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Abstract

India, a new entrant in shale gas exploration, has proved the potential by launching the maiden shale gas project in India near Durgapur, and surfacing the first ever shale gas as a mark of success.

The paper deals with the important geochemical evaluation of shale gas exploration from Barren Measure Formation. The Rock Eval and TOC analysis carried out at KDMIPE on Barren Measure shale core samples indicate very good organic richness (TOC: 4.56-10.5%) and good remaining hydrocarbon generation potential (S2: 3.3-12.34mgHC/g rock). The thermal maturity based on Tmax values indicate peak to late oil generation window (Tmax: 459-471°C). HI and OI values indicates the type III organic matter. The VRo studies indicate shale falling in late oil generation (VRo 0.86 to 1.01%) maturity window suitable for shale gas venture. The paper will bring out the workflows, methodologies, applicable in shale gas geochemical analysis & interpretation for potential assessment.

Introduction

Sixty percent of the Earth's sedimentary crust consists of shale and it is the primary source rock for most of the conventional hydrocarbon deposits in the world. These have very tight porosity and ultralow permeability but still commercially production is possible largely, due to the advancement in drilling and stimulation technique (1 and 2). The predominant evaluation of a shale facies from source perspective involves intense geochemical evaluation. Assessing the shale gas prospect and potential thus incorporates a number of geochemical studies which in turn gives inferences about its generation and gas storage capacity of the rocks. Shale contains sufficient amount of organic matter which subject to the geologic processes needed to convert organic material to oil and/or gas. Important geochemical evaluation associated with the assessment of shale gas plays involves the predominant play type like thermal, biogenic or mixed, organic richness of the rock, kerogen type, lighter hydrocarbon adsorption to methane, specificity of the hydrocarbon, maturity of the organic matter, burial history, transformation ratio and balance generation potential, cracking behavior of kerogen, gas composition and type, gas dryness, isotopic studies, biomarkers etc. (3, 4 and 5). Different organic material generates different kerogen types, namely, oil, wet gas, dry gas and nonhydrocarbons (6).

Characterisation of organic –rich matured source rock is the first step for the success of shale gas plays (7). There are many factors that affect the producibility of hydrocarbons from shale source/reservoir rocks. Basic geochemical data goes a long way toward characterizing these plays and their likelihood of high-graded commercial success. Geochemical evaluation requires holistic and integrated analysis of available field datasets. Geochemical properties to adequately characterize shale resources including total organic carbon (TOC), gas volume and capacity, thermal maturity, permeability and mineralogy (4). Thermal maturity is a function of depositional history. As kerogen is exposed to progressively higher temperatures over time, vitrinite- a cell wall material and woody plant tissue preserved in the rock- undergoes indicative of immatured kerogen, not having been exposed to sufficient thermal conditions over adequate time for conversion of organic matter to hydrocarbons.VRo value ranges from 0.6% to 0.8% indicate oil and 0.8% to 1.11 indicate wet gas. Measurements in excess of 1.5 are a sign of dry gas- generating source rock, a positive indicator of shale gas.

Gas is adsorbed on the surface of the kerogen in the shale and is also freely distributed in the primary and secondary porosity. Total gas-in-place is combination of adsorbed gas and the free gas. Depending upon the initial pressure of the reservoir as free gas is produced and the pore pressure falls, adsorbed gas will be liberated or desorb from the surface of the kerogen. Recent study (9) indicate that desorption phenomenon must be consider while estimating resource potential of shale gas. To determine adsorbed gas from shales Langmuir Adsorbed Isotherm is used by canister desorption test. The gas is removed from the canister, volumetrically measured and compositionally analysed as a function of time. A plot of gas produced over time can be used to estimate the GIP for the core samples at reservoir condition. This analysis is sensitive to the time it takes to retrieve the core from the downhole. The above results suggest three different relations of Langmuir volume and TOC. These relations are used in computation of adsorbed gas from TOC computed from log. The adsorbed gas content range between 1-3 scf/ton which is considered to be quite low with respect to shale gas exploration consideration.

India, a new entrant in shale gas resources, is the front runner and has already proved in its potential of existence. A systematic approach was initiated to identify, characterize and prioritize the promising basins drawing analog from US basins and results of Damodar valley basin. ONGC ventured by spudding the First shale gas well in Ichhapur near Durgapur of West Bengal, which has resulted in success.KDMIPE took an initiative on Shale Gas Exploration and carried out analytical studies for prospectivity assessment of shales in the HC bearing basins to establish the potential of the thick, organically rich, mature and relatively shallower Barren Measures Formation in the Damodar Basin (10).

The present work envisaged independent assessment of critical geochemical parameters from core samples of Well-SGAA of Damodar Basin, associated with the assessment of shale gas plays, synthesizing the generated output with international standard of results and thus validating the methodology and practices which involves Rock Eval, TOC and VRo studies of core samples, Gas compositional studies (upto C5), Isotopic analysis (Carbon and hydrogen) and Integrations of G & G data with available public domain results.

Experimental Details

Rock- Eval Analysis: The samples were washed, dried, crushed to powder and screened through BSS 60 mesh sieve. The crushed samples were well homogenized before carrying out experiments. The crushed samples were analysed on Rock Eval-VI. Analysis requires about one gram of core sample. Total carbon in shale sample includes organic and inorganic carbon. By using combustion technique, inorganic carbon is isolated by treating with phosphoric acid followed by drying at 13500C in oxygen rich environment. The organic rich carbon oxidized to CO2, which flow through a nondispersive infrared detector cell tuned to response to CO2. The measured gas volumes are converted to TOC measurement and recorded as a weight percent of rock.

Vitrinite Reflectance Study: The Vitrinite reflectance studies were carried out on Fluorescence Microscope with Image Analysis System (Leica Model DM6000M with MSP 200 Photometer, DFC 500 Digital Camera and Quin Imaging Software). The system was calibrated with glass standard of known reflectance in oil medium. Samples were scanned for Vitrinite macerals and reflectance was measured on maximum number of Vitrinite macerals. The result of Vitrinite reflectance (VRo) was originally developed to rank coal maturity, but presently in is used for identifying shale gas maturity. VRo is determined by microscope measurements of the reflectivity of at least thirty grains of vitrinite from rock samples, values ranging from 0- 3%.

Core Adsorption Lab Study: The samples were grinded, sieved with 60-mesh sieve and desorbed in glass desorber by adding 50% H_3PO_4 CO₂ gas evolved during reaction is absorbed by KOH solution and the hydrocarbon gases (W/V) will be measured in the graduated tube of desorber. The further analysis to detect light hydrocarbons (C1 to C5) was carried out by injecting the 0.5ml gas into GC (Chemito-1000).

Stable Carbon Isotopic Study: Stable carbon isotopic studies were carried out on Thermo Scientific Delta V Plus continuous flow-isotope ratio mass spectrometer (CF-IRMS) interfaced with Ultra Trace GC, which is equipped with a fused silica coating Poraplot- Q, 25m x 0.32mm coated 10 µm column. The gas samples ('40µl) were injected into the GC inlet using a micro syringe, in an isothermal GC run program at

 20° C.The elluents from the GC were passed through a Cu/Ni/Pt reactor which was maintained at 960°C which in turn was connected in series to a pure copper wire reduction furnace maintained at 650°C. Helium was used as a carrier gas. The water vapors were removed through an online Nafion membrane water trap and finally the purified CO₂ introduced into the source of mass spectrometer. A CO₂ gas pulse was employed as reference to calibrate the isotope ratios of samples measured. The mass spectrometer is standardized using NIST (USA) gas standards NGS-1 and NGS-2 natural gas mixtures. The instrument is run through Isodat instrument control and acquisition software. Results of isotopic values for natural gases are reported as δ^{13} C ‰ with respect to PDB (Table 7 and 11). The isotopic ratio was expressed in the usual delta (δ notation as follows)

$$\delta^{13}C (\%) = \begin{pmatrix} {}^{13}C/{}^{12}C_{sample} \\ {}^{13}C/{}^{12}C_{standard} \\ \end{pmatrix} \times 1000$$

Results and Discussions

Geochemical characterization has a significant role to play in shale gas exploration. Its generation history, composition and potential risk of production depends entirely on the geochemical aspect. The Rock Eval analysis data shown in Table 1 suggests significant TOC (total organic content) from the areas in the range of 4-12 wt% indicating highly organic rich Barren Measure shale. In general an increase of TOC has been observed with depth but at places lesser conformance in the extrapolation is noted. The amount of organic material present in sedimentary rocks is almost always measured as the total organic carbon (TOC) content. Exploration targets of shale gas have TOC value in the range of 2% to 10%. Rocks with TOC value above 10% are usually too immature for development (5) al). The S2 values (Figure 1) indicate good remaining hydrocarbon generation potential (S2: 3.3-12.34mgHC/g rock) with maturity in late oil generation/gas window, which is in the acceptable range of agreement with resource base (GIP) assessed as shown in hydrocarbon Generation Potential (S2) vs TOC profile of Well-SGAA. Figure 2 depicts the microscopic view of VRo of average value 0.86%. The thermal maturity based on Tmax values indicate late oil generation window except one sample (1081.13-1081.2m) which is in early generation stage (Tmax: 438°C) as depicted in Tmax v/s HI plot in Figure 3 showing Type III kerogen. The present day HI & OI values as well as Tmax vs HI and OI vs HI plots indicates the type III organic matter (Figure 4). Presence of free hydrocarbons (S1: 0.82-2.35mgHC/g rock) in Table 1 substantiate the maturity of the samples.

The VRo studies indicate early oil generation maturity (VRo 0.67%) whereas shale samples from 1550m to 1757m are in peak to late oil generation maturity (VRo 0.86 to 1.01%) (**Table 1**) with type III organic matter. Dull yellow to orange yellow fluorescing liptinite macerals are common siderite of average VRo of vitrinite is 0.86 %(**Figure 2**). It is observed that abundant terrestrial organic matter, inertinite and vitrinite, occurred as irregular fragments and in chaotic orientation.Vitrinite looks oxidized and recycled with reflectance ~1,00%.

Results of desorbed core samples from laboratory condition show appreciable concentrations of Methane and C2+ gases indicating thermogenic characteristics of the hydrocarbons (**Table 2**). Ratio values of light hydrocarbon(C1/C2, C2/ C3 etc) suggests petroliferous origin of the gas which is substantiated by the isotopic studies of the core samples.

Molecular composition based on isotopic data of desorbed shale gas in **Table 2** indicate that gases are immature and of predominance of mixed origin (i.e., petroliferous and bacterial methane).

The measured VRo data is used for calibration to address the difference in heat flow. The heat flow trend generated from this match is used to simulate a one dimensional basin model **(Figure 5)**. The modeled temperature and vitrinite reflectance shows good match with measured VRo and temperature. Therefore, the heat flow calculations can be considered representative. Considering Type III kinetic with HI and porosity value, the resource potential may be estimated.

Conclusions:

Geochemical evaluation constitutes the most essential parameters for evaluation of shale plays. Synthesis of G & G lab analytical data carried out by M/s Terra Tek, USA and the geochemical data generated by KDMIPE Labs indicate that the Raniganj Area, shale have very good organic richness (TOC: 4.56-10.5%) and good remaining hydrocarbon generation potential within late oil generation window and being dominant type III kerogen, substantial gas quantities is expected to be generated. It may also be inferred that shale lithological attributes showing large clay percentage and high organic richness, may be supportive of a large proportion of adsorbed gas in the system which is typical of Antrim and Albany shales in USA. Presence of free hydrocarbons (S1: 0.82-2.35mgHC/g rock) substantiate the maturity of the samples. The VRo studies indicate late oil generation maturity (VRo 0.86 to 1.01%). Showing of appreciable conc. of Methane and C2+ gases in all samples indicate thermogenic characteristics of the hydrocarbons.The desorbed gas isotopic data indicate that gases are immature and of mixed origin.

Based on the G & G data and already modelled results of 1D modelling and Surfacing of gas from the 1st shale gas well in India during testing wherein it is indicated that the Barren Measure formation did enter into adequate maturity window to produce shale gases comprising of adsorbed and free gases, therefore, warrants further exploratory and developmental activities for shale gas.

Acknowledgement

Authors are indebted to the ONGC management for their kind permission to publish this paper. The views expressed in the paper are those of authors only and not necessarily of the organization they belong to.Authors also acknowledged the contribution of Dr Trilok Chand, Shri A K Sinha, Shri Ashok Raina, Shri D.K Singh for their help in geochemical analysis.

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SI No	Dept h (m)	тос (%)	S1	S2	S3	S2/ S3	Tma x oC	н	ОІ	PI	Min C%	Av VRo (%)
1	1081	4.56	1.28	7.7	0.6	12	438	169	14	0.14	1.16	0.67
2	1549	5.54	2.35	5.7	0.8	7	459	102	15	0.29	1.21	0.86
3	1570	8.04	1.73	6.1	0.9	7	460	76	11	0.22	1.91	0.91
4	1581	4.99	0.89	3.3	0.6	6	461	66	12	0.21	1.36	0.91
5	1587	6.92	1.36	5.7	0.8	8	462	83	11	0.19	1.66	0.91
6	1598	7.78	1.47	7.1	0.7	10	464	92	9	0.17	0.86	0.92
7	1612	9.22	2.07	8.4	0.8	10	465	91	9	0.20	1.68	0.93
8	1745	6.26	1.22	6.4	0.6	11	468	103	10	0.16	0.64	1.0
9	1754	5.1	0.82	4.7	0.7	7	470	92	14	0.15	1.28	1.01
10	1756	10.5	1.98	12.4	0.9	13	471	118	9	0.14	0.83	1.01

Table 1 Rock Eval analysis & VRo data on shale samples of Well SGAA (S1:(mg.HC/g rock),S2:(mg.HC/g rock),S3:(mg.CO2/g rock),HI: mg.HC/g TOC, OI:mg.CO2/g TOC)%.

SI.	Depth (m)	C ₁	C ₂	C ₃	iC ₄	nC₄	iC ₅	nC₅	Isotopic Composition		
No.									$\delta^{13}C_1$	$\delta^{13}C_2$	$\delta^{\!13}\text{CO}_2$
1	1081	153.55	10.37	1.21	0.2	0.29	0	0	-68.1	-	-9.9
2	1549	506.29	33.44	3.7	0.41	0.63	0.19	0.13	-55.7	-35.6	-
3	1570	372.21	24.01	2.69	0.44	0.62	0.25	0.37	-54.7	-34.4	-
4	1581	766.13	60.29	5.07	0.78	0.8	0.49	0.21	-64.7	-	-
5	1587	304.02	31.84	3.17	0.48	1.09	0.27	0.23	-64.7	-35.6	-
6	1598	284.01	31.46	3.87	0.5	1.57	0.29	0.26	-65.9	-	-
7	1612	359.66	27.55	2.98	0.38	0.65	0.2	0.19	-58.6	-37.5	-11.8
8	1745	42.85	3.16	0.9	0.2	0.4	0	0	-58.8	-35.7	-
9	1754	5859.8	336.44	26.6	2.77	3.42	0.87	0.38	-46.1	-30.1	-
10	1756	76	7.92	1.56	0.3	0.63	0.25	0.3	-66.7	-	-10.9

Table 2Adsorbed gas analysis and isotopic composition of desorbed gas of shale samples from Well-
SGAA (#all concentration in ppm vol/wt%)



Figure 1. Hydrocarbon Generation Potential (S2) vs TOC profile of Well-SGAA



Figure 2 Vitrinite Reflectance (%) fluorescence view



Figure 3. Tmax v/s HI plot showing Type III gas samples of Well-SGAA

Figure 4. OI v/s HI plot showing Type III OM for shale OM for shale gas samples of Well-SGAA



Figure 5. Vitrinite reflectance (VRo) and temperature calibration in 1D model along Well SGAAA and hydrocarbon zone using Type III kinetics.