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Review article

Cause of shale gas geochemical anomalies and mechanisms for gas enrichment and depletion in high-maturity shales

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ABSTRACT

This article reviews the abnormal characteristics of shale gases (natural gases produced from organic-rich shales) and discusses the cause of the anomalies and mechanisms for gas enrichment and depletion in high-maturity organic-rich shales. The reported shale gas geochemical anomalies include rollover of iso-alkane/normal alkane ratios, rollover of ethane and propane isotopic compositions, abnormally light ethane and propane $\delta^{13}C$ values as well as isotope reversals among methane, ethane and propane. These anomalies reflect the complex histories of gas generation and associated isotopic fractionation as well as in-situ "mixing and accumulation" of gases generated from different precursors at different thermal maturities. A model was proposed to explain the observed geochemical anomalies. Gas generation from kerogen cracking at relatively low thermal maturity accounted for the increase of iso-alkane/normal alkane ratios and ethane and propane $\delta^{13}C$ values (normal trend). Simultaneous cracking of kerogen, retained oil and wet gas and associated isotopic fractionation at higher maturity caused decreasing iso-alkane/normal alkane ratios, lighter ethane and propane $\delta^{13}C$ and corresponding conversion of carbon isotopic distribution patterns from normal through partial reversal to complete reversal. Relatively low oil expulsion efficiency at peak oil generation, low expulsion efficiency at peak gas generation and little gas loss during post-generation evolution are necessary for organic-rich shales to display the observed geochemical anomalies. High organic matter richness, high thermal maturity (high degrees of kerogen-gas and oil-gas conversions) and late-stage (the stage of peak gas generation and post-generation evolution) closed system accounted for gas enrichment in shales. Loss of free gases during post-generation evolution may result in gas depletion or even undersaturation (total gas content lower than the gas sorption capacity) in high-maturity organic-rich shales.

1. Introduction

Shale gases are unconventional gas systems in which the shale is both the source of, and the reservoir for, natural gases, which are derived from the organic matter within the shale through biogenic and/or thermogenic processes (Curtis, 2002; Hill et al., 2007a; Strąpoć et al., 2010). Shale gas production in the USA has increased rapidly in the last 12 years, from 0.39 tcf (110.43×10^8 m^3) in 2000 to 4.80 tcf (1359.22×10^8 m^3, about 23% of U.S. dry gas production) in 2010 (EIA, 2011). The nine major gas-producing shales display varying total organic carbon (TOC) contents (0.45–25%) and varying thermal maturities (vitrinite reflectance (R_o) between 0.4 and 4.0%, Fig. 1, data from Curtis, 2002; Ground Water Protection Council (GWPC), 2009). These properties seem to suggest that organic-rich shales, from early mature to highly overmature with varying organic matter richness, may contain enough natural gas for commercial production, which raises high expectations for shale gas potential in other countries short of conventional oil and gas resources. In addition, high-maturity ($R_o > 1.1$–1.3%) organic-rich shales in the USA have high gas contents (Fig. 1) and high gas flow rates (Jarvie et al., 2007). This begs the questions that are commonly asked by explorers: whether all high-maturity organic-rich shales have high gas contents and what controls gas enrichment and depletion in high-maturity organic-rich shales?

Chemical and isotopic compositions are the most important parameters for characterizing natural gases (e.g., James, 1983; Schoell, 1983; Jenden et al., 1988; Prinzhofer and Huc, 1995; Galimov, 2006; Dai et al., 2008, 2012). Theoretical and empirical

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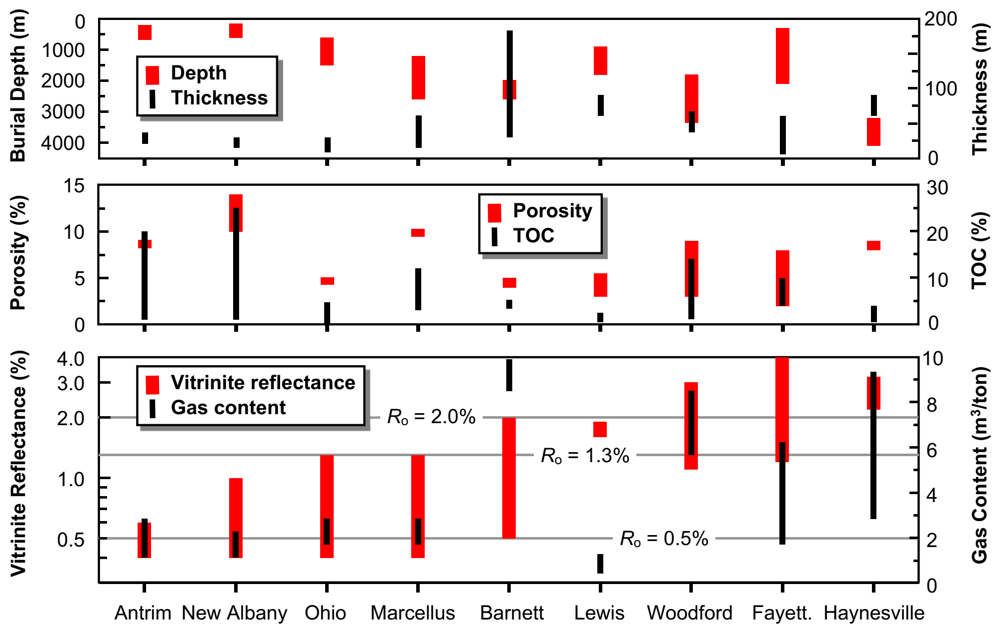

Figure 1. General properties of the nine major shale gas systems in the United States. Fayett. = Fayetteville. Data from Curtis (2002) and Ground Water Protection Council (2009).

evidence indicates that cogenetic gases (gases generated from a common source) usually obey the relationship methane $\delta^{13}C$ ($\delta^{13}C_1$) < ethane $\delta^{13}C$ ($\delta^{13}C_2$) < propane $\delta^{13}C$ ($\delta^{13}C_3$) (e.g., Des Marais, 1981; James, 1983). Full ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3$) or partial (such as $\delta^{13}C_2 < \delta^{13}C_1 < \delta^{13}C_3$, $\delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_1$) isotopic reversals have been found in natural gas samples from hydrothermal fluids, crystalline rocks and conventional gas reservoirs. Isotope reversals in hydrothermal fluids and crystalline rocks are associated with contribution from abiogenic hydrocarbons (e.g., Dai et al., 2004, 2005; Taran et al., 2007; Sherwood Lollar et al., 2008; McCollom et al., 2010). Carbon isotope reversals among hydrocarbons in conventional petroleum reservoirs have been attributed to mixing of natural gases generated from different source rocks and/or at different maturities (e.g., Jenden and Kaplan, 1989; Jenden et al., 1993; Dai et al., 2004), migration fractionation (Prinzhofer and Huc, 1995) or in-reservoir cracking of oil and gas (e.g., Hao et al., 2008).

In the last few years, abnormal geochemical characters have been found in unconventional gas reservoirs including highly productive gas shales (Ferworn et al., 2008; Rodriguez and Philp, 2010; Tilley et al., 2011; Zumberge et al., 2012; Slatt and Rodriguez, 2012) and deep-basin tight reservoir gas systems (Burruss and Laughrey, 2010). These abnormal characters include the "rollover" (deviation from the initial thermal maturation trends) of iso-butane/normal butane (iC_4/nC_4) ratios, "rollover" of ethane and propane $\delta^{13}C$ values and carbon isotope reversals. The physicochemical processes accounting for these abnormal characteristics in these unconventional gases are poorly understood. Recent studies focused on the cause of isotopic reversals, and at least four opinions have been proposed. (1) Ferworn et al. (2008) found rollover of iC_4/nC_4 and ethane $\delta^{13}C$ in natural gases from the Barnett, Haynesville and Marcellus organic-rich shales and attributed these abnormal characters to in-situ cracking of C_{2+} gas components. Rodriguez and Philp (2010) found isotopic reversals ($\delta^{13}C_1 > \delta^{13}C_2$) in high-maturity Barnett Shale gases and also attributed the isotopic reversal to in-situ oil or gas cracking. (2) Tilley et al. (2011) observed isotopic reversals in gases from the fractured Permian and Triassic reservoirs in the foothills at the western edge of the Western Canada sedimentary basin (WCSB). They believed that these gases were actually shale gases and explained the isotopic reversals as a result of simultaneous cracking of kerogens, oils and gases in a closed system. (3) Zumberge et al. (2012) systematically illustrated the geochemical anomalies in gases from the Barnett and Fayetteville organic-rich shales, and proposed a two-stage reaction scheme to explain these anomalies: water reacts with methane to generate isotopically light carbon dioxide and hydrogen, and carbon dioxide and hydrogen further react to form isotopically light ethane. (4) Burruss and Laughrey (2010) found complete isotopic reversals in gases from the unconventional fractured carbonate and tight sandstone reservoirs of Ordovician and Silurian age in the northern Appalachian basin. Based on calculation for gas mixing and isotopic fractionation, they concluded that Rayleigh fractionation during redox reactions at elevated temperatures and thermal maturities (about 5.0% R_o) caused the observed isotopic reversals.

Shale gases represent gases at their site of generation (Price and Schoell, 1995) and therefore provide representative in-situ samples to investigate the complex physicochemical processes in the kerogen-hydrocarbon-water-matrix systems at varying temperature and pressure. More importantly, isotope reversals (and other abnormal geochemical characteristics as will be discussed in the following section) appear to be a common feature for high-maturity organic-rich shales that have high total gas contents and high gas production rates (Ferworn et al., 2008). Understanding the causes and mechanisms of the geochemical anomalies of shale gases would shed light on the conditions under which highly productive gas shales might be formed and preserved. The purpose of this article is to review the abnormal properties of shale gases, to discuss the mechanisms for gas enrichment and depletion in overmature organic-rich shales, and to analyze the major risk for gas exploration in overmature organic-rich shales having complex evolution histories.

2. Data set

Chemical and isotopic data for 368 shale gas samples (Table 1), from six (i.e., the Antrim, New Albany, Barnett, Fayetteville, Haynesville and Marcellus shales) of the nine major producing shales in