Using integrated noble gas and hydrocarbon geochemistry to constrain the source of hydrocarbon gases in shallow aquifers in the northern Appalachian Basin

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I. Abstract

Rising demands for domestic energy sources, mandates for cleaner burning fuels for electricity generation, and concerns about global climate change and production are driving the transformation from coal to natural gas from unconventional energy resources. This trend has been facilitated by innovations in low-cost exploration technologies, which have substantially increased the potential for the recovery of natural gas and oil from organic-rich black shales globally. Nonetheless, public and political sensitivities are tempered by various concerns regarding the environmental risks associated with shale gas development, specifically drinking-water-quality concerns, natural gas hydrate formation, thin shales, and escape of dissolved constituents (i.e., Cl, Ba) and hydrocarbon molecular and isotopic composition (e.g., ethane, propane). Here, we present our initial assessment of the dissolved gas (noble gas and hydrocarbon molecular and isotopic) geochemistry of shallow aquifers in the northeastern PA and southeastern NY.

Utilizing noble gas and hydrocarbon molecular and isotopic tracers, we determine the sources of methane from naturally elevated CH4 levels in groundwater and shallow aquifers in the northeastern PA and southeastern NY.

II. Sampling and Methods

We examine the dissolved gas isotopic compositions of 72 domestic groundwater wells within a seven county area of PA (Bradford, Sullivan, Susquehanna, and Wayne counties) and NY (Broome, Delaware, and Sullivan counties). The study area is part of the Appalachian Plateau physiographic province as gently dipping strata (overall dip magnitudes of ~1-3 degrees) that are broadly folded due to salt core detached folds, and further deformed by layer parallel shortening, reverse faults, and fracturing (e.g., Lash and Engelder, 2009). The oldest lithologies of interest in the study area consist of the interbedded limestones and shales of the Middle Ordovician/Black River Group. These rocks, and the overlying and eroding organic-rich Utica shale, represent Taconic orogenic sediments (Milici and Witt, 1988). The Marcellus Formation is shown in purple. The three principal shallow Upper Devonian gas producing formations are the Utica, Marcellus, and Utica. The oldest lithologies of interest in the study area consist of the interbedded limestones and shales of the Middle Ordovician/Black River Group. These rocks, and the overlying and eroding organic-rich Utica shale, represent Taconic orogenic sediments (Milici and Witt, 1988). The Marcellus Formation is shown in purple. The three principal shallow Upper Devonian gas producing formations are the Utica, Marcellus, and Utica (Figure 3): A generalized stratigraphic column (left), areal extent of the Marcellus Formation (right), and Map showing the county of interest. In our study area, these joint sets are sub-rectangular in shape and characterize gas flow. Figure 1: Copper tube sampling method originally devised by Werner (1984) and modified. This standard technique for groundwater gas sampling, specifically dissolved gas composition (e.g., USGS), the sample method ensures minimal air contamination of inorganic constituents including helium, hydrocarbons, etc.

III. Geological Background

The Appalachian Basin is an architecturally-controlled hydrocarbon producing basin that has evolved in response to complex tectonic processes and climatic changes since the Precambrian (Figure 1). The Marcellus at ~380 ± 15Ma, and age and burial depths were sufficient for the production of mature thermogenic hydrocarbon gases (Engelder and Whitehouse, 2000). The UD consists of thick synorogenic deposits including the Brauler, Lock Haven, and Catskill Formations. The older to younger sequence of the Catskill Formation is shown in purple. The three principal shallow Upper Devonian gas producing formations are the Utica, Marcellus, and Utica (Figure 3): A generalized stratigraphic column (left), areal extent of the Marcellus Formation (right), and Map showing the county of interest. In our study area, these joint sets are sub-rectangular in shape and characterize gas flow.

IV. Dissolved Gas and Inorganic Tracers

The potential for elevated methane concentrations from both natural geological processes and from natural gas development and elevated methane concentrations in shallow aquifers, other suggest that the presence of methane in shallow groundwater aquifers is common, natural, and unrelated to shallow gas development (e.g., Molofsky et al, 2011). Indeed, examples of natural methane seeps are identified in the northern Appalachian Basin (e.g., Salt Spring State Park, Morrisville, PA). Although published reports on methane concentrations higher than 0.5 cc/L have been observed in shallow aquifers in the northeastern PA (Bradford, Sullivan, and Wayne counties). The study area is part of the Appalachian Plateau physiographic province as gently dipping strata (overall dip magnitudes of ~1-3 degrees) that are broadly folded due to salt core detached folds, and further deformed by layer parallel shortening, reverse faults, and fracturing (e.g., Lash and Engelder, 2009). The oldest lithologies of interest in the study area consist of the interbedded limestones and shales of the Middle Ordovician/Black River Group.

V. Noble Gases: Conservative Fingerprint Tracers

While these findings suggest a correlation between areas of shale gas development and elevated methane concentrations in groundwater, others suggest that the presence of methane in shallow groundwater aquifers is common, natural, and unrelated to shallow gas development (e.g., Molofsky et al, 2011). Indeed, examples of natural methane seeps are identified in the northern Appalachian Basin (e.g., Salt Spring State Park, Morrisville, PA). Although published reports on methane concentrations higher than 0.5 cc/L have been observed in shallow aquifers in the northeastern PA (Bradford, Sullivan, and Wayne counties). The study area is part of the Appalachian Plateau physiographic province as gently dipping strata (overall dip magnitudes of ~1-3 degrees) that are broadly folded due to salt core detached folds, and further deformed by layer parallel shortening, reverse faults, and fracturing (e.g., Lash and Engelder, 2009). The oldest lithologies of interest in the study area consist of the interbedded limestones and shales of the Middle Ordovician/Black River Group.

VI. CONCLUSIONS:

Stray gas investigations should first constrain the geochemical and hydrogeological basin for a target area. As a result, radiogenic noble gases provide conservative tracers of gas source that are unaffected by microbial or subsequent hydrocarbon geochemical reactions. Here we show an example of how paired stable carbon isotopes and radiogenic noble gases can be used to determine the gas source and post-genetic migrational history of Devonian and Ordovician natural gases (Hunt et al., 2012; Darragh et al., 2013).

Figure 1: Copper tube sampling method originally devised by Werner (1984) and modified. This standard technique for groundwater gas sampling, specifically dissolved gas components (e.g., USGS), the sample method ensures minimal air contamination of inorganic constituents including helium, hydrocarbons, etc.

Figure 2: Digital elevation map of groundwater samples (n=72), sorted by location (county). Shaded brown areas represent the northern PA gas development, while the blue-green demarcate lower lying areas (valley). All samples from this study were collected from public wells after active shale gas development at the time of sample collection across four counties (Bradford, Sullivan, Susquehanna, Wayne, and Delaware) (Figure 3). Dissolved noble gases were collected in refrigeration-grade copper tubes that were flushed with water prior to sealing with refrigeration-grade copper tubes that were flushed with water prior to sealing.

Figure 3: A generalized stratigraphic column (left), areal extent of the Marcellus Formation (right), and a structural analysis of hydrocarbon geochemistry. Herein, we present our initial assessment of the dissolved gas (noble gas and hydrocarbon molecular and isotopic) geochemistry of shallow aquifers in the northeastern PA and southeastern NY.

Figure 4: The release of radiogenic isotopes (He, Ne,*Ar*) is a function of the temperature of the source formation of radiogenic noble gases (Hunt et al., 2012). As a result, radiogenic noble gases provide conservative tracers of gas source that are unaffected by microbial or subsequent hydrocarbon geochemical reactions. Here we show an example of how paired stable carbon isotopes and radiogenic noble gases can be used to determine the gas source and post-genetic migrational history of Devonian and Ordovician natural gases (Hunt et al., 2012; Darragh et al., 2013).