



Relationships between water and gas chemistry in mature coalbed methane reservoirs of the Black Warrior Basin



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ABSTRACT

Water and gas chemistry in coalbed methane reservoirs of the Black Warrior Basin reflects a complex interplay among burial processes, basin hydrodynamics, thermogenesis, and late-stage microbial methanogenesis. These factors are all important considerations for developing production and water management strategies. Produced water ranges from nearly potable sodium-bicarbonate water to hypersaline sodium-chloride brine. The hydrodynamic framework of the basin is dominated by structurally controlled fresh-water plumes that formed by meteoric recharge along the southeastern margin of the basin. The produced water contains significant quantities of hydrocarbons and nitrogen compounds, and the produced gas appears to be of mixed thermogenic-biogenic origin.

Late-stage microbial methanogenesis began following unroofing of the basin, and stable isotopes in the produced gas and in mineral cements indicate that late-stage methanogenesis occurred along a CO₂-reduction metabolic pathway. Hydrocarbons, as well as small amounts of nitrate in the formation water, probably helped nourish the microbial consortia, which were apparently active in fresh to hypersaline water. The produced water contains NH₄⁺ and NH₃, which correlate strongly with brine concentration and are interpreted to be derived from silicate minerals. Denitrification reactions may have generated some N₂, which is the only major impurity in the coalbed gas. Carbon dioxide is a minor component of the produced gas, but significant quantities are dissolved in the formation water. Degradation of organic compounds, augmented by deionization of NH₄⁺, may have been the principal sources of hydrogen facilitating late-stage CO₂ reduction.

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1. Introduction

Natural gas is produced from coal by lowering reservoir pressure, and this lowering is achieved primarily by reducing the hydrostatic pressure component through the coproduction of formation water (e.g., McKee et al., 1988; Seidle, 2011). Accordingly, significant volumes of water are produced from many coalbed methane (CBM) reservoirs, and the quantity and composition of this water varies greatly (e.g., Ayers and Kaiser, 1994; Pashin et al., 1991; Reddy, 2010). Management of coproduced water is thus a central issue in CBM development, because the water must be processed and disposed in an environmentally responsible manner. The quantity and quality of formation water in coal, moreover, is intimately related to the architectural framework and geologic history of the host sedimentary basin. For this reason, basin hydrodynamics is thought to have a significant influence on the generation and alteration of natural gases in coal. Thus, basin hydrology

and geochemistry are fundamental considerations in the design and implementation of reservoir development protocols (e.g., Kaiser et al., 1994; Pashin, 2007, 2008; Pashin et al., 1991; Scott, 2002).

CBM has been produced commercially in the Black Warrior Basin of Alabama since 1980, with cumulative production exceeding 69×10^9 sm³ of gas and 1.6×10^9 bbl of water. In 2011, more than 5500 wells were active, producing more than 2.7×10^9 sm³ of gas and 69×10^6 bbl of water. Analysis of production data indicates that a typical CBM well in the Black Warrior Basin produces cumulatively between 3×10^6 and 14×10^6 sm³ of gas and 26,000 and 300,000 bbl of water (Pashin, 2010a). Initial research efforts in the 1970s focused on mitigating methane hazards in underground coal mines (Elder and Deul, 1974). The potential for production from multiple seams outside of mining areas was proven by the mid 1980s (Graves et al., 1983). With a rich history of production and reservoir data, the Black Warrior is an exceptional basin to explore the interrelationships among reservoir geology, water chemistry, and gas composition.

This study employs a variety of geological and geochemical techniques to characterize these interrelationships along a corridor from Brookwood Field, which is dominated by fresh formation water,

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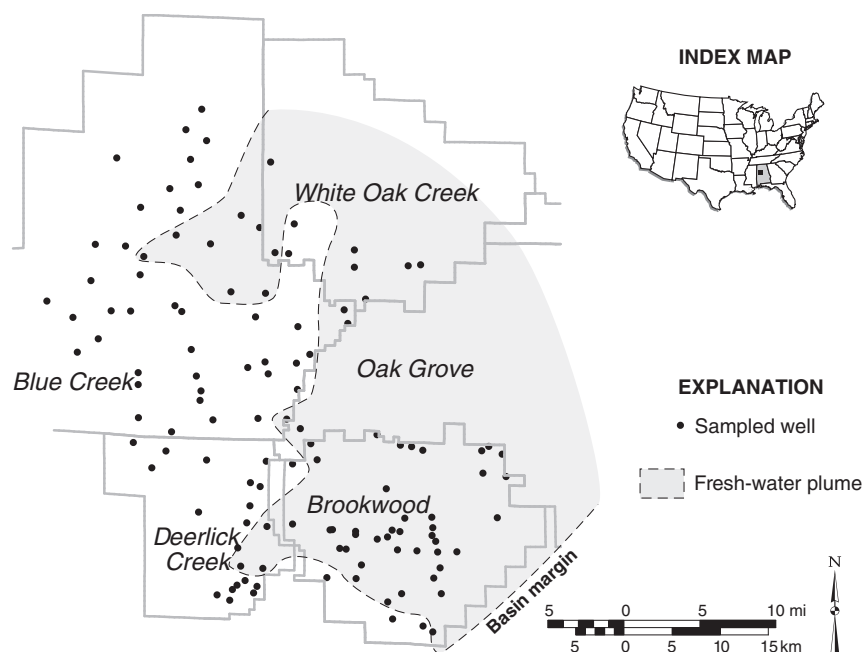


Fig. 1. Map of study area in the Black Warrior basin of Alabama showing locations of wellhead samples in Brookwood, Oak Grove, White Oak Creek, Blue Creek, and Deerlick Creek fields.

to Blue Creek Field, where saline formation water is preserved in the interior of the basin (Fig. 1). This research is part of a multi-year study that is sponsored by the U.S. Department of Energy and is focused on the sampling and characterization of reservoir fluids in CBM reservoirs of the Black Warrior Basin. The primary goals of this research are to increase understanding of water and gas chemistry in CBM reservoirs and to use this understanding to develop improved produced water and reservoir management strategies.

2. Analytical methods

This research draws on a database that includes 91 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 measurement.

Samples were prepared for laboratory analysis at the Geological Survey of Alabama, the University of Alabama, 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$, and a Perkin-Elmer 2380 CVAAS was used to determine Hg with a sensitivity of detection of 0.010 $\mu\text{g/L}$. 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 every 10th sample, and ionic concentrations were checked for charge balance. Reproducibility of measurements was high, with an error of $<2\%$ 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 et al. (2007) and in a supplemental file that is included with this publication.

Wellhead gas samples were collected from 56 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 $\pm 5\%$ for most gases and of $\pm 10\%$ for C_{4-6} 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 $\delta^{13}\text{C}_1$ and δD determinations. Isotopic determinations were made on a GC-C-IRMS unit with analytical precision of 0.3‰ for $\delta^{13}\text{C}_1$ 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

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