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 the approach of peak global hydrocarbon production are driving the transformation from coal to natural gas from unconventional energy resources. This transit has been aided by recent advances in horizontal drilling and hydraulic fracturing 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 enthusiasm and consent is tempered by various concerns regarding the environmental risks associated with shale gas development, specifically drinking-water quality (e.g. contamination from hydraulic fracturing fluids, production/flow back waters, and/or stray combustible gases). Thus, questions and concerns regarding the significance of elevated levels of combustible gas in shallow aquifers has been at the forefront of these concerns.

Previously, Osborn et al 2011 identified 17-times higher concentrations of thermally mature methane (CH_4) and aliphatic hydrocarbons (e.g. ethane (C_2H_6)) in drinking water wells within 1km of shale gas development sites producing from the Marcellus Shale in northeastern Pennsylvania. While these findings suggest a correlation between areas of shale gas development and elevated methane concentrations in shallow aquifers, others suggest that the presence of methane in shallow groundwater aquifers is common, natural, and unrelated to shale 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, Montrose, PA) (Warner et al, 2012).

The potential for elevated methane concentrations from both natural geological migration and anthropogenic activities highlights the need to develop and validate advanced geochemical systematics (e.g. integrated noble gas and hydrocarbon molecular and isotope geochemistry) capable of evaluating the source, timing, and migration history of hydrocarbon gases currently present within shallow aquifers. Herein, we present our initial assessment of the dissolved gas (noble gas and hydrocarbon molecular and isotopic) geochemistry of shallow aquifers in the northeastern tier of Pennsylvania and southeastern tier of New York State.

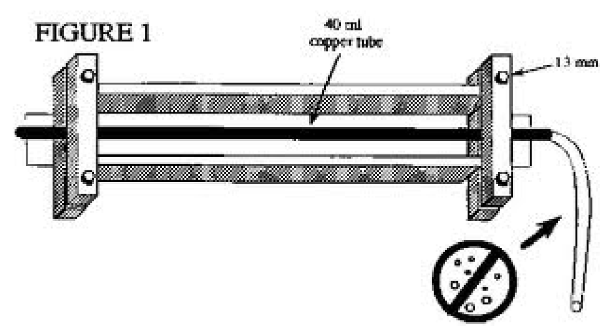
II. Sampling and Methods

We examine the dissolved gas isotopic compositions of 72 domestic groundwater wells and one natural methane seep within a seven county area of PA (Bradford, Sullivan, Susquehanna, and Wayne counties) and NY (Broome, Delaware and Sullivan counties). The study area is within the NAB Plateau region underlain by the Marcellus Shale (~800-2200m depth) (Figure 2). We integrate our data with previous work on the principal aquifers of the region (Alluvium, Catskill, and Lock Haven) including salt concentrations (i.e., Cl, Ba) and hydrocarbon molecular and isotopic composition (Warner et al., 2012). We place these data within the geological history of the NAB. This study includes only data from wells located >1km from active shale gas development sites including samples targeted for naturally occurring CH_4 along with other nearby domestic wells in order to characterize geological context of naturally elevated CH_4 in the NAB.

All groundwater samples (n=73) were analyzed for their major gas abundance (e.g., CH_4, C_2H_6, N_2, O_2) and noble gas composition (He, Ne, Ar, Kr). The stable carbon isotopic composition of methane ($\delta^{13}C$-CH_4) was determined for all samples with [CH_4] exceeding 0.5 cc/L (n=36), while paired stable hydrogen isotopic composition (δ^2H-CH_4) is available for 30 of the samples included in this study.

Before sampling, wells were purged to remove stagnant water and then monitored for pH, electrical conductance, and temperature until stable values were obtained. Water samples were collected prior to any treatment systems and were filtered and preserved following USGS protocols (USGS, 2011). The analysis of inorganic constituents (e.g., Cl, Ba) was reported in (Warner et al., 2012). Dissolved gas samples were collected for hydrocarbon molecular and stable isotopic composition (e.g., Isotech, 2011; Osborn et al., 2011a). Noble gas samples were collected in refrigeration-grade copper tubes that were flushed with water prior to sealing with stainless steel clamps (e.g., Dowling et al., 2004). Major gas components (N_2, O_2, Ar, CH_4) were measured using a Dycor quadrupole MS and a SRI GC (e.g., Darrah et al., 2012; Hunt et al., 2012). The isotopic analyses of noble gases were performed using a VG 5400 MS (e.g., Darrah and Poreda, 2012; Poreda and Farley, 1992).

Figure 1: Copper tube sampling method originally devised by Weiss, 1967 is a standard and accepted technique for groundwater gas sampling, specifically dissolved gas components near saturation (e.g., USGS). The sample method ensures minimal air contamination, accurate assessment of dissolved constituents including helium, hydrocarbons, etc.



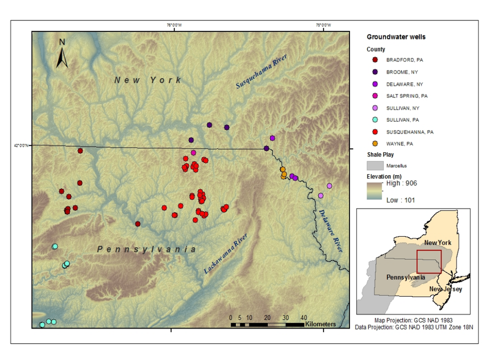


Figure 2: Digital elevation map of groundwater samples (n=72), sorted by location (county). Shaded brown areas represent higher elevations, while the blue-green demarks lower lying areas (valleys). All samples from this study were collected at distances >1km from active shale gas development at the time of sample collection across four counties in Pennsylvania (Bradford, Susquehanna, Wayne, Sullivan) and 3 counties (Delaware, Sullivan, Broome) in New York. Previous work identifies increasing [CH_4] and salt concentrations in valley bottoms (Warner et al, 2012, Molofsky et al, 2011).

III. Geological Background

The Appalachian Basin is an archetypal energy-producing foreland basin that has evolved in response to complex tectonic processes and climatic conditions since the Paleozoic (e.g., Faill, 1997). In the NAB, the Paleozoic sedimentary rocks were deposited during the Taconic and Acadian orogenies and deformed in the subsequent Alleghanian orogeny (Ettensohn and Brett, 2002). Today the complex depositional and tectonic history of this area is subtly expressed within the northern section of Appalachian Plateau physiographic province as gently dipping strata (overall dip magnitudes of ~ 1-3 degrees) that are broadly folded due to salt cored detachment folds, and further deformed by layer parallel shortening, reverse faults, and fracturing (e.g., Davis and Engelder, 1985; Engelder, 1979; Sak et al., 2012).

The oldest lithologies of interest in the study area consist of the interbedded limestones and shales of the Middle Ordovician Trenton/Black River Group. These rocks, and the overlying organic-rich Utica shale, represent Taconic orogenic sediments (Milici and Witt, 1988). The lower most Silurian age strata contains the fine-grained Tuscarora Formation sandstones, while the Upper Silurian is characterized by the transition from the Silurian Lockport Dolomite/McKenzie argillaceous limestone to the Bloomsburg red sandstone and evaporitic Salina Group (Straeten et al., 1994). The Salina Group consists of interbedded shales, dolomites, and salt deposits that act as the regional decollement for Alleghanian structures (Scanlin and Engelder, 2003). As a result, structural folds and faults above the decollement (i.e. Devonian and younger stratigraphic units) bear little resemblance in deformation style to those present beneath the Salina Group (e.g., Scanlin and Engelder, 2003).

The transition from Upper Silurian to Lower Devonian is comprised of the Upper Silurian Helderberg Group (layered dolomites and limestones) and Lower Devonian Oriskany Sandstone. At the base of the Middle Devonian sits the Onondaga/Selinsgrove limestones, which lies directly beneath the Middle Devonian aged Hamilton Group (Straeten et al., 2011). The Hamilton Group is an eastward to southeastward thickening wedge of marine sediments that includes the organic- and siliciclastic-rich, hydrocarbon producing Marcellus subgroup at its base (Straeten et al., 2011). The Marcellus at is ~380 ± 15Ma; its age and burial depths were sufficient for the production of mature thermogenic hydrocarbon gases (Engelder and Whitaker, 2006). The UD consists of thick synorogenic deposits including the Brallier, Lock Haven, and Catskill Formations (Figure 3). The latter two formations constitute the two primary lithologies that serve as aquifers in northeastern PA, along with the overlying glacial and sedimentary alluvium.

In the Appalachian plateau physiographic province, the rocks above the Silurian-aged Salina formation (including the Marcellus formation) deformed by stably sliding along their basal decollement as part of the Appalachian plateau detachment sheet (Davis and Engelder, 1985). Deformation within the Appalachian plateau detachment sheet is significantly less intense than the Valley and Ridge and is accommodated by a combination of layer parallel shortening, folding that lead to the broad anticline/syncline sequences, duplex/thrust faulting structures, and jointing (Lash and Engelder, 2009; Scanlin and Engelder, 2003). Each of these deformation features is present and observable within our study area. A combination of thrust-load-induced subsidence, clastic loading, and Alleghanian deformation led to the onset of thermal maturation and eventually catagenesis for the Marcellus Formation. This same hydrocarbon maturation and resulting fluid over-pressuring is suggested as the force that initiated the pervasive and systematic joint sets in the Devonian sediments throughout the Appalachian plateau (i.e. J_1 and J_2) (Engelder et al., 2009; Lash and Engelder, 2009). In our study area, these joint sets often cross-cut and are un-mineralized (Lash and Engelder, 2009).

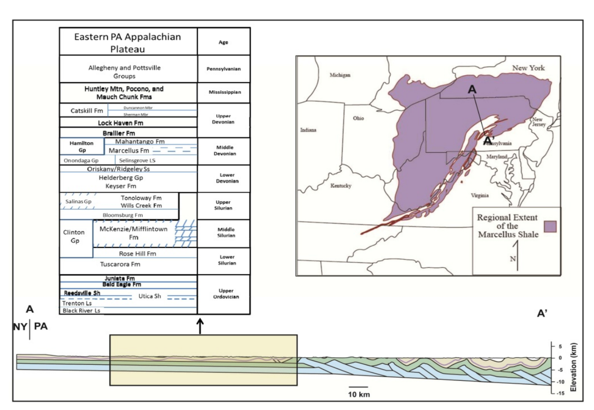


Figure 3): A generalized stratigraphic column (left), areal extent of the Marcellus Formation (right), and a simplified structural cross-section (reproduced from Sak et al, 2012) of the northern Appalachian Basin (NAB) plateau in northeastern PA and southeastern NY. The Marcellus Formation outcrop belt (upper right) is highlighted in red and the areal extent of the Marcellus Formation is shown in purple. The three principal shallow Upper Devonian aquifers include the Catskill, Lock Haven, and surficial alluvium. The generalized structural cross-section (bottom right) spans from the intensely deformed Valley and Ridge (southeast) to the Appalachian Plateau (to the north and west) across the Appalachian Structural Front (ASF). Samples in this study were collected within the yellow box at distances ranging from ~20-80km from the ASF.

Rifting of the Atlantic ocean, that began in the tertiary and continues today, led to rapid exhumation/unloading, erosion, and neotectonic jointing (i.e. often termed J_3) in at least the top 0.5km of the crust (Engelder, 2008). One additional factor that may influence the permeability of aquifers within our study area is Pleistocene glacial cycles. Ice loading and retreat led to an additional cycle of shallow crustal compaction, glacial isostatic rebound, and likely neotectonic fracturing within NE PA. As a result, previously deeply buried lithologies such as the Catskill and Lock Haven Formations in our study area are often highly naturally fractured, dual permeability aquifers today. The majority of stratigraphic sequences above the Catskill Formation are eroded in our study area and therefore not discussed. More complete reviews of Carboniferous Age deposition (Mississippian and Pennsylvanian) are available elsewhere (e.g., Faill, 1997).

IV. Dissolved Gas and Inorganic Tracers

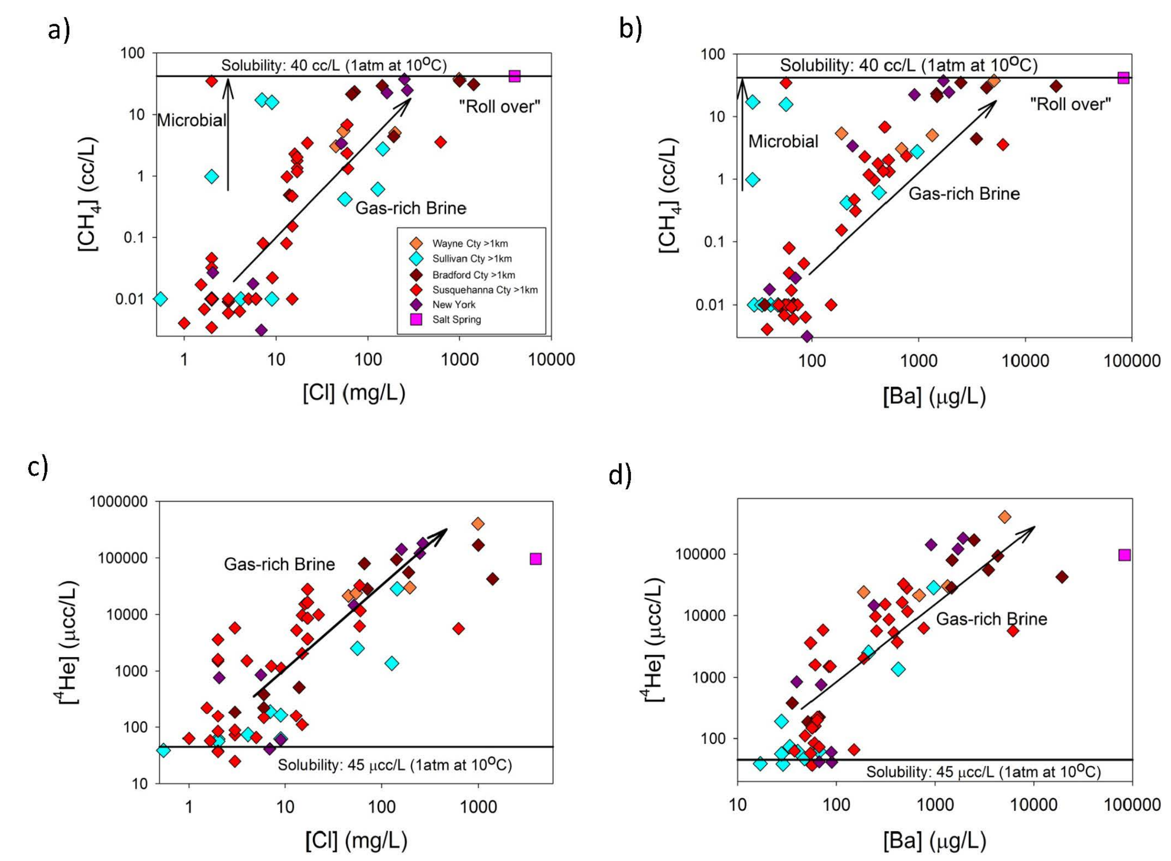
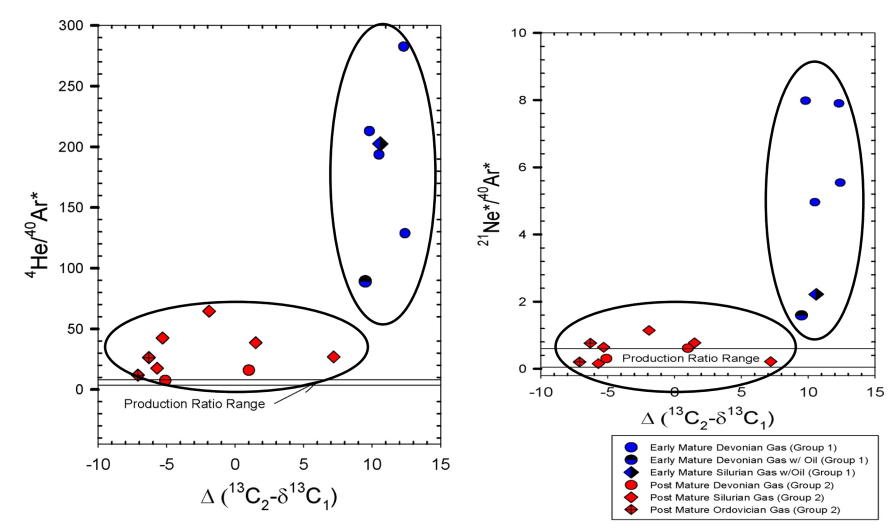


Figure 5: Variations of [Cl], [Ba], [CH_4], and [He] in groundwater and natural salt-rich spring located >1km from active shale gas drilling in Pennsylvania and New York. Sample colors indicate the county where samples were located. CH_4 and ^4He concentrations increase with Cl and Ba across the study area. The Cl-rich fluids contain elevated Br^-/Cl^- and Ba/Sr, as well as $^{87}Sr/^{86}Sr$ consistent with Middle Devonian Formation brines (i.e., Marcellus-type) (Warner et al, 2012). Notice that the increase in [CH_4] "rolls over" as methane concentrations approach saturation levels for shallow groundwater. The upper limit (solubility saturation = 40 cc/L at 1 atm) for [CH_4] demonstrates how groundwater solubility limits the maximum dissolved gas concentrations. The positive correlations of [^4He] with [Cl], [Ba], and [CH_4] suggests previous migration of a gas-rich, saline fluid from deeper formations into Upper Devonian aquifers across the region. The coexistence of CH_4 and [^4He] suggests a thermogenic source of methane.

V. Noble Gases: Conservative Fingerprint Tracers

Figure 4: The release of radiogenic isotopes (^4He, $^{21}Ne^*$, and $^{40}Ar^*$) is a function of temperature of the source formation (Hunt et al, 2012). As a result, radiogenic noble gases provide conservative tracers of gas source that are unaffected by microbial activity or subsequent chemical reactions. Here we show an example of how paired stable carbon isotopes and radiogenic noble gas isotopes can be used to fingerprint the genetic source and post-genetic migrational history of Devonian and Ordovician natural gases (Hunt et al, 2012; Darrah et al, 2013).



VI. CONCLUSIONS:

- Stray gas investigations should first constrain the geological and hydrogeological background of a basin targeted for drilling.
- Stray gas investigations should utilize the full compliment of dissolved gases
- Gas chemistry should be paired with dissolved constituents
- Noble gases provide conservative tracers of natural gas: a) source; b) migration; and c) geological history
- Combining noble gas, stable isotopes, and inorganic components allow us to better constrain the geological history of fluid migration in unconventional energy basins (Darrah et al, 2013)