Chemical and isotopic composition of gases released by crush methods from organic rich mudrocks

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ABSTRACT

We report on the composition of mudrock gases released under vacuum by ball-mill rock crushing and pressure induced fracturing. Nine core samples from organic rich Barnett Shale were used in this study. TOC content varies from 3.3–7.9%; thermal maturity varies from 0.58–2.07 %R_o.

Our results show that both thermal maturity and gas desorption contributes to changes in the CH_4/CO_2 ratio of gases released during rock crushing. CH_4/CO_2 ratios of these gases are lower at low thermal maturities and higher at high thermal maturities because more CH_4 rich gas is generated at higher maturity levels. CH_4/CO_2 ratios decrease with longer rock crushing times because of the increase in the CO_2 rich gas contribution. However, no obvious compositional fractionation occurs among C_1, C_2 and C_3 of crushed-rock gas and C_1/C_2 and C_2/C_3 ratios remain nearly constant during crushing although these ratios are greatly increased overall when the level of thermal maturity is high. Gas geochemical parameters (C_1/C_2, C_2/C_3, and $i\text{-}C_4/n\text{-}C_4$) of released gas are good indicators of thermal maturation of organic rich shales. The CH_4/CO_2 ratio is a function of selectivity, partition coefficients and (possibly but less likely) sorption kinetics between CH_4 and CO_2 molecules in shales.

Trends in released gas yield and gas chemistry during rock crushing relate to gas storage states and pore connectivity. The $\delta^{13}C_1$, $\delta^{13}C_2$ and $\delta^{13}C_3$ values of gas released from particles of coarser size (> 250 μm) are similar to values of gas produced from Barnett shales after hydraulic fracturing. CH_4 dominated gas appears to be stored in larger connected pores and is therefore released during the initial stages of crushing. The carbon isotope values of methane, ethane and propane are heavier in the more thermally mature samples, suggesting that this released gas is representative of the gas chemistry of subsurface rocks. Retrieval of gas chemistry data from existing core samples provides information of great relevance for understanding deep shale gas reservoirs.

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1. Introduction

Organic rich shales have received renewed research focus in the past few years because of their emergence as hydrocarbon reservoirs (Curtis, 2002; Montgomery et al., 2005; Loucks and Ruppel, 2007; Rowe et al., 2008; Ruppel and Loucks, 2008; Mohr and Evans, 2011; Bernard et al., 2012a,b). Gas shale reservoirs are unconventional gas systems in which the shale is both the source of, and the reservoir for, methane, which is derived from organic matter through biogenic and/or thermogenic processes (Hill et al., 2007; Jarvie et al., 2007; Strapoc et al., 2010). Natural gas stored in shale-gas reservoirs partitions, depending on fluid properties, pressure and temperature into: (1) free gas in pores and fractures, (2) sorbed gas in organic matter and inorganic minerals, and (3) dissolved gas in oil and water (Zhang et al., 2012; Gensterblum et al., 2014). Understanding the relative proportions of gas stored in these different forms as a function of pressure and temperature is critical to an accurate assessment of shale-gas resources and design of effective production strategies. In this study, compositional analyses of the gases released through a series of ball-mill rock-crushing iterations using Barnett Shale samples of differing thermal maturities were conducted in order to understand gas storage mechanisms in organic rich shales.

Accurately determining gas in place (GIP) is critical to an evaluation of shale-gas plays, but estimation of gas volumes in shales is challenging (Ambrose et al., 2010, 2011). Organic matter content and type, mineral composition and pore characteristics are all

factors crucial to controlling GIP (Sondergeld et al., 2010; Chalmers et al., 2012; Ji et al., 2012; Modica and Lapierre, 2012; Zhang et al., 2012). Strapoc et al. (2010) reported a strong positive correlation between total organic carbon (TOC) and total gas content from canister desorption of fresh cores from the Devonian–Mississippian New Albany Shale in the Illinois Basin, indicating that organic matter content is primarily responsible for total GIP in these rocks. Moisture content also plays a role, although the detailed mechanism of fluid–rock surface interaction is still unclear (Ross and Bustin, 2009; Gensterblum et al., 2014). Recent research has shown that the most favorable areas for Barnett Shale gas production are those having higher thermal maturity, greater pay-zone thickness, higher TOC and further distance from major faults and areas underlain by porous, water-bearing Ellenburger carbonates (Zhao et al., 2007). Most of the wells in Tarrant and northern Johnson counties exhibit high thermal maturity and high gas productivity. Southwestern Denton, Tarrant and northern Johnson counties, contain more than 70% of the most productive (top 10%) producing wells in the Barnett Shale play (LaFollette and Holcomb, 2011). Gas geochemistry, in particular isotope geochemistry, is part of standard assessment for organic matter type, maturity and fluid type for basin modeling, and is now a key tool for shale gas exploration, largely due to the association of isotope reversals with mature, highly productive shale gas (Tilley and Muehlenbachs, 2013). Geochemical characterization of produced gases has been conducted on rocks from several sedimentary basins in North America, including the Barnett and Fayetteville shales (Rodriguez and Philp, 2010; Zumberge et al., 2012), fractured reservoirs in the Appalachians (Burruss and Laughrey, 2010), and shale and low permeability sandstones from the Western Canada Sedimentary Basin (WCSB) (Tilley et al., 2011; Tilley and Muehlenbachs, 2013). Analysis of the molecular and carbon and hydrogen isotopic compositions of the produced gases indicate that gases from sealed, self-contained petroleum systems share a common maturation history of conventional open-system gases (Tilley and Muehlenbachs, 2013). The maturation history of shale gas systems comprises three distinct stages: pre-rollover zone, rollover zone and post-rollover zone. Each zone has characteristic carbon and hydrogen isotopic trends (Tilley and Muehlenbachs, 2013).

Canister gas and mud drilling gas samples are useful for determining shale gas chemistry in subsurface reservoirs. A significant amount of gas loss from canister gas desorption during core transportation from the drilling target depth to the surface (Javadpour et al., 2007; Javadpour, 2009) causes concerns over whether the chemistry of canister gas is representative of produced gas chemistry. Recent imaging of shale pores by ion-beam milling and field-emission scanning-electron microscopy shows that nanosize pores in organic matter are dominant in the Barnett and Marcellus shales (Ruppel and Loucks, 2008; Loucks et al., 2009, 2012; Bernard et al., 2012a,b; Milliken et al., 2012, 2013). These tiny pores provide space for gas storage and the gas that fills these pores can be released when the rock is crushed. Released gas can provide a method of studying shale-gas using older cores, bridging a gap that is caused by the scarcity of fresh canister core desorption data.

In this study, we describe the design of a gas tight cell equipped with a valve to collect the gas released during rock crushing. Chemical and isotopic compositions of the collected gas are measured for an indication of gas thermal maturity. We have tested this method on mudstones of the Barnett Shale, a producing shale-gas play in the Fort Worth Basin, Texas. The main objectives of this study are to: (1) evaluate whether the crushed-rock gas from pre-existing core samples retains information indicative of thermal maturity and gas chemistry in subsurface reservoir conditions; (2) evaluate the main controls on the variation of crushed-rock gas chemistry, including thermal maturation and post-coring alteration; (3) compare the gas chemistry between the produced gas and the crushed-rock gas from Barnett shales; and (4) develop a geochemical method for utilizing crushed-rock gas chemistry for gas quality prediction in subsurface reservoirs. Our experimental findings have important implications for shale-gas resource assessments and recovery technologies.

2. Materials and methods

2.1. Sample selection

As shown in Table 1, nine organic rich shale core samples, having a wide thermal maturity ranging from 0.58–2.07 %R_o, were collected from the Barnett Shale in the Fort Worth Basin, Texas. The Barnett Shale is a succession of organic rich, black mudstones deposited under conditions of low oxygenation in a marine foreland basin along the southern margin of the Laurussian paleocontinent during the Mississippian (Loucks and Ruppel, 2007; Rowe et al., 2008; Ruppel and Loucks, 2008). Visual assessments of kerogen indicate the presence of 95–100% amorphous (structureless) organic matter with occasional algal *Tasmanites*, confirming the presence of Type II kerogen (Jarvie et al., 2007). Vitrinite reflectance (R_o) values are calculated for Lee C-5-1, Tarrant #3-A and Young W.C. #2 based on T_{max} values according to the formula of Jarvie et al. (2005). The measured vitrinite reflectance (R_o) values for T.P. Sims #2 well have been reported by Loucks et al. (2009). The measured vitrinite reflectance (R_o) values for Blakely #1 were provided by Humble Geochemical Services.

The locations of the five wells from which cores were obtained for this study are shown in Fig. 1. Three highly mature samples (R_o = 1.96–2.07%, TOC = 4.1–6.6%) were collected from a gas producing well (Texas United Blakely #1) at depths of 7112 ft, 7191 ft, and 7223 ft (2153.5 m, 2177.4 m, 2187.1 m) in the Newark East gas field, currently the largest gas field in Texas and the second largest in the United States. Two mature samples (R_o = 1.60%, gas condensate zone) were collected from the Mitchell Energy T.P. Sims #2 well at depths of 7634 ft and 7742 ft (2311.6 m, 2344.3 m). Three moderately mature oil window samples were collected from the Young, W.C. #2 well in Wise County, TX at a depth of 6918 ft (2094.8 m) and from the Tarrant #3-A well in Jack County at depths of 6164 ft and 6168 ft (1866.5 m, 1867.7 m). An immature sample (R_o = 0.58%, TOC = 7.9%) was collected at 1250 ft (378.5 m) in the Lee C-5-1 well in Brown County. Core samples were crushed with a hammer to gravel size (0.5–2.0 cm) and homogenized.

2.2. Experimental methods

The Spex 8000M Mixer/Mill ball-mill was used for a time series of rock crushing. Released gases from each time increment of grinding were directly introduced into the gas chromatograph (GC) for gas compositional analysis. A standard 65 ml hardened steel grinding vial with a screw-on cap was fitted with O-rings to serve as a vacuum seal (Fig. 2). The hardened steel vial was further modified by adding a plug valve for a connection to a vacuum line and online gas chromatograph (GC) sample injection. A hole was drilled on the side of the vial, and a combination of a 2 μm in-line filter and a Swagelok ¼ in. SS quarter-turn instrument plug valve was inserted and welded to the vial (Fig. 2). The gas-tight vial is used to release gas from rocks by ball-mill crushing.

Approximately 10 g of gravel size rock sample was loaded into the specially fitted ball-mill vial set. The vial containing the sample was evacuated overnight through a connection to the GC vacuum gas injection line. After evacuation of the vial, samples were initially milled for 10 s, and then the vial was connected to the GC vacuum injection line through a 1/16 in. Swagelok tube fitting.