

Geochemistry and Geologic Analysis in Shale Gas Play

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Abstract

The understanding from the conventional geochemistry and geology analysis is very different when trying to apply them to shale gas plays. This paper is a summary for U.S. shale gas plays on geochemistry and geologic analysis application, and real field data from active U.S. shale gas plays was used in the discussion for different concepts.

Introduction

Shale gas plays have become so successful in the U.S. that the whole world energy scenario is in flux. There are so many critical geological, engineering, and economic issues that need to be considered for a successful shale gas play. In this paper, the application of geochemistry and geological methods and technologies for shale gas plays are discussed.

Geologic Age, Burial History, and Overburden

In North America the proven economic shale gas plays are Mississippian/Devonian (318 to 416 MM years) with the Jurassic (160 MM years) and Upper Cretaceous (99 MM years) currently in evaluation. Assuming the necessary organic content, these rocks generally have a burial and temperature history that provides for optimum thermal maturity of the organic matter and present economically accessible depths. The overburden type, thickness and structural complexity becomes important due to its influence on direct drilling costs. While deposited in different geologic times, these shales share similar depositional environments. Black shales accumulate in depositional settings in which there is little or no oxygen present in the water (usually deep water anoxic environments). Shales of the Devonian and Mississippian in North America were deposited at a time when an interior seaway was present across much of the continental U.S. from the Appalachian mountains westward providing continuity of deposition environment. Burial history can be determined by use of geochemistry data.

Geologic Drilling and Completion Challenges

To date, shale gas plays have been most successful in basinal areas where there is minimal overlying and associated structural complexity. The best Barnett Shale production in North Texas is where faulting and karsting is not present. The best Fayetteville Shale production in eastern Oklahoma and western Arkansas is where reverse faulting is minimal. Large areas of the Appalachian region of the Marcellus have complex fault structuring and, even though they have excellent source rock and maturity profiles, are not yet areas of the most aggressive development. Regions where there is minimal complex geologic overburden, little to no faulting and consistent lateral depositional history within the shale gas target have had the most success. Complex structure above the shale gas target usually increases the vertical drilling costs due to

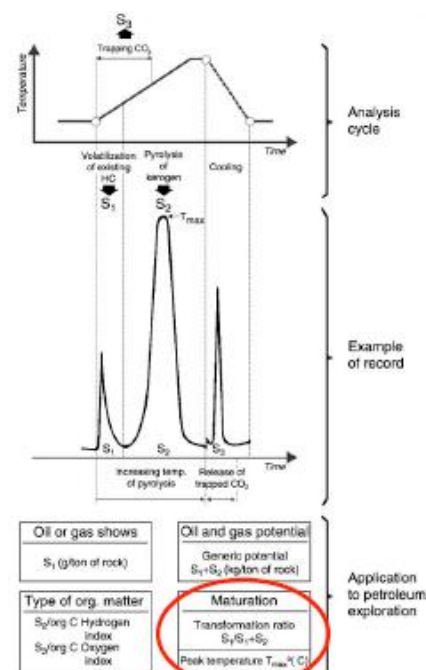
excess hole deviation caused by high geologic dips and fault planes. Air drilling can overcome some of these operational and economic challenges.

Completion challenges can be caused by faulting and karsting. Faults adjacent to the horizontal wellbores can capture the hydraulic stimulation fluid and open fracture systems in overlying or underlying strata out of zone that can preferentially route water into the gas shale zone and overwhelm gas production. Karsts (collapsed carbonate cave systems) often have local fracture systems that act similar to fault systems and can route water into the gas shale zone.

Geochemistry for Thermal Maturity and Organic Content

This subject is the initial step in the determination of the producibility of gas shales. Much of this material is from various papers by Dan Jarvie from 2003 through 2009. Some gas shale systems are of biogenic origin but the most prolific are thermogenic. The distribution, gas saturation, oil risk and productivity of thermogenic gas shales are strongly dependant on geochemical factors. These factors are original organic richness, basin locale dependant thermal maturity and burial history. There are a number of geochemical analyses relevant to gas shale evaluation that can describe these three factors.

Thermal maturity is the measure of heat produced carbon and hydrogen loss from the shale due to hydrocarbon generation leading to lower TOC and hydrogen values. Rock Eval pyrolysis is used to identify the type and maturity of organic matter and to detect petroleum potential in sediments. Samples are heated, evolved gas volumes are measured and maximum cracking temperature is observed. S1 (free oil and gas present in the shale) and S2 (remaining kerogen in the shale) ratios are determined. These estimate hydrocarbon volume potential. Figure 1 shows the Rock Eval process.



In summary, the four basic parameters obtained by pyrolysis are as follows:

S1 = the amount of free hydrocarbons (gas and oil) in the sample (in milligrams of hydrocarbon per gram of rock). If $S_1 > 1$ mg/g, it may be indicative of an oil show. S1 normally increases with depth. Contamination of samples by drilling fluids and mud can give an abnormally high value for S1.

S2 = the amount of hydrocarbons generated through thermal cracking of nonvolatile organic matter. S2 is an indication of the **quantity of hydrocarbons that the rock has the potential of producing should burial and maturation continue.**

S3 = the amount of CO2 (in milligrams CO2 per gram of rock) produced during pyrolysis of kerogen. **S3 is an indication of the amount of oxygen in the kerogen and is used to calculate the oxygen index.** Contamination of the samples should be suspected if abnormally high S3 values are obtained. High concentrations of carbonates that break down at lower temperatures than 390°C will also cause higher S3 values than expected.

Tmax = the temperature at which the maximum release of hydrocarbons from cracking of kerogen occurs during pyrolysis (top of S2 peak). Tmax is an indication of the stage of maturation of the organic matter.

Figure 1: Key Parameters from Rock Eval Pyrolysis (Wallis, et al, 2009).

Rock Eval Tmax is the temperature at maximum S2 yield indicating thermal maturity. Hydrogen Index (HI) characterizes the origin of the kerogen and amount of hydrogen remaining in the shale. Low HI indicates initial higher original TOC. HI is determined from Rock Eval and TOC.

Kerogen Types

Total Organic Content (TOC) describes the organic richness (kerogen content) of the shale. Measured TOC low maturity outcrop values are often double that of subsurface values. This is common for gas shales and represents the burial of the organic material through time with higher temperatures present with increasing depth and pressure providing the conversion of the kerogen to hydrocarbons. The TOC for gas shales should be greater than 2% and in some shales ranges over 10%. TOC may be modified (usually upward) to correct for sampling inconsistencies.

Kerogen is a complex mixture of disseminated organic compounds in sediments that release hydrocarbons upon the application of heat and pressure. It consists of altered remains of marine and lacustrine compacted organic material, such as algae and other low plant forms, pollen, spores and spore coats, and insects with differing amounts of terrigenous debris. It converts to various liquid and gaseous hydrocarbons at a depth of seven or more kilometers and a temperature between 50° and 100 °C. The type and amount of hydrocarbons released is also dependant on the kerogen type, whether of marine or non-marine origin.

Type I kerogen has high HI, is lacustrine sourced, oil prone on maturation and usually rare, often found in southeast and continental Asia. It is a good source for gas shales with correct thermal history. Type II has high HI, is marine and generates both oil and gas, sourcing many giant conventional fields worldwide. Type III has low HI, mostly terrigenous and is gas prone. Type IV has lowest HI and is rare. Kerogen can be qualitatively identified on wireline logs since source rock intervals generally show a higher gamma ray, lower density, higher sonic transit time, higher porosity and higher resistivity than other sedimentary layers. Note that dependant on maturation parameters, the kerogen type may not be related to overall generated gas volumes.

Vitrinite Reflectance

Vitrinite Reflectance (%Ro) indicates the thermal maturity level of the kerogen. It is derived by measuring the amount of heat destruction of the kerogen of terrigenous origin using light reflectance measured under microscope. %Ro typically ranges from 0.2 to 3.0. The higher the reflectance, the higher the thermal maturity. %Ro is not valid for pre-Silurian rocks as land plants had not yet developed. It is not a measurement of kerogen conversion that is required to assess the maturity of shale gas targets so it must be used with other maturation indices (Jarvie, 2008). %Ro can be calculated from Tmax. Transformation Ratio (TR) is the extent of kerogen conversion and is calculated from the HI. TR values approaching one have highest gas production potential.

As described above, kerogen type can determine the type of hydrocarbons produced during the primary phase of hydrocarbon generation,

however, under further maturation as shown in Figure 2, what was initially an oil source rock can produce large volumes of gas after secondary cracking.

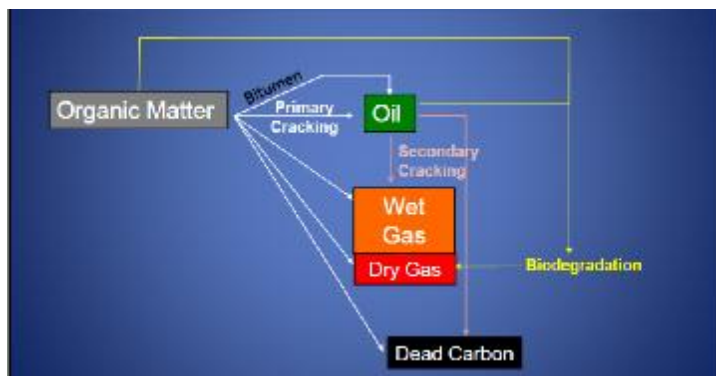


Figure 2: Primary and secondary cracking producing gas (Jarvie, 2008).

The Barnett shale is an example of this as it is the source for oil in the Ft Worth basin as well as the gas. It contains primarily Type II kerogen and can be described as “a burnt out oil source rock.” Figure 3 summarizes geochemical maturation parameters for North American shale gas plays. Direct application of geochemical maturation parameters for shale gas risk assessment is shown in Figure 4. A typical relationship between Kerogen type, HI and Tmax is shown in Figure 5. For rapid evaluation of a basin potential for shale gas, burial history plots can be constructed from formation tops, ages, lithologies, deposition water depth, porosities as a function of depth, bottom hole temperatures, kerogen content and %Ro data versus depth. This data can be sourced from core analyses, well logs, well reports, geologic papers and seismic sections (Guidish et al, 1985 and Figure 6, Camphor, 2004).

Shale	Interpreted Thermal Maturity Window	TOC (wt.%)	Estimated TOC _o (wt.%)	HI (mg HC/g TOC)	Estimated TR	%R _o from Tmax	Measured %R _o	S1/TOC (mg HC/g TOC)	Count	Dry Gas Ratio (C1/C1+C4)	δ ¹³ C methane (ppt)	δ ¹³ C ethane (ppt)	δ ¹³ C propane (ppt)
Antrim	Immature to early oil	5.27	5.35	432	10-20%	0.87	0.51	53	181	98%	-55		
New Albany	Oil	7.06	7.28	428	5-40%	0.65	na	21	58	52%	-53	-44	-37
Woodford	Oil	9.23	9.61	503	10-50%	0.76	0.54	52	31				
Marcellus	Dry gas	3.37	5.27	16	>90%	2.16	na	20	33				
Utica	Dry gas	1.71	2.67	18	>90%	nr	na	33	21				
Fayetteville	Dry gas	1.86	2.91	24	>90%	nr	2.0-2.5	15	538				
Woodford	Late oil-early gas	2.04	3.19	73	>80%	0.92	na	17	40				
Barnett	Immature-early oil	5.21	5.37	380	12%	0.62	0.55	42	3				
Barnett	Early oil	4.70	5.28	289	31%	0.86	0.77	78	25				
Barnett	Gas	4.45	6.50	45	90%	1.72	1.67	19	90				
Avokan	Late oil-early gas	3.11	4.86	23	>70%	1.4	na	27	18				
Barnett	Late oil-early gas	4.04	6.31	87	>70%	0.76 - 1.48	0.86-2.15	33	858				
Woodford	Late oil-early gas	3.93	6.14	87	>70%	1.02	1.20 - 2.10	70	32				
Bossier	Dry gas	1.81	2.33	13	>90%	nr	1.40	18	28				
Lewis	Dry gas	1.48	2.28	22	>90%	NR	1.60	18	22				
Waltman	Oil	2.53	4.22	322	50%	0.75	0.69	6	43	87%	-35	-23	-22
Bakken	Oil	11.37	13.87	298	10-70%	.50 - 1.00	0.55 - 0.95	43	349				
Monterey	Oil	6.77	7.95	480	10-20%	0.40	0.45	88	12				
Antelope	Oil	3.02	3.18	433	10-30%	0.55	na	70	70				

All values are average values from Humble database and may include variable thermal maturities

TOC_o total organic carbon, original value
HI hydrogen index (S2/TOC x 100; mg HC/g TOC)
TR transformation ratio ((HI_o - HI_{ps})/HI_o) where HI_o is original HI and HI_{ps} is present-day HI value
%R_o vitrinite reflectance in oil submersion
%R_{eq} vitrinite reflectance equivalent; calculated from Rock-Eval Tmax value
ppt parts per thousand or parts per mil

Figure 3: Geochemical Summary of North American Shale Gas Plays (Jarvie, 2008).

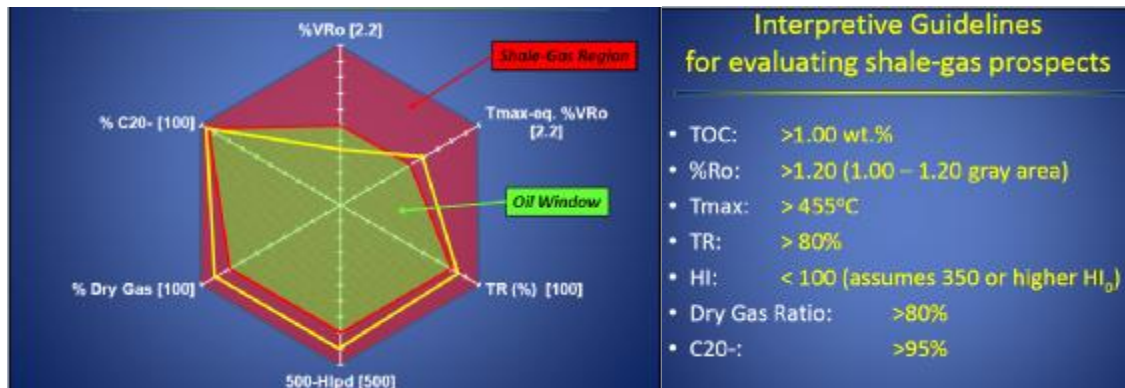


Figure 4: Visual plot and complete list for geochemical assessment of gas risk (Jarvie, 2008).

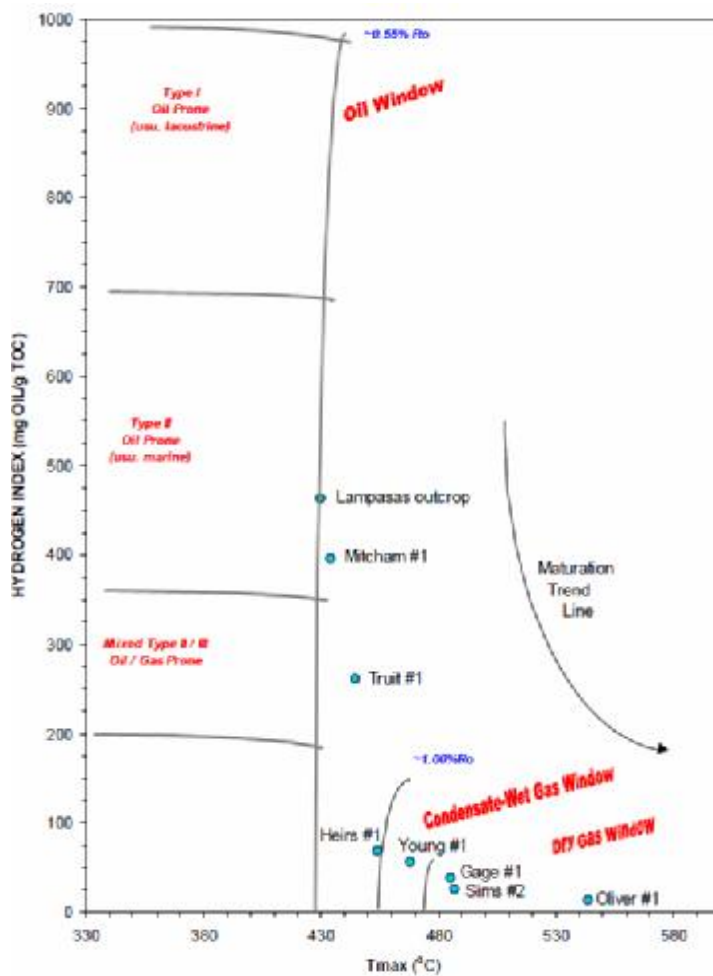


Figure 5: Typical Hydrogen Index versus Tmax (Jarvie, 2008).

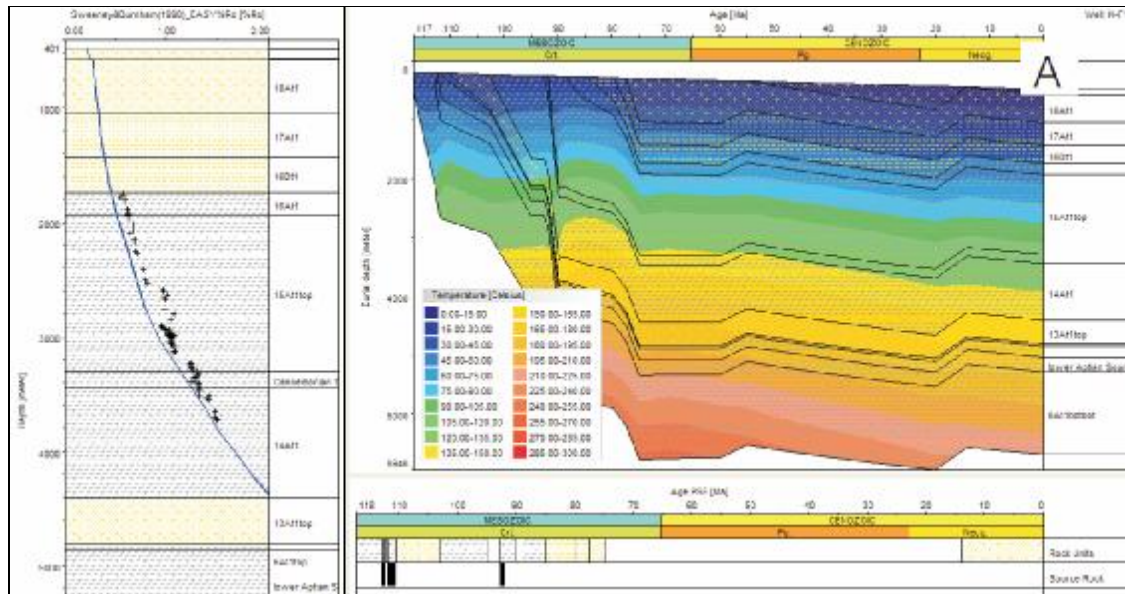


Figure 6: Burial History Plot (Camphor, 2004).

Porosity, Permeability and Gas Storage

Gas shales usually exhibit average porosities in the single digits and permeabilities in the nanodarcy range (10^{-3} to 10^{-6} millidarcies). Porosity is mostly governed by silica content. Much of the shale gas is stored in this porosity and this is where much of the early production of a shale gas well is derived. Permeabilities are generally poor whether vertical or horizontal. The compaction of clay particles that occurs during post-deposition as additional overburden accumulates above these particles results in formation of thin laminae (layers) as the clay particles rotate and lie parallel due to compaction. Massive, multi-stage slick water hydraulic fracturing has proved to be the only economically viable method for increasing the vertical and horizontal permeabilities to allow economic gas recovery. The natural matrix permeability of shales is sometimes overcome by formation of natural fracture networks which develop when overburden pressure is reduced as a result of erosion of overlying rock formations. Fractures are often key sources of permeability facilitating fluid migration through these fine grained rocks (modified from ALL Consulting, 2008).

Gas in shale reservoirs is stored two basic ways: by sorption and by compression of free gas in natural fractures or other available macroporosity. Sorption refers to gas that is stored in adsorbed state. Adsorbed gas is held on the surfaces of solid material, either organic matter or minerals, in the reservoir. It is this portion of the gas that is attached to the kerogen and clay platelets in the shale and is released over a long time period (generally 30 to 40 years) to move to the pressure sink at the well bore. The Langmuir adsorption equation is,

$$q = \frac{(a * P)}{(1 + a * P)}$$

Equation 1

where θ is the percent surface coverage, P is the gas pressure or concentration, α is a constant.

The constant α is the Langmuir adsorption constant and increases with an increase in the binding energy of adsorption and with a decrease in temperature. Figure 7 shows Antrim shale and Barnett Shale different isotherm behaviors. Physical controls on adsorption include the type of solid sorbent, temperature, and the rate of gas diffusion. Free gas, however, exists in a dissolved state, e. g., as solution gas in liquid petroleum. It is this gas that exists within the porosity or within any naturally occurring open fractures within the gas shale and is produced at high rates early within the life of the well (modified from Jarvie et al, 2007).

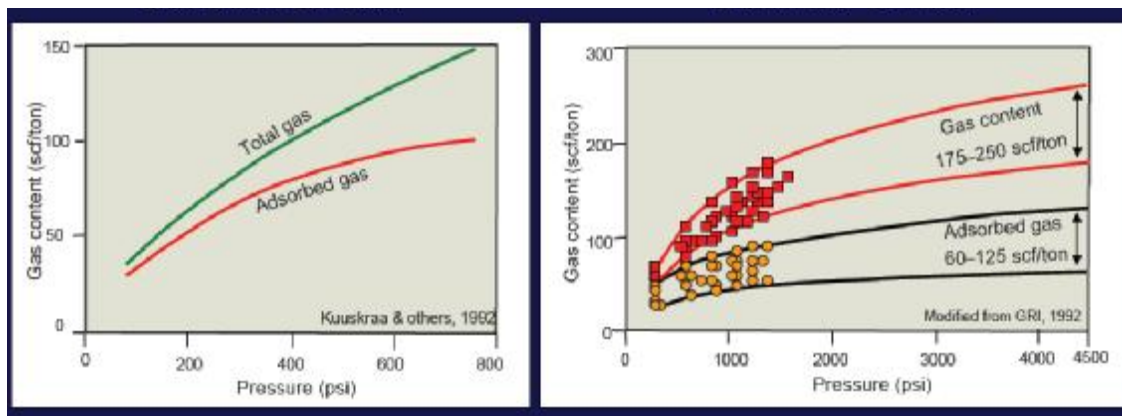


Figure 7: Effect of Pressure on Free Gas and Adsorbed Gas (left is Antrim Shale; right is Barnett). Difference between Total and Adsorbed is the Free Gas. Both increase with Pressure. Note that Barnett has higher pressure and double the Total Gas at the higher pressure (Wang, 2008).

Core, Cuttings and Log Analyses

Core and cuttings from new drill or older wells can be analyzed for geochemistry, rock properties, petrology, rock mechanics and biostratigraphy to perform geochemical and geological analyses of the samples. Depending on the quality and preservation of the samples, these studies can determine free and adsorbed gas volumetrics, type and quality of organic material, thermal history, test petrophysical models for prediction, determine mechanical suitability for hydraulic fracturing, identify depositional environments and diagenesis and geochemical analysis: Total Organic Carbon (TOC), thermal maturity (Vitrinite Reflectance and/or TAI), RockEval/TMax (how much of the organic material has been converted to gas).

To frac the shale formation is a routine process to make shale formations productive. To evaluate the potential for shale formation success, the brittleness parameter can be used for evaluation. Brittleness is a function of mineral composition and diagenesis. Jarvie et al (2007) define the brittleness formula:

$$B = \frac{Q}{(Q + C + CL)}$$

Equation 2

where B is brittleness, Q is quartz, C is carbonate and CL is clay. Wang (2008) modified the above brittleness function and added the effect of diagenesis to brittleness, which caused by changes in temperature and fluid composition related to tectonic and burial history, and thermal maturity. The vitrinite reflectance was considered to be the most stable parameter to reflect the maturity change in a shale formation, and it is used to the brittleness formula:

$$B = \frac{(1 + a(R_0 - b))Q}{(Q + C + CL)} \quad \text{Equation 3}$$

where R_0 is vitrinite reflectance and a and b are constants to be determined. Figure 8 shows gas rate and brittleness as a function of vitrinite reflectance using equation 2.

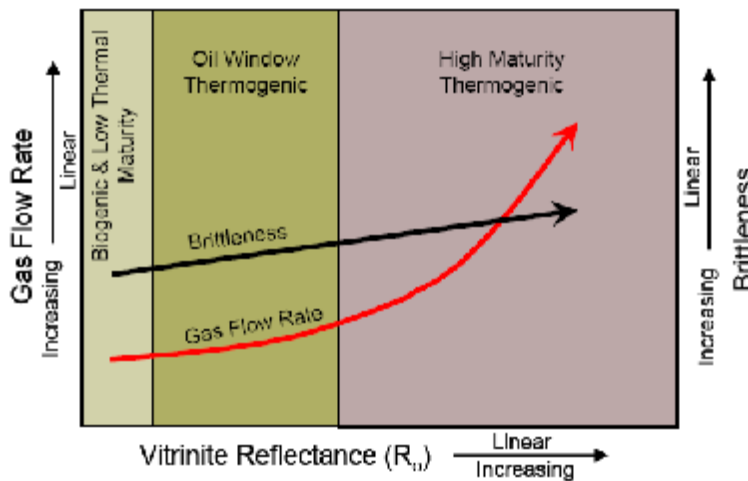


Figure 8: Gas flow rate, brittleness, and vitrinite reflectance relation (Wang, 2008).

Shale gas reservoirs are most often characterized as mudstones rather than pure shales as, along with the clays, they also usually have large amounts of quartz, carbonate debris and pyrite. The quartz is usually present as mechanically derived silts and organically derived sponge spicules and radiolaria. The quartz content and vertical distribution is often key to porosity and potential gas storage directly affecting well expected ultimate recoveries. The carbonate debris may be present as disseminated or as distinct layers. Pyrite occurs due to the oxygen starved, reducing nature of the depositional environment, often concentrated along depositional layering presenting challenges to efficient horizontal drilling. These mudstones generally exhibit high gamma ray due to the abnormally large volume of organic material (kerogen) present, low density (again mostly due to abnormally high kerogen) and high resistivity due to the direct gas content and usually low water saturation. There is often neutron-density log gas effect when the neutron log is run with a carbonate matrix. The high density disseminated pyrite can influence log analysis if not properly identified. These parameters can vary in magnitude

throughout the vertical section. Appendix 1 shows the basic shale gas well logging combinations.

Gas Analysis and Recovery

Access to analyses of the gases present in the shales can provide significant insight as to the expected ultimate recovery (EUR) of the wells. Generally, the gases with lower BTU content (mmbtu per mcf), primarily composed of methane and ethane will have higher EURs due to the smaller molecular size of the shorter chain gases. This is because the smaller methane molecules can more easily move through the clay plates and kerogen particles within the mudstone toward the pressure sink at the wellbore. The longer chain hydrocarbons are more easily trapped. This is why the more thermally mature gases are expected to have the higher EURs and is especially true in the Barnett shale in North Texas. It also explains why most oil shales (with the exception of the Bakken Shale in Montana and North Dakota) have to date not been economically exploited with the current tools that work so well for the gas shales, primarily the slick water multi stage hydraulic fracturing. Often these oil shales, when fractured in horizontal wells, exhibit high initial production rates of oil that quickly decline in volume to the point where they are not economic to produce.

There are several methods for determining shale gas-in-place in terms of standard cubic ft of gas in place per ton of shale. They are all based on extrapolation and modeling of simple or sophisticated conventional core analysis. Petrophysical analysis, both simple and sophisticated is one branch. The simplest approach is to relate shale density to gas-in-place via tying log density data to core analysis results and developing a linear transform. This method can provide low resolution gas-in-place by rock volume but can not separate gas filled porosity volumes and adsorbed gas volumes. A more rigorous petrophysical approach is to tie multi-log inversion analysis to a conventional core database. In this method the gas filled porosity and the adsorbed gas ratios can be estimated to provide total gas-in-place. Recovery factors are usually determined by reservoir simulation of the horizontal well using the reservoir and fluid properties, pressure and temperature and hydraulic stimulation efficiency. Permeability enhancement via the hydraulic stimulation can be modeled to quantify the estimated recovery versus permeability changes. It is a non-linear relationship.

Shale gas reservoirs usually exhibit hyperbolic production declines on a semi-log plot of production rate versus time. This characteristic is due to the generally low vertical and lateral permeability of the rock. Production periods may last over 40 years due to the long term, low volume gas adsorption discussed earlier. There are usually isolated layers of quartz constituents with higher permeability either present within the rich source rock or closely connected. These are generally thin but may be volumetrically significant. When vertically connected by hydraulic fracture stimulation, these isolated permeability layers are the main contributor to well producibility and overall higher EUR. Often a shale gas well may produce 50% of its EUR within the first three to five years. Generally, wells with higher initial production rates will have higher EURs, but this can vary widely dependant on the hyperbolic decline parameters related to the success of the hydraulic fracture stimulation. After a

number of wells have been on stream, type decline curves can be developed within geographic areas that indicate expected EURs based on the initial production rates. EURs with high degree of confidence can be determined from as little as three months of full production when these type decline curves are available. Figure 9 shows a typical Barnett shale gas production well decline curve.

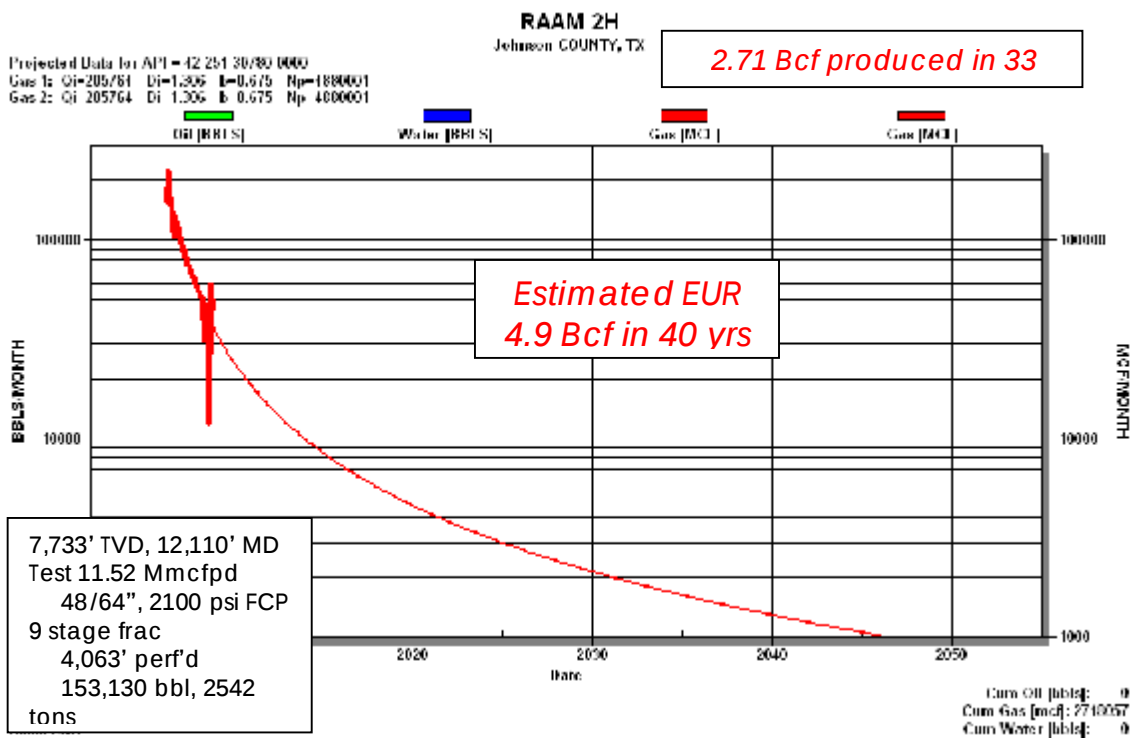


Figure 9: Typical Barnett Shale Horizontal Well Decline Curve.

Conclusion

To evaluate the shale gas potential by using geological and geochemistry methods and technologies is a challenge since there are so many parameters controlling the final results.

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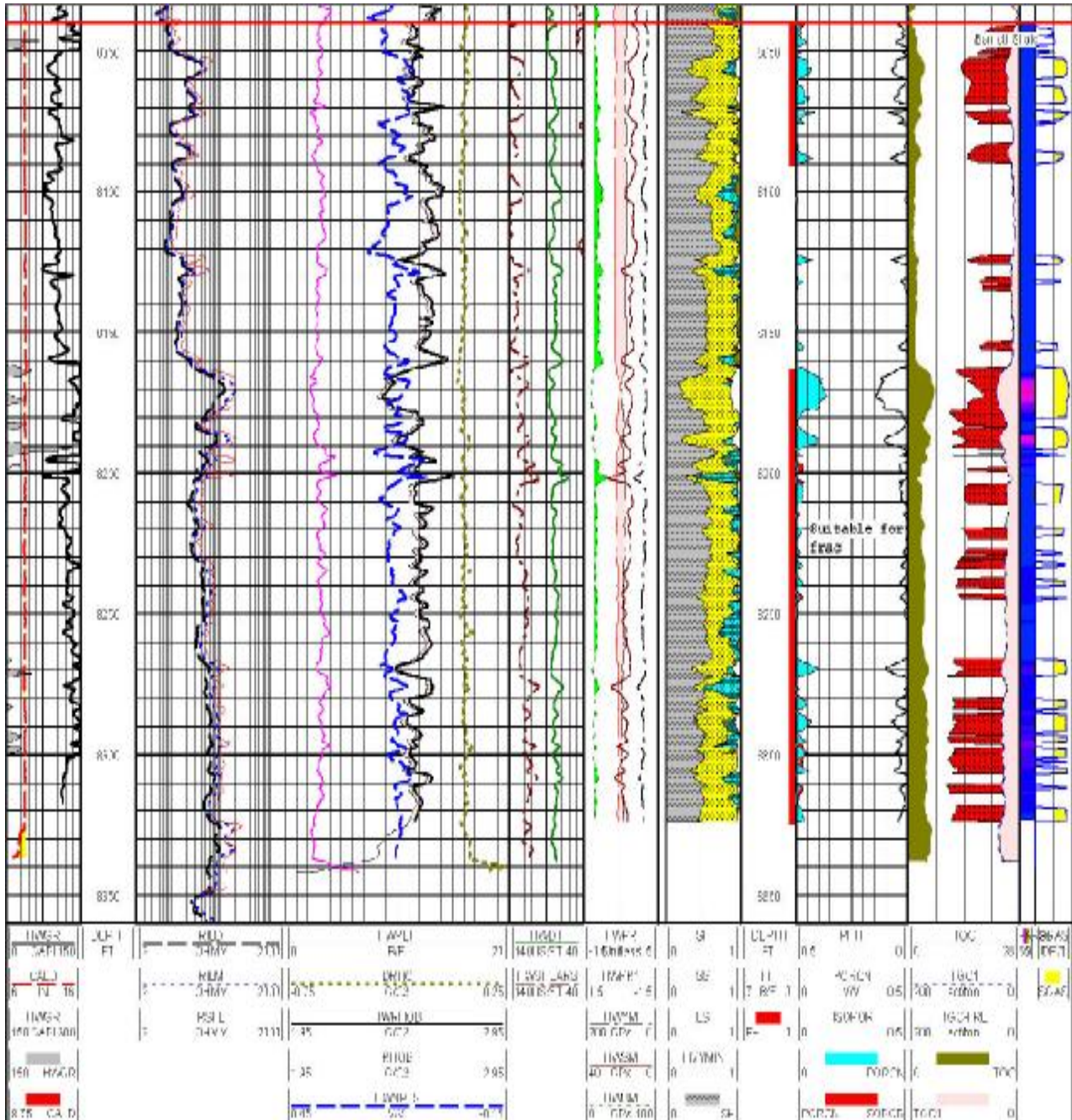
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About the Principal Author

Before Harding & Shelton Group, Wenwu Xia worked as a research scientist at University of Oklahoma. His research areas included digit modeling the fracturing fluids and formation reaction during hydraulic fracturing, Reservoir simulation, real time algorithm analysis. He held management, technology development and technical leadership positions within China National Petroleum Corporation (CNPC) from 1982 to 1995. His research projects included basin sedimentary environment and history, lithology analysis, and reservoir protection for basins in south of China on shore. He earned an MS in Petroleum Engineer from the University of Oklahoma in 1999, an MS in Computer Science from the University of Oklahoma in 2000, and BS from the China University of Geoscience in 1982. He lives in Norman, Oklahoma.

Appendix 1



The well log curve of Barnet Shale Well MITX # 1H (Harding & Shelton Group, 2006).