

Abnormal isotopic enrichment of carbon dioxide in natural gas reservoirs of coal beds: A case study of biogenic activity in thermogenic gas unconventional reservoirs of Damodar Valley

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Keywords

Damodar valley Basin, Secondary microbial reduction, Stable carbon isotopic, Coal bed Methane

Abstract

The Damodar Valley Basin is the largest coal bed gas producing sites in India. However, the gas isotopic composition of this Basin was not well studied. The exploration has been focused on mature coals with a high content of thermogenic methane. The present study decipher that although the gas is thermogenic, but with significant contribution of microbial gas. The gas samples from wells R-1, R-2, R-3, R-4, R-5, R-6, R-7, J-1, J-2, J-3, B-1, B-2, B-3, B-4 and B-5 show $\delta^{13}C_1$ -50.3 to -38.3% and C_2+ 0.08 – 2.11% , indicate their thermogenic to mix origin and dry nature. However observed isotopic enrichment in carbon di oxide, $\delta^{13}CO_2$ ~ 2.3 to 21.8% and significant difference between stable carbon isotopic value of methane and ethane ($\delta^{13}C_1 - \delta^{13}C_2$) $\sim 20\%$, indicate secondary alteration of methane and its generation through CO_2 reduction pathway instead of acetate fermentation pathway.

Introduction

Coal bed Methane (CBM), an unconventional source of natural gas is considered as an alternative source for augmenting India's energy resource. India has the fifth largest proven coal reserves in the world and thus holds significant prospects for exploration and exploitation of CBM. In Indian prospective, the Damodar Valley Basin holds the significant coal bed gas producing sites although the gas stable carbon isotopic composition of this basin is not well understood. So far the thermogenic methane producing mature coal beds are in centre of exploration and exploitation strategies.

Present study based on stable carbon isotopic characteristics of coal bed gas reveals that although the gas is thermogenic in origin along with significant effect of microbial activities in gas

generations which are duly supported by the biogenic gas signatures observed in studied gas samples. It is evident that in subsurface, microorganisms have generated biogenic methane in many hydrocarbon environments including coal, organic-rich shale, and petroleum reservoirs at scales that impact global energy cycles (Hoehler et al 2013).

The general geology of study area.

Damodar River Basin has a total catchment area of 25,820 km² and is a part of the Ganges River System. Drainage area of Damodar Basin extends from 22° 45'N to 24° 30'N and 84° 45'E to 88° 00'E and is covering about 11.8% of the total geographical areas of Jharkhand and 8.6% of West Bengal states. Geology of the basin is characterized by the rocks consisting of granites and granitic gneisses of Archaeans, sandstones and shales of the Gondwanas and the recent alluvial (Figure 1). Damodar basin is known for its coal deposits, accounting for 46% of the country's coal reserves and commonly referred as the 'store house of Indian coal.

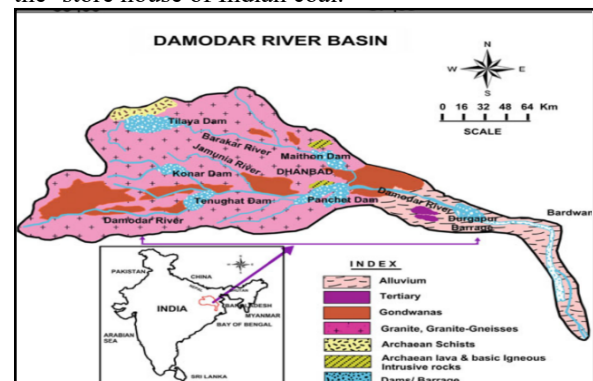


Figure 1: Geological map of Damodar River basin (Mondal G.C., et al., 2010).

The three coalfields viz. Raniganj, Jharia and Bokaro form the eastern extremity of the Damodar Valley

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Basin which holds high rank and superior quality of coals (**Figure 2**).

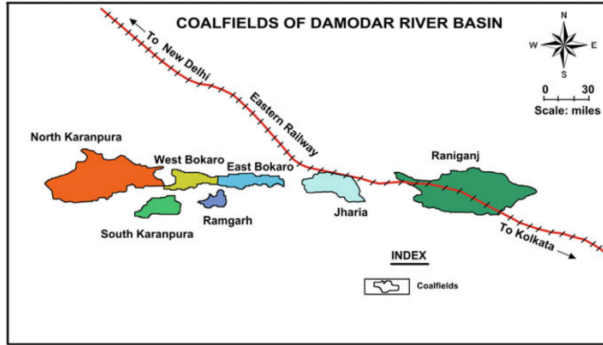


Figure 2: Major coalfields of Damodar River basin (Mondal, G.C., et al., 2010).

The three aforesaid coalfields, each with considerable number of coal horizons of enhanced rank, became the early target areas for probing. Most of the CBM reserve in India is confined mainly to Jharia and Bokaro coalfields in Jharkhand and Raniganj coalfield in West Bengal. The Gondwana sediments of eastern India host the bulk of India's coal reserves. The majority of the best prospective areas for CBM development are in eastern India, situated in Damodar Valley. Stratigraphically the Permian Gondwana of Damodar Basin includes Talchir, Karharbari, Barakar, Barren Measures and Raniganj formations (**Figure 3**). Lithologically different sedimentary sequences in Damodar Basin are characterized by the association of coal, organic rich carbonaceous shale, siltstone and sandstone.

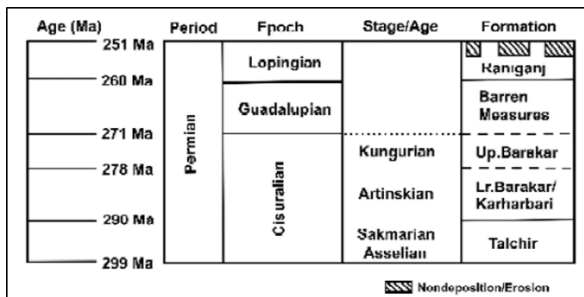


Figure 3: Stratigraphy of Permian Gondwana in Damodar Basin (after Mukhopadhyay et al., 2010).

Experimental methods

Chemical composition of gases

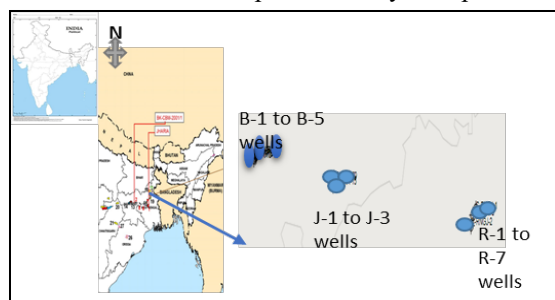
The natural gas samples were analysed for their molecular composition on Perkin Elmer Clarus 680 Natural Gas Analyzer equipped with three columns namely, Molecular Sieve 5Å capillary column (for hydrogen and helium analysis), Elite M1 capillarycolumn (for hydrocarbon analysis) and Molecular Sieve packed column (for nitrogen, oxygen and carbon dioxide analysis), dual TCD and one FID, using helium and nitrogen as carrier gases. The dual TCD was used to analyse inorganic gases including helium and hydrogen whereas the FID was used for the analysis of hydrocarbons from C₁-C₆₊ through a single injection. The oven having capillary columns was programmed for an initial temperature of 35°C with a hold time of 7.5 minutes. A temperature ramp of 25°C per minute was followed up to a final temperature of 150°C with final hold time of 6.4 minutes. The oven with packed column was maintained at 130°C for the entire analysis period. The injector and TCD temperature were maintained at 200°C whereas the FID temperature was maintained at 250°C during the entire analysis. The Chemical composition analysis span of gases was of 18.5 minutes.

Isotopic composition of gases

Stable carbon isotopic studies were carried out on CF-IRMS (Thermo Fisher Delta V Plus) interfaced with Trace Ultra GC, which is equipped with a fused silica coating Poraplot-Q; 25m x 0.32mm x 25µm column. The gas samples were injected through a loop system, which takes 100µl of the sample into the injection port. The eluents from the GC were passed through a Cu/Ni/Pt oxidation reactor 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 carrier gas. The water

$$\delta^{13}\text{C}(\text{‰}) = \left(\frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}}}{^{13}\text{C}/^{12}\text{C}_{\text{standard}}} - 1 \right) \times 1000$$

vapours were removed through an online Nafion membrane water trap and finally the purified CO₂



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was introduced into the source of mass spectrometer. A reference CO₂ gas pulse was employed to calibrate the isotope ratios of samples analysed. The mass spectrometer was calibrated using secondary reference gas standardized through NIST (USA) primary reference gas standards: NGS-1 and NGS-2. The instrument is run through Isodat instrument control and acquisition software. The isotopic ratio was expressed in the usual delta (δ) notation in permil (‰) with respect to PDB as follows:

Figure 4: Tentative location of studied CBM wells

Results and Discussions

Sample details

A total fifteen gas samples of wells R-1, R-2, R-3, R-4, R-5, R-6, R-7, J-1, J-2, J-3, B-1, B-2, B-3, B-4 and B-5 have been used during the study for detail geochemical analysis (Figure 4). The geochemical analysis of studied gas samples suggests thermogenic to mix origin with dry in nature ($\delta^{13}C_1$ -50.3 to -38.3‰ and C_{2+} 0.08 - 2.11%) (Figure-5).

S.No	Well Name	Chemical Composition (% Mol)					Stable Carbon isotopic values ($\delta^{13}C$ ‰)			
		C ₁	C ₂	C ₃	C ₂₊	CO ₂	$\delta^{13}C_1$	$\delta^{13}C_2$	$\delta^{13}C_3$	$\delta^{13}CO_2$
1	R-1	98.99	0.08	0.00	0.08	0.30	-49.6	-	-	-
2	R-2	98.88	0.13	0.12	0.24	0.42	-50.3	-	-	8.2
3	R-3	99.11	0.11	0.01	0.12	0.21	-50.4	-	-	13.4
4	R-4	98.33	0.23	0.05	0.27	0.49	-42.0	-20.2	-	15.4
5	R-5	98.27	0.99	0.08	1.07	0.42	-43.0	-25.7	-26.6	15.5
6	R-6	97.68	1.40	0.18	1.58	0.28	-45.2	-28.0	-26.3	11.5
7	R-7	98.67	0.20	0.02	0.21	0.21	-49.7	-26.0	-	6.6
8	J-1	91.96	1.36	0.02	1.39	0.78	-40.9	-23.6	-	14.7
9	J-2	89.69	1.55	0.02	1.57	2.61	-38.3	-22.3	-	14.4
10	J-3	95.11	0.46	0.02	0.47	1.92	-40.2	-	-	9.9
11	B-1	93.80	0.21	0.00	0.21	3.15	-44.2	-	-	13.9
12	B-2	87.91	1.40	0.07	1.47	8.71	-41.2	-21.8	-	6.5
13	B-3	86.84	1.53	0.03	1.57	7.03	-41.6	-20.5	-	12.6
14	B-4	90.56	0.84	0.04	0.89	5.76	-41.3	-21.1	-	4.2
15	B-5	86.08	1.97	0.14	2.11	10.63	-40.5	-22.1	-	2.3

Table 1: Geochemical details of studied gas samples (Choudhary N., et al., 2023)

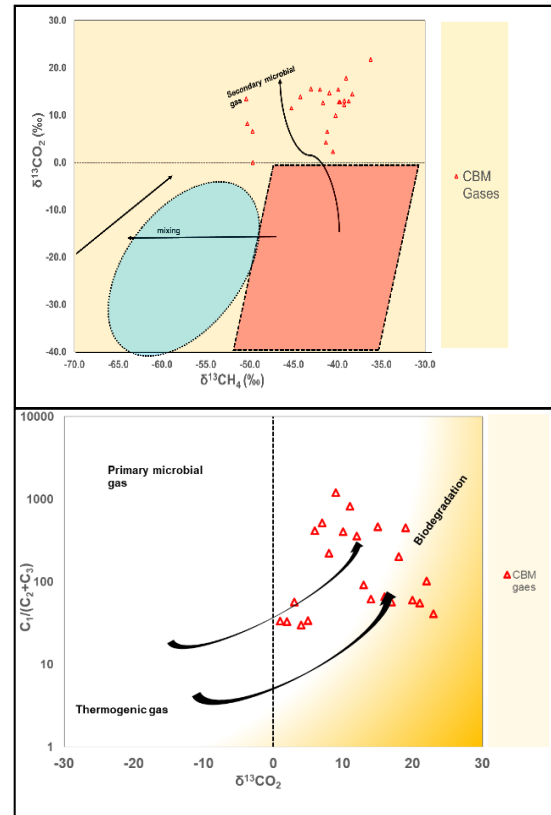
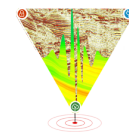


Figure 5: $\delta^{13}CH_4$ vs. $\delta^{13}CO_2$; $\delta^{13}CO_2$ vs. $C_1/(C_2 + C_3)$ cross plots showing the occurrence of secondary microbial gas generation in CBM gases (from Whiticar, 1999; Milkov, 2011).

Evidence of secondary microbial gases

An unusual isotopic enrichment phenomenon in stable carbon isotopic value of carbon dioxide ($\delta^{13}CO_2 \sim +2.3$ to $+15.5$ ‰) as well as significant isotopic difference between carbon delta value of methane and ethane [$(\delta^{13}C_1 - \delta^{13}C_2) \sim 20$ ‰] have been observed, which indicates secondary alteration of methane and also corroborates, microbial methane gas generation through secondary carbon dioxide reduction pathway (Pallasser, 2000; Boreham et al., 2001; Jones et al., 2008, Milkov and Dzou, 2007; Jones et al., 2008; Milkov, 2011) (Table 1, Figure 6) To deconvolute studied stable carbon isotopic values of methane and carbon dioxide gases, a conceptual model given by Wang et.al. , (2022) was followed, which helps in understanding the carbon isotopic



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composition of the studied gases where biodegradation, methanogenesis and mixing processes are considered (Figure.6)

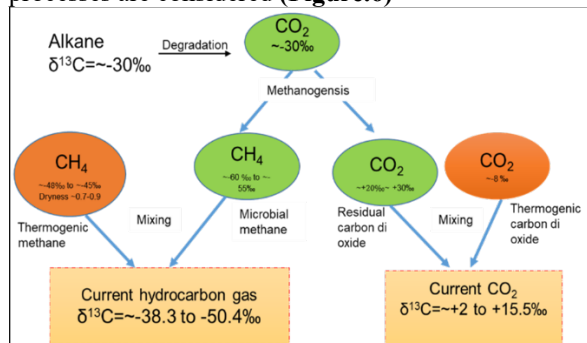
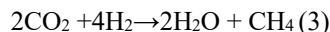
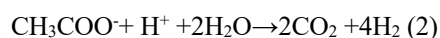
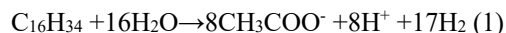


Figure 6: A conceptual model showing the origin and isotopic composition of carbon dioxide and methane during degradation, methanogenesis and mixing processes (Wang et al., 2022).

In Damodar valley certain C₂₊ enriched coal seams exists where higher alkanes are available as substrate for bacteria to produce gas via biodegradation process (Table -4, Choudhary, N. et, al. ONGC unpublished report, March 2023). Methanogenic biodegradation of higher hydrocarbons is an anaerobic process, which involves microbial degradation of higher alkanes to produce CO₂ and subsequent reduction of CO₂ to methane (Equations 1 to 3; (Head et al., 2003; Larter et al., 2005).



The methane initially generated by CO₂ reduction has lighter carbon and hydrogen isotopes, but when it mixed with thermogenic gas the actual isotopic values could be buffered to much heavier values, which is observed in current case study, the δ¹³C value of methane varies between -38‰ to -50.4‰.

CO₂, which can be generated from the thermal cracking of organic matter and consumed during methanogenesis, or mixing of any of these sources of CO₂ besides its removal via dissolution in pore water and precipitation as carbonates (Jones et al., 2008; Huang and Larter, 2014) can be distinguished on basis of δ¹³C Isotopic values.

CO₂ from thermal degradation of organic matter, decomposition of carbonates, and degassing of the

mantle, have distinct carbon isotopic signatures from the secondary microbial CO₂ (Connan et al., 1996; Dai et al., 1996). The CO₂ derived from the thermal decarboxylation of organic matter generally has a light carbon isotopic composition with δ¹³CO₂ < -8‰, while mantle-derived CO₂ have δ¹³C values ranging from -4 to -7‰ (Dai et al., 1996). The δ¹³C values for CO₂ derived from the decomposition of carbonates would be close to that of limestone with an average bulk rock δ¹³C value of +1.8‰ (Cai et al., 2001). CO₂ due secondary reduction phenomenon, has δ¹³C values in range of +2‰ to +20‰ (Milkov, 2011; Pallasser, 2000; Boreham et al., 2001; Jones et al., 2008, Milkov and Dzou, 2007;).

In present case, positive δ¹³C values of carbon dioxide (+2‰ to +15‰) substantiates that initially, gases are thermogenic in nature but due to presence of microbial activity and mixing phenomenon, its δ¹³C values become shifts towards positive side.

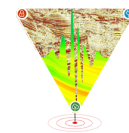
Conclusions

The compound specific stable isotopic study of the coal bed gas indicate that gases are thermogenic in origin with a component of microbial gas.

Although the high thermal maturity of the coal had led to the generation of thermogenic gas initially, it would have been altered by a methanogenic pathway. Studied gases generated through methanogenic hydrocarbon degradation predominantly via CO₂ reduction to generate secondary microbial gas with CO₂ enriched in δ¹³C. The secondary microbial gas then mixed with thermogenic gas in the reservoir, leading to a positive shift in methane δ¹³C gas. The secondary microbial gas then mixed with thermogenic gas in the reservoir.

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