International Journal of Coal Geology 126 (2014) 106–119

Contents lists available at ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/ijcoalgeo

Carbon isotope characterization of powder river basin coal bed waters: Key to minimizing unnecessary water production and implications for exploration and production of biogenic gas☆

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ARTICLE INFO

Article history:
Received 1 April 2013
Received in revised form 27 September 2013
Accepted 1 October 2013
Available online 17 October 2013

Keywords:
Coalbed methane
Carbon isotope
Powder River Basin
Biogenic gas
Produced water
Reservoir characterization

ABSTRACT

Compared to other natural waters, water associated with biogenic natural gas is enriched in 13-carbon. Shallow coal seams regularly contain abundant resources of biogenic gas; as such water associated with biogenic gas in these coal beds is isotopically distinct from other waters. The production of gas from coal beds requires the removal of large volumes of produced water. Thus a method of discerning coalbed reservoir water from other natural waters (surface and groundwater) is important to both the coalbed natural gas (CBNG) industry and associated environmental and regulatory agencies.

Although isotopic tracers have been employed to identify coalbed natural gas produced waters, the isotopic variability within the reservoir has not been documented and explained. In this study, we present the isotopic compositions of dissolved inorganic carbon, oxygen and hydrogen for water produced from 197 CBNG wells in the Powder River Basin of Wyoming and Montana. This extensive database allows us to distinguish variations in isotopic compositions that may occur by multiple processes. These include variations that identify efficient dewatering of coal beds, variations characterizing incomplete hydraulic isolation of coal beds from adjacent strata and the subsequent mixing of groundwaters, variations related to well completion design, and variations associated with geochemical and biogenic processes that occur along groundwater flow paths.

These data suggest that little change in $\delta^{13}C_{DIC}$ occurs within the reservoir as a result of water and gas production; thus, the carbon isotopic composition informs other processes within the reservoir unrelated to coalbed natural gas recovery. The $\delta^{13}C_{DIC}$ and δD of groundwater vary along flow-path across the basin, reflecting different methanogenic pathways that are associated with different isotopic fractionations, and the pathways that dominate in different areas within the basin. In areas where several producing coal seams are present, the $\delta^{13}C_{DIC}$ and δD of produced waters from each seam are distinct. Therefore on a local scale, the isotopic composition of produced water can identify the particular coal seam from which water and gas are withdrawn. The methods and results presented in this case study provide examples that illustrate how water quality and isotopic data can be used to determine the hydraulic connectivity between coal and non-coal strata, identify and quantify water from individual coal horizons, as well as predict and understand the isotopic variability of the reservoir.

1. Introduction

Strongly positive $\delta^{13}C_{DIC}$ (>10‰) have been documented in produced water from several biogenic gas-producing fields, including the Antrim Shale, New Albany Shale, Forest City Basin shales and coals, Atlantic Rim coals, and the Powder River Basin coals (Martini et al., 1998, 2003; McIntosh et al., 2008; McLaughlin et al., 2011; Quillinan et al., 2012; Sharma and Frost, 2008). Studies have used this diagnostic characteristic of water associated with biogenic gas generation to trace produced water on the surface (Sharma and Frost, 2008) and in the subsurface (Martini et al., 1998; McLaughlin et al., 2011; Sharma and Frost, 2008). The basis for the tracer lies in the fact that most natural waters have negative $\delta^{13}C_{DIC}$ (−12 to −7‰; Mook and Tan, 1991) while waters associated with biogenic gas are positive (+10 to +30‰; Grossman et al., 1989). Enriched $\delta^{13}C_{DIC}$ are recorded in reducing environments where the production of biogenic methane, either by acetate fermentation or by CO_2 reduction, removes ^{12}C, leaving ^{13}C-enriched CO_2 in the system, which accounts for the positive $\delta^{13}C_{DIC}$ in formation waters (Grossman et al., 1989). Intermediate

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http://dx.doi.org/10.1016/j.coal.2013.10.006

values may reflect mixing of these two types of natural waters (Martini et al., 1998; McLaughlin et al., 2011; Quillinan et al., 2012; Sharma and Frost, 2008). This study seeks to understand both the natural isotopic variations of water within a biogenic natural gas reservoir along with any that are induced as a result of gas production. We have selected the Powder River Basin (PRB) of Montana and Wyoming for our study, a mature and well-studied biogenic coalbed natural gas (CBNG) field, which contain thousands of producing CBNG wells (Fig. 1).

The PRB in northeastern Wyoming and southeastern Montana is an asymmetric syncline formed during the Laramide orogeny in Late Cretaceous to Early Eocene times. The coals in the PRB are found within the Tongue River member of the Paleocene Fort Union Formation and the overlying Eocene Wasatch Formation (Love and Christiansen, 1985). The Tongue River Member of the Fort Union Formation hosts the thick, laterally continuous coal beds that are mined on the eastern side of the basin and contain CBNG across the basin (WOGCC, 1987–2010). Jones (2008) has identified 10 distinct coal zones that contain 26 mappable coal beds within the Tongue River Member and in the Wasatch Formation (Fig. 2). The natural gas resource from these coal beds is estimated to hold more than 30 trillion cubic feet (TCF, 850 billionm^3) of recoverable methane (Wyoming State Geological Survey, 2010) of which <5 TCF (141 billion m^3) has been recovered (WOGCC, 1987–2010).

2. Background

PRB coals are primarily subbituminous. Because of their low rank, PRB coals have not generated large quantities of thermogenic gas (Montgomery, 1999). CBNG from the Fort Union Formation has C1 / C2 + C3 ratios from 1000 to 4000 with a few lower values in the deepest part of the basin (Flores et al., 2008), indicating that it is almost exclusively of biogenic origin.

Biogenic gas is commonly associated with shallow (less than 600 m), organic-rich rocks that are thermally immature (Shurr and Ridgley, 2002). Two metabolic pathways have been identified to produce biogenic gas: acetate fermentation and CO_2 reduction (Jenden and Kaplan, 1986; Schoell, 1980; Whiticar et al., 1986; Woltemate et al, 1984). Gasses originating from the fermentation pathway are generally more enriched with respect to carbon-13 and more depleted in deuterium than gas generated via CO_2 reduction. In CO_2 reduction the carbon isotope ratio of the methane is controlled by the initial carbon isotope composition of the CO_2 (Shurr and Ridgley, 2002).

$$CH_3COOH \rightarrow CH_4 + CO_2 (\text{Acetate fermentation}) \quad (1)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O(CO_2 \text{ reduction}) \quad (2)$$

CO_2 is readily available in most coal beds as a result of carbonate dissolution and bacterial processes (Freeze and Cherry, 1979). Most bacteria generate methane through CO_2 reduction (Rice, 1993), although several species utilize the fermentation pathway most commonly acting on an acetate substrate. The metabolic pathway also varies with time: biogenic gas that is generated early in the coal bed burial history likely results from the carbonate reduction pathway (Rice, 1992 and Rice and Claypool, 1981). Biogenic gas formed long after deposition can be a result of either acetate fermentation or by carbonate reduction (Barker and Fritz, 1981; Carothers and Kharaka, 1980; Coleman et al., 1988; Grossman et al., 1989; and Rice and Threlkheld, 1982) and is found in coal beds of all ranks (Rice, 1993).

Montgomery (1999) noted that Fort Union coal beds contain significant quantities of biogenic gas. On the basis of this observation Shurr and Ridgley (2002) suggest that the PRB coals have remained at depths suitable for biogenic gas production for extensive periods, allowing for both ancient and recent biogenic gas generation. Recent bacterial gas generation has been documented on the basin margins, whereas early-stage (older) gas generation is theorized to have occurred across the basin (Flores et al., 2008; Shurr and Ridgley, 2002). Similar to the San Juan (U.S.), Surat (Aus.), and Sydney (Aus.) basins, recent biogenic gas on the margins of the PRB has been found to form by the acetate fermentation and CO_2 reduction pathways (Faiz et al., 2003; Flores et al., 2008; Gorody, 1999; Moore, 2012; Rice, 1993 and Whiticar et al., 1986).

The shallow nature of PRB coals also leads to low sorbed gas content. Gas content from these coals ranges from 22 to 74 cubic feet per ton (0.6 to 2 m^3/t). The chemical composition of the gas in Fort Union coal beds of the Powder River Basin is, on average, 86% methane, 6% carbon dioxide, and 4% nitrogen (Flores et al., 2008).

The methane produced from the Powder River Basin has a $\delta^{13}C_{CH4}$ of −83.4‰ to −53.4‰ and a δD_{CH4} of −333‰ to −283.4‰ (Flores et al., 2008; Gorody, 1999; Rice, 1993). Flores et al. (2008) observed depleted CH_4 with respect to carbon on the basin margins and enriched gas in the center of the basin. They suggested that this is a result of methanogenesis by mixed acetate fermentation and CO_2 reduction pathways on the basin margins and dominantly by CO_2 reduction in the center of the basin.

Isotopes of hydrogen of the formation water also are fractionated during methanogenesis, creating isotopically light methane. During acetate fermentation, 25% of the hydrogen is supplied from the formation water as compared to 100% for CO_2 reduction (Whiticar et al., 1986). The δD of formation water may be enriched by methanogenesis (Clark and Fritz, 1997; Quillinan, 2011; Siegel et al., 1990) to a greater degree by CO_2 reduction than by acetate fermentation. However δD is not considered a reliable indicator of methanogenic pathways (Waldron et al., 1999).

The δD and $\delta^{18}O$ of precipitation lie along the global meteoric water line ($\delta D = 8\delta^{18}O + 10‰$; from Craig, 1961). Produced water that originates as meteoric water should also lie approximately along this line. The exact position is a function of temperature (Craig, 1961).

Meteoric recharge for Fort Union coal beds in the PRB takes place on the basin margins (Bartos and Ogle, 2002 and references therein; Quillinan and Frost, 2012). These models suggest that residence times of water in coal bed aquifers increase with increasing depth and distance from the outcrop. On the basis of limited tritium data and simple ground water flow models, Pearson (2002) suggested that the residence time for water to flow from eastern recharge to the central part of the basin was between 7000 and 70,000 years. ^{14}C dating by Frost and Brinck (2005) further refined this estimate to less than 20,000 years.

Water derived from coal beds in the Powder River Basin have $\delta^{18}O$ that ranges from −21.5‰ to −16.15‰ and δD ranging from −158.4‰ to −121.3‰ (Bartos and Ogle, 2002; Flores et al., 2008; Gorody, 1999). The $\delta^{13}C_{DIC}$ of waters measured from the Upper and Lower Wyodak coal zone range from 12‰ to 22‰ (Sharma and Frost, 2008). These waters are strongly sodium bicarbonate-type, with total dissolved solid (TDS) concentrations that range from 500 to 5600 mg/L (Bartos and Ogle, 2002; Campbell et al., 2008; Frost et al., 2002; Pearson, 2002; Quillinan, 2011; Rice et al., 2000). The TDS of these waters is found to increase along approximate groundwater flow paths from the southern and eastern margins toward the basin center. This geospatial trend is observed in all coal zones (Quillinan and Frost, 2012).

3. Methods

Samples were collected from the major exploited coal zones for CBNG development (Quillinan and Frost, 2012): the Wyodak Rider, Upper Wyodak, Lower Wyodak, Cook and Wall coal zones (Fig. 2). We analyzed 181 produced water samples from wells in Wyoming and 16 from wells in Montana for stable isotopic compositions of