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Using Production Gas Carbon and Hydrogen Stable Isotope Signatures to Predict Fluid Quality: Wattenberg Field, Colorado, USA

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Abstract

Stable carbon ($\delta^{13}C$) and hydrogen ($\delta^{2}H$) isotopes have been used to characterize hydrocarbons for exploration, development and production since the 1960s, and have re-emerged as predictive tools with the development of unconventional "tight" oil and gas plays. Here we report on publicly available Colorado Oil and Gas Conservation Commission (COGCC) and U.S. Geological Survey (USGS) datasets of production gases collected from the Greater Wattenberg Area (GWA) of Colorado.

The $\delta^{13}C$ and $\delta^{2}H$ of natural gas can be used to interpret gas origin (i.e., bacterial versus thermal), hydrocarbon maturity, migration and reservoir compartmentalization, and production allocation. Maturities derived from carbon and hydrogen isotopes can serve as controls in regional maturity maps, which are used to help define areas of oil, wet gas and dry gas production. Stable isotope analysis can be executed pre-completion on samples obtained from mud gas and/or gas desorbing from cuttings and core. These data can help predict fluid type, API gravity, and gas-oil ratio (GOR), all of which can help guide land acquisition and development decisions.

Production gases from the lower to upper Cretaceous Muddy "J" Sand, Codell, Niobrara and Sussex formations are characterized isotopically as early-mature to post-mature oil-associated gases. Progressing from shallow to deeper formations, $\delta^{13}C$ of methane, ethane, propane and $\delta^{2}H$ of methane components all increase, reflecting increasing maturity with depth, and the presence of multiple, discrete petroleum systems (Sherwood et al., 2013). Stable carbon and hydrogen isotope values show a strong correlation to both initial and cumulative GOR for the unconventional Niobrara and Codell intervals of Wattenberg Field. While this relationship does not hold for wells actively producing from the Muddy "J", this could be a result of geologic compartmentalization in this interval due to faulting, natural migration and other factors.

Validation of the correlation between Niobrara and Codell production GOR and stable isotope composition was provided by an independent geochemistry dataset from the USGS. The predicted GOR values were then used to accurately distinguish reservoir fluid classification. These results demonstrate the potential of natural gas stable isotope signatures as a useful and reliable fluid quality prediction tool.

Introduction

Accurately determining rock and hydrocarbon fluid properties is imperative in developing a sound understanding of any petroleum reservoir system, especially in the case of unconventional reservoirs. Reservoir fluid quality parameters, such as gas-oil ratio (GOR) or fluid type, can have a tremendous effect on asset value and development plans. In the absence of robust laboratory pressure-volume-temperature (PVT) data, two relatively inexpensive techniques for predicting fluid properties are the analysis of composition and carbon and hydrogen stable isotopes of associated natural gases. Besides low cost, a distinct advantage is that the gas samples of interest can be collected from the mudgas stream during drilling, from desorbing core or cutting samples, or from production streams at pre-described intervals. This allows one to make fluid quality predictions at any point in the life cycle of a well. Additionally, production gases sampled over a regional area of interest, as demonstrated here, can provide further control in the construction of predictive regional fluid-quality maps.

Statement of Theory and Definitions

Greater Wattenberg Area (GWA), located within the west-central portion of the Denver-Julesburg Basin of Colorado (Figure 1), represents an ideal locality for developing the proposed fluid-quality prediction tool. The field was first discovered in 1970 and is now well established. As such, there is a wealth of publicly available geochemical and production data with which to develop fluid quality prediction models. Secondly, oil and gas is actively produced in the field from multiple conventional and unconventional reservoirs - the low permeability "tight" reservoirs of the Muddy "J" Sandstone of the Dakota Group, Codell Sandstone Member of the Carlisle Shale, Niobrara Formation and the Sussex Sandstone Member of the Pierre Shale (Higley and Cox, 2007; Figure 2). Finally, GWA is located on a thermal anomaly within the Denver Basin, with the thermal gradient greatest towards the center of the field and decreasing away from this center (Higley and Cox, 2003). As a consequence of this lateral thermal gradient, produced natural gases preserve a range of chemical and isotopic compositions from across the field, making it an ideal locality for the present study.

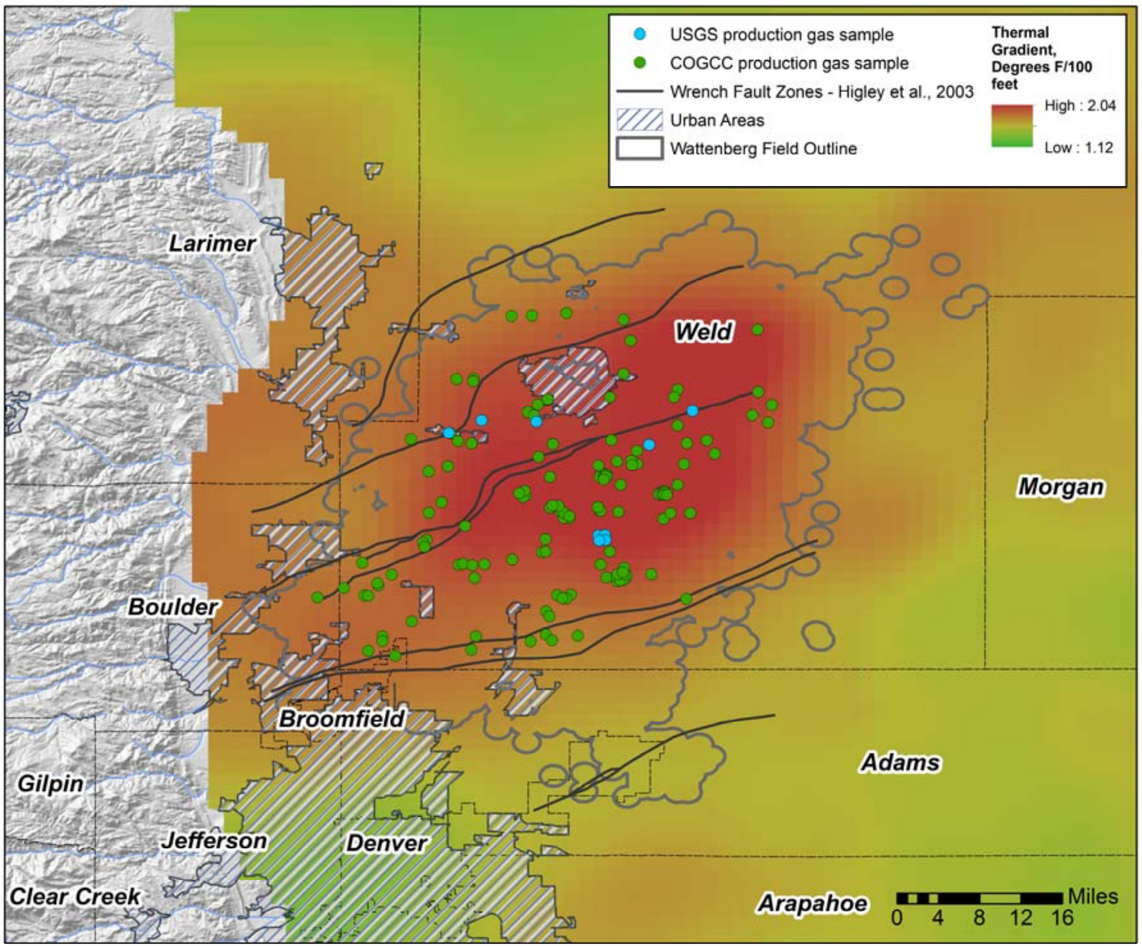

Figure 1: Map of Greater Wattenberg Area, located within the Denver-Julesburg Basin of Colorado. Thermal gradient is derived from well bottomhole temperatures (Dixon, 2002). Included are the COGCC and USGS production gas sampling points used in this study, as well as Wrench Fault Zones as described by Higley and Cox, 2003.

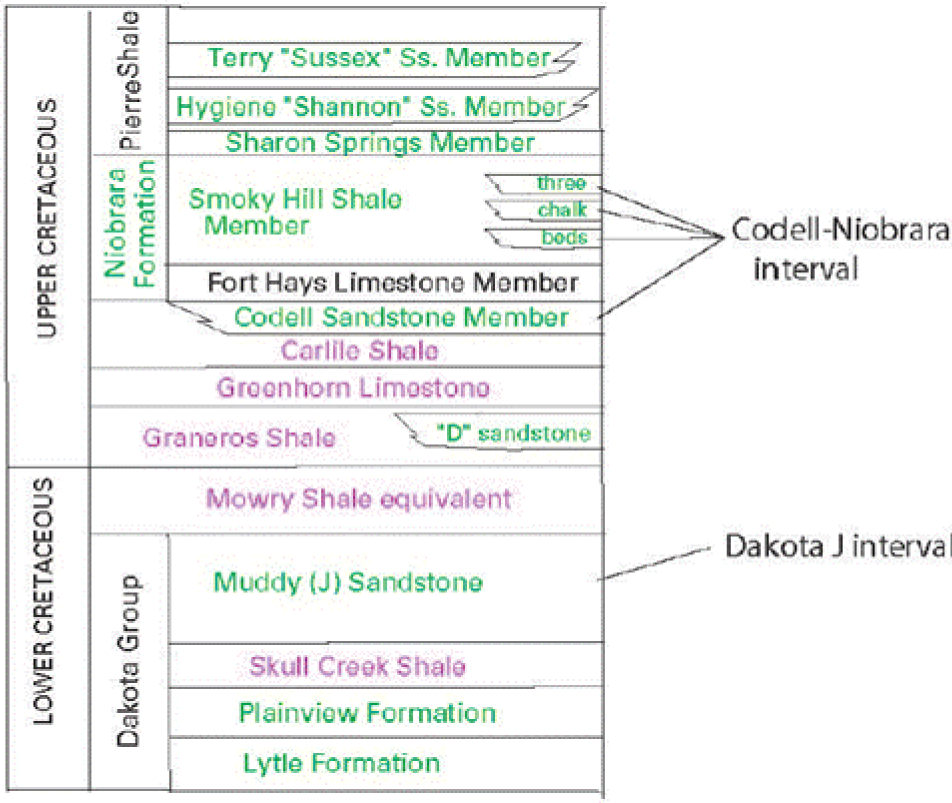

Figure 2: Denver-Julesburg Basin Stratigraphy (Nelson and Santus, 2011).

The compositional and isotopic analysis of natural gas is a powerful tool and can be used to interpret gas origin (i.e., bacterial versus thermal; Figure 3A), hydrocarbon maturity (Figure 3B), migration and reservoir compartmentalization. The relative proportion of C_1-C_5 n-alkanes from standard gas composition analysis by gas chromatography, reported in molar percentage, provides an initial characterization of the gas through the use of ratios such as gas character and wetness. Stable isotopes, measured using gas chromatography isotope ratio mass spectrometry (GC-IRMS) techniques, add an additional level of more detailed natural gas characterization.

In the case of hydrocarbon molecules, two stable isotopes are of particular interest: hydrogen-2 or deuterium (^{2}H) and carbon-13 (^{13}C). For practical purposes, stable-isotope values are expressed as a ratio in the conventional delta (δ) notation in parts per thousand (‰) relative to a standard:

$$\delta^{13}C\ (‰) = [(^{13}C/^{12}C)_{sample} \div (^{13}C/^{12}C)_{standard} - 1] \times 1000 \quad (1)$$

$$\delta^{2}H\ (‰) = [(^{2}H/^{1}H)_{sample} \div (^{2}H/^{1}H)_{standard} - 1] \times 1000 \quad (2)$$

where the reference standard for carbon is Vienna Pee Dee Belemnite (VPDB) and the hydrogen standard is Vienna Standard Mean Ocean Water (VSMOW).

The additional neutron in the atoms of ^{13}C and ^{2}H and the associated mass difference results in slightly different atomic properties that impact physical and chemical reactions. These reactions typically favor one isotope, thus changing the relative stable-isotopic composition of the products and reactants. This process, called fractionation, is the basis for distinguishing natural gases by their isotopic signature (Kendall and Caldwell, 1998). The distribution of stable carbon and hydrogen isotopes in natural gas components is controlled by several factors, of particular importance being the isotopic composition of the source material and kinetic isotope effects, which predict that ^{12}C-^{12}C or ^{1}H-^{1}H bonds will break more easily than ^{12}C-^{13}C or ^{1}H-^{2}H bonds, thus concentrating the heavier isotopes in the reactant pool (Whiticar, 1997; Chung, 1988). These effects allow for the determination of empirical relationships between the stable-isotopic composition of natural gas components and the thermal maturity level of the active source rock from which the gases were derived (Dolan et al., 2007; Whiticar, 1997; Figure 3B). Considering that gas-oil ratio (GOR) is also related to thermal maturity, among other factors, stable-isotope geochemistry may be an appropriate tool for predicting fluid quality parameters such as GOR and reservoir fluid type, especially in low-migration, tight petroleum systems.

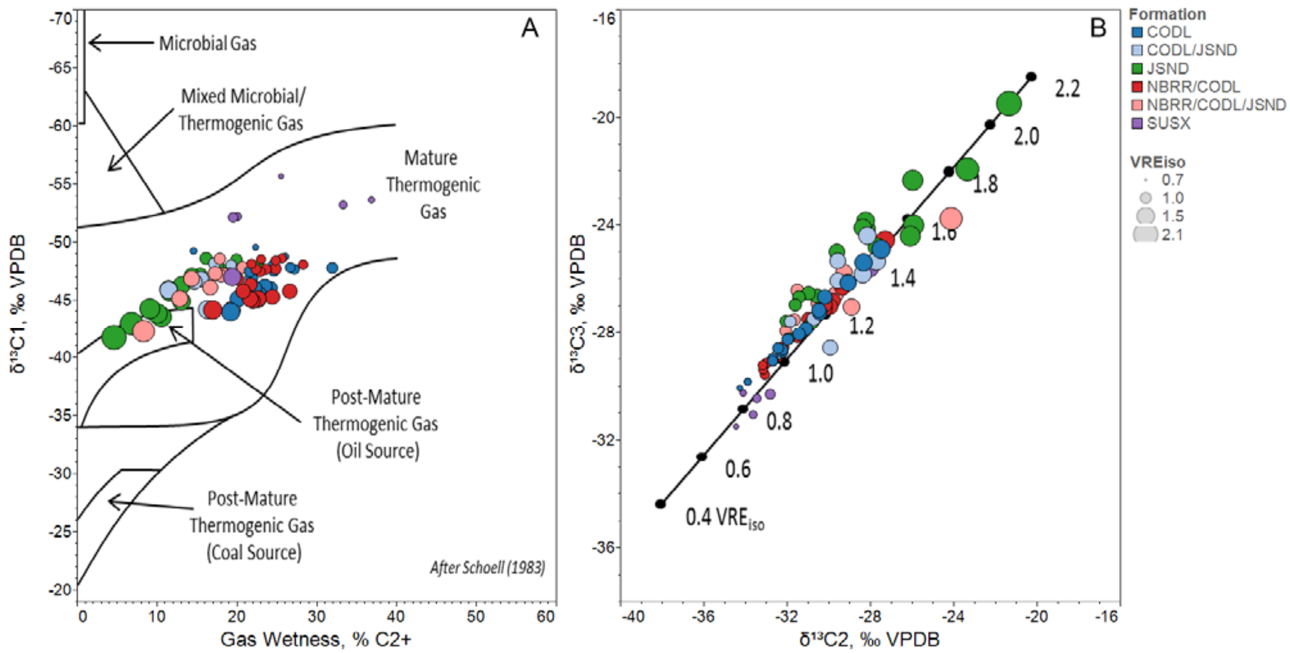

Figure 3: Genetic characterization and carbon-isotope thermal maturity plots after Sherwood et al. (2013). (A) Based on the classification scheme of Schoell (1983), all production gases from GWA are of thermogenic origin, with some Muddy "J" Sand gases classified as post-mature. (B) Propane $\delta^{13}C$ vs ethane $\delta^{13}C$ plot overlaid on a previously developed maturity calibration from a database of Rocky Mountain gases (Dolan et al., 2007). Calibration is based on Vitrinite Reflectance of depth-paired wellbore cuttings and $\delta^{13}C$ of mud gas components. Symbols are scaled by VRE_{iso}.

Description and Application of Process

In 2007, the Colorado Oil and Gas Conservation Commission (COGCC) published a baseline study of natural gas wells in the GWA in order to address concerns about potential oil and gas development activities and their impact on groundwater resources. As part of this study, hydrocarbon gases were sampled from 77 wells and analyzed for molecular concentration, $\delta^{13}C$ and $\delta^{2}H$ isotopic composition of methane (C_1), and $\delta^{13}C$ of ethane (C_2) and propane (C_3) (LT Environmental, 2007). This initial dataset was supplemented by additional gas sampling and analytical events within the GWA, the results of which were obtained from the COGCC's online GIS database (COGCC, 2013). Molecular and isotopic composition data from a total of 142 wells were analyzed in this study.

These gases were all collected from actively producing wells; however, the chemical and isotopic composition can also be analyzed on gases collected from desorbing core or cuttings samples and gases collected from the mud stream while drilling. As the isotopic signature is not dependent on gas concentration or volume, it provides a robust means for distinguishing the mudgas, which is thought to be dominated by free gas, to core or cuttings gas, which is predominantly bound gas, and the production stream throughout the lifecycle of the well (Goddard and Tang, 2013). Although they would likely provide better control than production gas signatures, which are often co-mingled between multiple producing reservoirs, these mudgas and desorbing gas data are not often publicly available, hence the use of publicly available production gas data.

While laboratory analyses are typically used to determine fluid quality, gas-oil ratio (GOR) can be an indicator of reservoir fluid type and quality, as defined in *The Properties of Petroleum Fluids* (McCain, 1990). GOR data are advantageous in that they are often available publicly from initial tests and monthly reporting. Cumulative production GOR values, reported in standard cubic feet per barrel (scf/bbl), were collected from the IHS Energy production database for the 142 wells referenced above (IHS Energy, 2014). While the cumulative production data is useful in minimizing the effects of small perturbations in production during the lifecycle of the well, the first six months of production data were also collected, where available, to understand the initial production period. Given that the wells vary in age and many older Muddy "J" or Dakota group wells have been recompleted into the Niobrara/Codell producing zone, it was necessary to verify the production data and producing formation through the COGCC well completion reports (COGCC, 2014). The complexities presented by comingling of production for numerous reservoirs and recompletions are not trivial and can be cause for concern when working with publicly reported production data, though well history and completion information was cross-checked to minimize those effects in this dataset.

Presentation of Data and Results

As stable carbon and hydrogen isotope ratios have been previously established as a proxy for thermal maturity, one would expect a positive trend where ^{13}C enriched gases are more mature and exhibit more gas-prone production (Whiticar, 1997). Cumulative GOR cross plotted with $\delta^{13}C$ values of C_1, C_2, C_3 and δ^2H of C_1 all demonstrate this relationship consistently, although there is considerable scatter above the main exponential trend line (Figure 4).

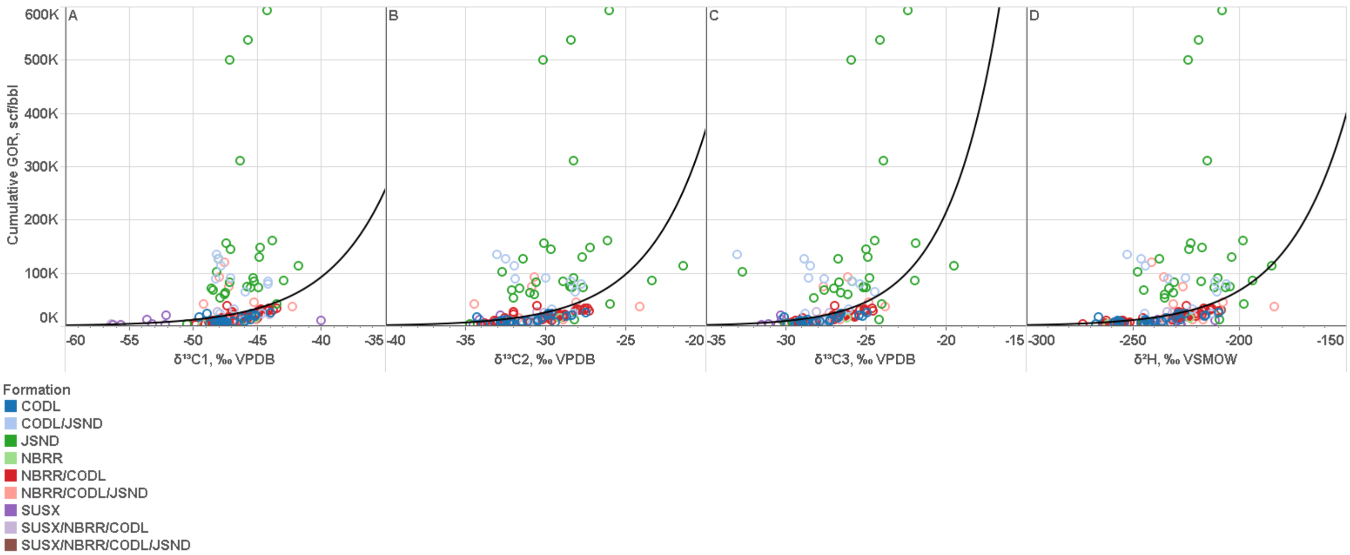

Figure 4: Plotted are cumulative GOR (scf/bbl) data vs $\delta^{13}C_{methane}$ (A), $\delta^{13}C_{ethane}$ (B), $\delta^{13}C_{propane}$ (C), and $\delta^2H_{methane}$ (D) for each well, color-coded by producing formation.

An important observation is that the outliers which fall above the main trend are, without exception, representative of wells that are actively producing from the Muddy "J" interval or comingled production between other zones and the Muddy "J". This observation agrees with previous findings from Wattenberg where the Dakota / "J" interval was found to produce gas on a per well basis at roughly three times the rate of the Niobrara and Codell intervals (Nelson and Santus, 2011). The median GOR for the 1900 wells producing from the Dakota and "J" intervals was 95.5 mcf/bbl, which is in good agreement with these data (Higley and Cox, 2003). Restricting the dataset to only wells producing from the Niobrara, Codell or a comingling of the two, cumulative GOR vs the stable carbon-isotope values of methane, ethane, propane and stable hydrogen-isotope values of methane yields a strong positive correlation in all four cases (Figures 5A, 5B, 5C, 5D). The same relationship holds when stable-isotope data are plotted against GOR derived from an initial production period of 6 months, though many of the initial production data were not available for older wells (Figures 5E, 5F, 5G, 5H).

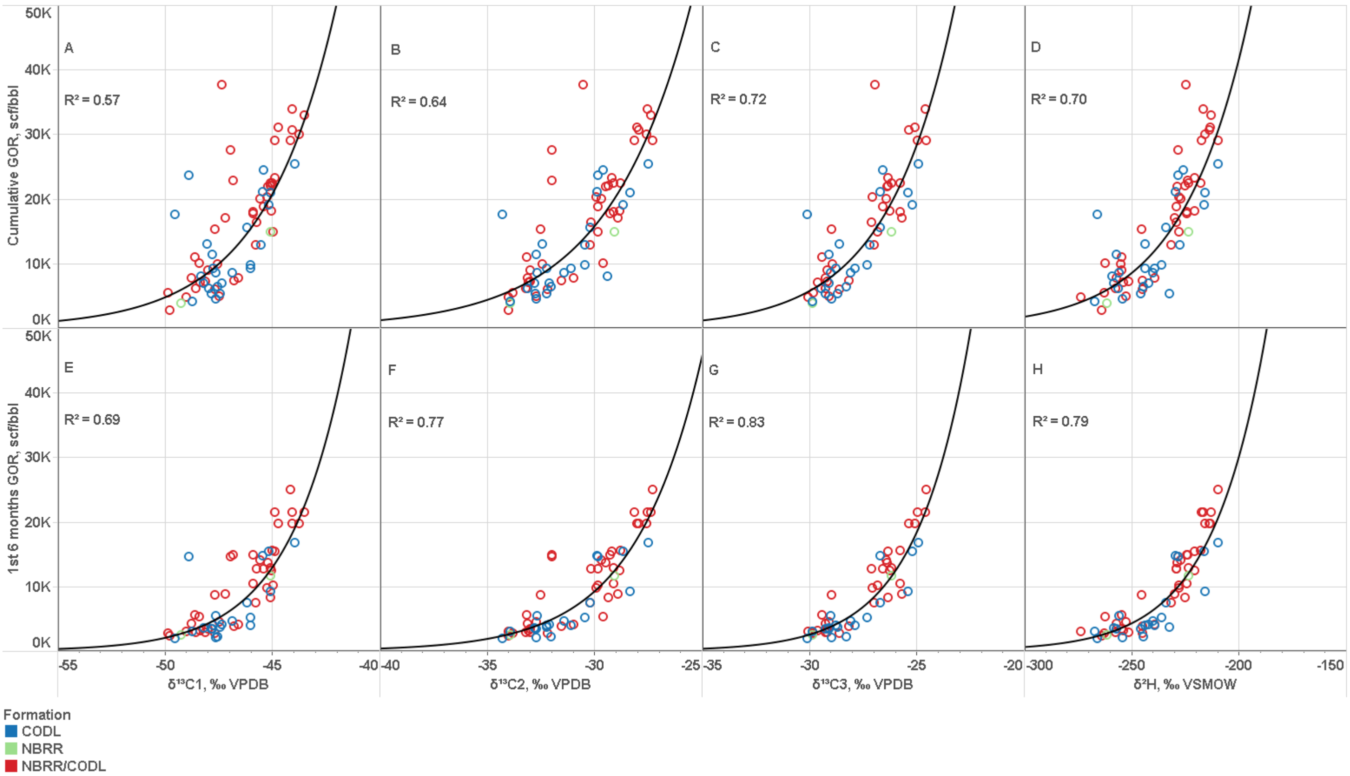

Figure 5: Plotted are cumulative GOR (scf/bbl) data vs $\delta^{13}C_1$ (A), $\delta^{13}C_2$ (B), $\delta^{13}C_3$ (C), and δ^2H of C_1 (D) and GOR data from the first six months of production (scf/bbl) vs $\delta^{13}C_1$ (E), $\delta^{13}C_2$ (F), $\delta^{13}C_3$ (G), and δ^2H of C_1 (H) for each Niobrara or Codell producing well, color-coded by formation. Displayed are the R-squared values for the exponential-regression model of each curve.

The strong correlations between stable carbon and hydrogen isotope composition and GOR for the Niobrara and Codell intervals and the lack thereof for natural gases collected from Muddy "J" production streams is not entirely understood, though there may be several potential factors at work. For example, in addition to gas production being overall higher than the shallower Niobrara and Codell intervals, the Muddy "J" is known to be associated with lobes of greater and highly variable GOR across the field, especially between the Longmont and Lafayette wrench fault zones (Higley and Cox, 2003; Figure 1). Variation in GOR is linked to areas of higher heat flow, with a narrow band of extremely high GOR in the western part of Wattenberg along a fault that was likely a conduit for higher heat flow in the past (Higley and Cox, 2003). Production gas isotope data confirms that maturity values significantly higher than the maximum for known lower and upper Cretaceous source rocks in Wattenberg exist; further corroborating the theory that gas may have migrated through faults from a deeper source (Sherwood et al., 2013). These migration and structural factors may contribute to the variability in GOR in the Muddy "J", but this variability is much less pronounced in the Niobrara and Codell intervals.

Though the Muddy "J" production data warrants further investigation, there is potentially significant value in the relationship defined by the Niobrara and Codell system. One application would be utilizing this relationship as a predictive tool to estimate GOR and reservoir-fluid type during drilling or when making development decisions. In order to prove the merit of such a tool, an additional independent dataset of production gas stable-isotope data from GWA was collected from the USGS Energy Geochemistry database (USGS, 2009). Ethane and propane $\delta^{13}C$ data is sparse in the USGS dataset for GWA, so deuterium isotope data is used to predict GOR in this case. With a much larger range of values relative to carbon isotopes, deuterium isotopic composition also has the advantage of a more favorable signal to noise ratio. Using the exponential-regression model calculated above (Figure 5D), a cumulative GOR was projected based upon the deuterium stable isotope values. The results were integrated with an established reservoir fluid classification scheme from *The Properties of Petroleum Fluid* (Figure 6; McCain, 1990). The modeled GOR compares favorably to the cumulative GOR data from IHS and allows for an accurate classification of reservoir fluid type; in the case of these samples, one would expect retrograde and condensate production. These correlations could also be modeled spatially at a resolution defined by sampling and production data density, resulting in predictive fluid quality maps to help guide development decisions.

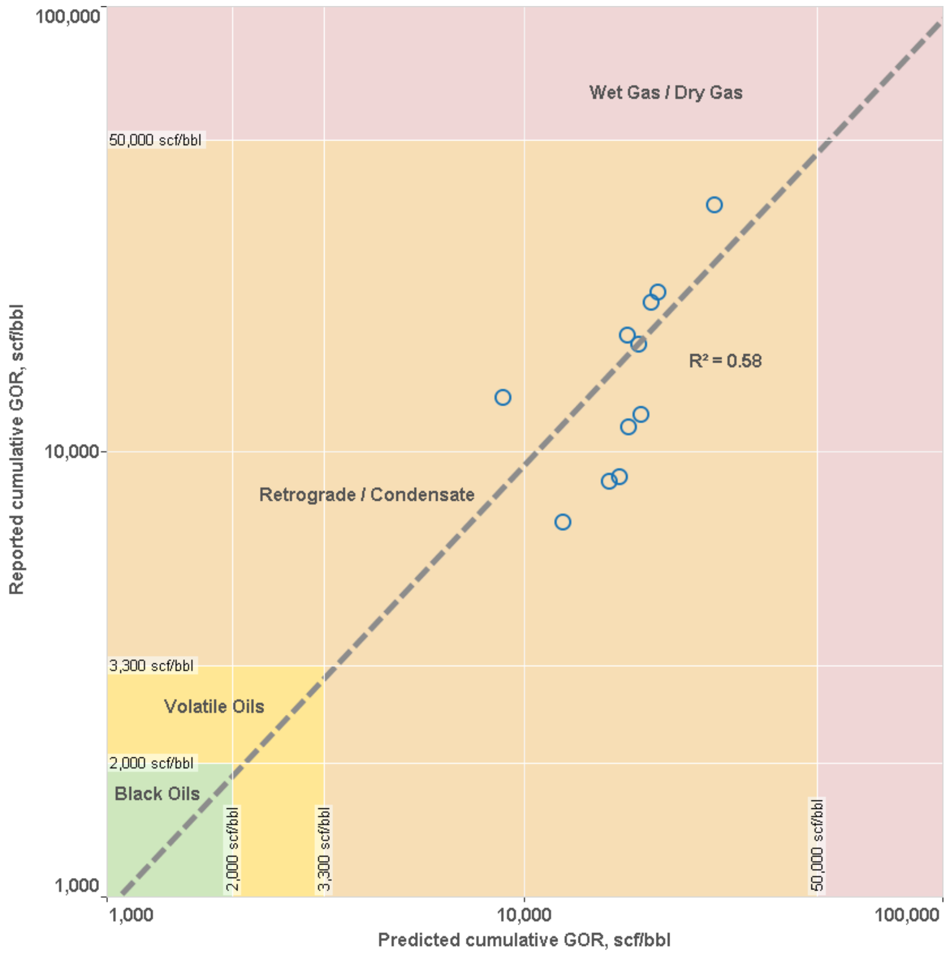

Figure 6: Plotted are actual cumulative GOR (scf/bbl) vs predicted cumulative GOR (scf/bbl) for 11 samples from the USGS Energy Geochemistry database (USGS, 2009). Predicted cumulative GOR is based upon production gas $\delta^2H_{methane}$ values.

Conclusions

Together, gas composition and stable isotope analyses of natural gas samples show promise as a predictive tool for fluid-quality parameters. Stable carbon and hydrogen isotope values show a strong correlation to both initial and cumulative GOR for the unconventional Niobrara and Codell intervals of Wattenberg Field. While this relationship does not hold for wells actively producing from the Muddy "J", this could be a result of geologic compartmentalization in this interval due to faulting, natural migration and other factors. Based upon the stable-isotope data, in some instances the Muddy "J" is likely producing vertically migrated gas originating from a deeper source. The relationship exhibited by the Niobrara and Codell interval production gas data is useful in predicting reservoir fluid type and GOR and this analysis could be used to predict reservoir fluid-quality from gas samples taken at any point in the life cycle of a well. It can also be used to build predictive fluid quality maps to guide land acquisition and development decisions. Further investigation should be pursued to evaluate whether this Niobrara and Codell calibrated model can be used to make accurate predictions outside the boundaries of the Greater Wattenberg Area.

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