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The evolution of Devonian hydrocarbon gases in shallow aquifers of the northern Appalachian Basin: Insights from integrating noble gas and hydrocarbon geochemistry

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Abstract

The last decade has seen a dramatic increase in domestic energy production from unconventional reservoirs. This energy boom has generated marked economic benefits, but simultaneously evoked significant concerns regarding the potential for drinking-water contamination in shallow aquifers. Presently, efforts to evaluate the environmental impacts of shale gas development in the northern Appalachian Basin (NAB), located in the northeastern US, are limited by: (1) a lack of comprehensive "pre-drill" data for groundwater composition (water and gas); (2) uncertainty in the hydrogeological factors that control the occurrence of naturally present CH_4 and brines in shallow Upper Devonian (UD) aquifers; and (3) limited geochemical techniques to quantify the sources and migration of crustal fluids (specifically methane) at various time scales. To address these questions, we analyzed the noble gas, dissolved ion, and hydrocarbon gas geochemistry of 72 drinking-water wells and one natural methane seep all located $\gg$1 km from shale gas drill sites in the NAB. In the present study, we consciously avoided groundwater wells from areas near active or recent drilling to ensure shale gas development would not bias the results. We also intentionally targeted areas with naturally occurring CH_4 to characterize the geochemical signature and geological context of gas-phase hydrocarbons in shallow aquifers of the NAB. Our data display a positive relationship between elevated

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[CH_4], [C_2H_6], [Cl], and [Ba] that co-occur with high [^{4}He]. Although four groundwater samples show mantle contributions ranging from 1.2% to 11.6%, the majority of samples have [He] ranging from solubility levels ($\sim 45 \times 10^{-6}$ cm^3 STP/L) with below-detectable [CH_4] and minor amounts of tritiogenic ^{3}He in low [Cl] and [Ba] waters, up to high [^{4}He] = 0.4 cm^3 STP/L with a purely crustal helium isotopic end-member (^{3}He/^{4}He = ~0.02 times the atmospheric ratio (R/Ra)) in samples with CH_4 near saturation for shallow groundwater (P(CH_4) = ~1 atmosphere) and elevated [Cl] and [Ba]. These data suggest that ^{4}He is dominated by an exogenous (i.e., migrated) crustal source for these hydrocarbon gas- and salt-rich fluids. In combination with published inorganic geochemistry (e.g., ^{87}Sr/^{86}Sr, Sr/Ba, Br^-/Cl^-), new noble gas and hydrocarbon isotopic data (e.g., ^{20}Ne/^{36}Ar, C_2+/C_1, δ^{13}C-CH_4) suggest that a hydrocarbon-rich brine likely migrated from the Marcellus Formation (via primary hydrocarbon migration) as a dual-phase fluid (gas + liquid) and was fractionated by solubility partitioning during fluid migration and emplacement into conventional UD traps (via secondary hydrocarbon migration). Based on the highly fractionated ^{4}He/CH_4 data relative to Marcellus and UD production gases, we propose an additional phase of hydrocarbon gas migration where natural gas previously emplaced in UD hydrocarbon traps actively diffuses out into and equilibrates with modern shallow groundwater (via tertiary hydrocarbon migration) following uplift, denudation, and neotectonic fracturing. These data suggest that by integrating noble gas geochemistry with hydrocarbon and dissolved ion chemistry, one can better determine the source and migration processes of natural gas in the Earth's crust, which are two critical factors for understanding the presence of hydrocarbon gases in shallow aquifers.

1. INTRODUCTION

The extraction of unconventional hydrocarbon resources, which has been enhanced by horizontal drilling and hydraulic fracturing, has rejuvenated American and international domestic energy development (Kerr, 2010; Tour et al., 2010). These new technologies have reduced electricity generation from coal and expanded oil and natural gas production by exploiting previously untapped black shales and tight sands (Kerr, 2010; Tour et al., 2010). Despite these economic benefits, potential risks for drinking-water contamination remain a concern (Molofsky et al., 2011, 2013; Osborn et al., 2011; Jackson et al., 2013; Vidic et al., 2013; Darrah et al., 2014; Vengosh et al., 2014; Heilweill et al., 2015; Siegel et al., 2015; Drollette et al., 2015). Specific environmental concerns include the presence of elevated levels of combustible, thermogenic gases in drinking-water wells <1 km from shale gas drilling sites (Osborn et al., 2011; Jackson et al., 2013; Darrah et al., 2014) in the northern Appalachian Basin (NAB) (Fig. 1).

A lack of information about: (1) comprehensive pre-drill groundwater data; (2) uncertainty in the timing and conditions of geological and hydrogeological migration of hydrocarbon-rich crustal brines and/or natural gas; and (3) a robust set of geochemical techniques that can accurately constrain the source, mechanism, and timing of fluid migration in the Earth's crust, limits our understanding of the environmental impacts of shale gas development, specifically whether the presence of natural gas in drinking-water is natural or anthropogenic (Molofsky et al., 2011, 2013; Osborn et al., 2011; Jackson et al., 2013; Darrah et al., 2014, 2015). In the NAB, geochemical evidence (e.g., Br^-/Cl^- and ^{87}Sr/^{86}Sr) suggests that cross-formational pathways may transmit diluted Middle-Devonian (i.e., Marcellus-like) gas-rich brines to shallow aquifers on yet undetermined time scales and by uncertain migration processes (Warner et al., 2012; Vengosh et al., 2014), while a subset of drinking-water wells may have elevated levels of methane because of the presence of poor gas-well integrity in areas <1 km from drilling (Osborn et al., 2011; Jackson et al., 2013; Darrah et al., 2014). Conversely, natural methane seeps (e.g., Salt Spring State Park, Montrose, PA) provide compelling evidence for natural geological gas migration, unrelated to shale gas development (Molofsky et al., 2011, 2013; Warner et al., 2012; Baldassare et al., 2014; Darrah et al., 2014). In this paper, we focus on understanding the natural mechanisms of migration for the emplacement of hydrocarbon gases into shallow aquifers by studying these processes in the NAB, which is an example of an archetypal unconventional energy basin located in the northeastern United States.

The occurrence, distribution, and composition of hydrocarbons in the Earth's crust, including Devonian hydrocarbon-bearing formations in the NAB (Fig. 1), result from the complex interplay between the tectonic and hydrologic cycles (e.g., Bethke and Marshak, 1990; Cathles, 1990; Ballentine et al., 1991). For example, tectonic processes induce catagenesis (by increasing burial) and drive the migration of hydrocarbons and "deep" crustal brines. Hydrocarbon migration, which is often accompanied by "deep" crustal ("oil field") brines, typically occurs by two major processes: (1) *primary migration* out of source rocks (e.g., black shales, which constitute modern-day unconventional hydrocarbon reservoir rocks) and (2) *secondary migration*, which transports hydrocarbons away from the hinterland (Oliver, 1986; Allen and Allen, 1990; Bethke and Marshak, 1990), where regional groundwater flow and buoyancy forces emplace them in stratigraphic or tectonically-induced structural traps (Cathles, 1990; Ballentine et al., 1991; Sherwood Lollar and Ballentine, 2009). Following primary and secondary migration, hydrocarbon- and brine-rich fluids may be restricted to deeply buried stratigraphic and structural traps or to "unconnected" fractures, limiting their interaction with the active hydrologic cycle (e.g., Selley, 1998; Engelder, 2012; Holland et al., 2013). For example, at the time of maximum burial, the Marcellus and overlying UD traps in the study area were likely buried 2–6 km below the surface (Evans, 1995).