199.

___1985b, Northern Alabama sections, *in* Woodward, N. B., ed., Valley and Ridge thrust belt: balanced structural sections, Pennsylvania to Alabama: University of Tennessee Department of Geological Sciences Studies in Geology 12, p. 54-60.

___1988, The Black Warrior basin, *in* Sloss, L. L., ed., Sedimentary cover - North American craton: Geological Society of America, The Geology of North America, v. D-2, p. 471-492.

___1995, Diachronous thrust loading and fault partitioning of the Black Warrior foreland basin within the Alabama recess of the Late Paleozoic Appalachian-Ouachita thrust belt: Society of Economic Paleontologists and Mineralogists Special Publication 52, p. 111-126.

___2001, Mushwad: Ductile duplex in the Appalachian thrust belt in Alabama: American Association of Petroleum Geologists Bulletin, v. 85, p. 1847-1869.

Thomas, W. A., Kanda, R. V. S., O'Hara, K. D., and Surles, D. M., 2008, Thermal footprint of an eroded thrust sheet in the southern Appalachian thrust belt, Alabama, USA: Geosphere, v. 4, p. 814–828.

Vail, P. R., 1987, Seismic stratigraphy interpretation procedure: American Association of Petroleum Geologists Studies in Geology 27, v. 1, p. 1-10.

Van de Graaf, A. A., Mulder, A., De Bruijn, P., Jetten, M. S. M., Robertson, L. A., and Kuenen, J. G., 1995, Anaerobic oxidation of ammonium is a biologically mediated process: Applied Environmental Microbiology, v. 61, p. 1246-1251.

Van Voast, W. A., 2003, Geochemical signature of formation waters associated with coalbed methane: American Association of Petroleum Geologists Bulletin, v. 87, p. 667-676.

Vinson, D. S., McIntosh, J. C., Ritter, D. J., Blair, N. E., Martini, A. M., 2012, Carbon isotope modeling of methanogenic coal biodegradation: metabolic pathways, mass balance, and the role of sulfate reduction, Powder River Basin, USA: Geological Society of America Abstracts with Programs, 44, no. 7, p. 466.

Wang, Saiwei, Groshong, R. H., Jr., and Pashin, J. C., 1993, Thin-skinned normal faults in Deerlick Creek coalbed-methane field, Black Warrior basin, Alabama, *in* Pashin, J. C., ed., New Perspectives on the Mississippian System of Alabama: Alabama Geological Society 30th Annual Field Trip Guidebook, p. 69-78.

Wanless, H. R., 1976, Appalachian region: U.S. Geological Survey Progessional Pepaer 853-C, p. 17-62.

Ward, W. E., II, Drahovzal, J. A., and Evans, F. E., Jr., 1984, Fracture analyses in a selected area of the Warrior coal basin, Alabama: Alabama Geological Survey Circular 111, 78 p.

Weisenfluh, G. A., and Ferm, J. C., 1984, Geologic controls on deposition of the Pratt seam, Black Warrior basin, Alabama, U. S. A., *in* Rahmani, R. A., and Flores, R. M., eds., Sedimentology of Coal and Coal-bearing Sequences: International Association of Sedimentologists Special Publication 7, p. 317-330.

Whiticar, M. J., 1996, Stable isotope geochemistry of coals, humic kerogens and related natural gases: International Journal of Coal Geology, v. 32, p. 191-215.

___, 1999, Carbon and hydrogen isotope systematic of bacterial formation and oxidation of methane. Chemical Geology, v. 161, p. 291-314.

Whiticar M. J., Faber E., and Schoell M., 1986, Biogenic methane formation in marine and freshwater environments: CO_2 reduction vs. acetate fermentation—Isotopic evidence: Geochimica et Cosmochimica Acta, v. 50, p. 693-703.

Whitis, T. N., 2007, Inland shrimp culture in Alabama: Encyclopedia of Alabama, http://www.encyclopediaofalabama.org/face/Article.jsp?id=h-1302, last accessed 1/5/2014.

Winston, R. B., 1990a, Vitrinite reflectance of Alabama's bituminous coal: Alabama Geological Survey Circular 139, 54 p.

___1990b, Preliminary report on coal quality trends in upper Pottsville Formation coal groups and their relationships to coal resource development, coalbed methane occurrence, and geologic history in the Warrior coal basin, Alabama: Alabama Geological Survey Circular 152, 53 p.

Zuber, M. D., and Boyer, C. M., II, 2001, Comparative analysis of coalbed methane production trends and variability—impact on exploration and production: Tuscaloosa, Alabama, University of Alabama, 2001 International Coalbed Methane Symposium Proceedings, p. 245-256.

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