Stable isotopic composition of coal bed gas and associated formation water samples from Raniganj Basin, West Bengal, India

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ABSTRACT

This study was carried out to document the source and stable isotopic characteristics of coal bed gas and associated coal bed water samples of the Raniganj Basin, West Bengal, India. The Raniganj Basin is one of the largest coal bed gas-producing sites in India. However, the gas isotopic composition of this basin was not well investigated until now. The exploration has been focused on mature coals with a high content of assumed thermogenic methane. Interestingly, the present study has revealed that although the gas is thermogenic, there is a significant effect of microbial activities in gas generation. The gas explored from this Basin contains almost 98–99% methane (CH_4) in general with very little portions of other hydrocarbons and thus, this gas can be considered as "dry gas". It is consistent also with late-stage microbial alteration of thermogenic gases. The $\delta^{13}C$ and δD values of CH_4 range from -47.4 to $-49.7‰$ and -207 to $-211‰$ respectively across the three wells as well as from -48.8 to $-50.1‰$ and -209 to $-211‰$ respectively in the gas samples collected from gas gathering station. The Whiticar style cross plot of these two parameters reveals that the gas samples have mixed thermogenic and biogenic sources and the microbial gas was generated through the CO_2 reduction pathway rather than the acetate fermentation pathway. The difference in δD values of water and methane samples [δD (H_2O-CH_4)], that varies from 173 to 175‰, may also exhibit that the biogenic methane was produced through reduction of CO_2. The stable hydrogen and oxygen isotopic signatures of formation water samples (δD and $\delta^{18}O$-H_2O) stand with the mixed origin of the gas. The cross-plot of these two parameters reveals that the water samples lie almost along the Global Meteoric Water Line (GMWL), which may suggest the combined effect of methanogenesis due to mixing of coal seam formation water with modern meteoric water. In summary, the produced coal bed gas from the Raniganj Basin, although being largely thermogenic in origin, has been influenced by secondary microbial alteration.

1. Introduction

Coal bed methane (CBM) is an important source of energy in a number of countries, most notably the USA, Australia and Canada, and a developing energy source in countries such as China and India. This gas may be thermogenic, biogenic or have a mixed origin (Golding et al., 2013). The origin of this coal bed gas can be distinguished on the basis of the stable isotopic characteristics of gas and associated formation water. Methane, ethane, carbon dioxide and nitrogen are the primary constituents of coal bed gas (Golding et al., 2013). Dry gas is defined as having a high methane content, while wet gas is defined as having substantial concentrations of ethane and liquid condensates (Tissot and Welte, 1984). Generally, analysis of stable isotopes of carbon and hydrogen ($\delta^{13}C$ and δD of CH_4) is applied to determine the

origin of the coal bed gas whether it is thermogenic or microbial (Golding et al., 2013). The microbial gases are characterized by $\delta^{13}C$-CH_4 values less than $-50‰$ (Hamilton et al., 2014; Strapoć et al., 2011; Whiticar, 1996, 1999; Whiticar et al., 1986) whereas the thermogenic gases show comparatively heavier $\delta^{13}C$-CH_4 values ($> -50‰$) (Hamilton et al., 2014; Sackett, 1978; Schoell, 1980). If the gas is microbial, then it would have followed any one of the two pathways—CO_2 reduction or acetate fermentation pathway—which also affect the isotopic composition of the gas. The Whiticar style plot of $\delta^{13}C$-CH_4 against δD-CH_4 can differentiate these two pathways (Whiticar, 1996, 1999; Whiticar et al., 1986). The stable hydrogen isotopes of methane and water also play a significant role here by discriminating the two microbial pathways (Golding et al., 2013). The cross–plots of stable hydrogen and oxygen of coal bed formation water

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(δD and δ^{18}O-H_2O) can be used again as supportive parameters for the source and characteristics of the coal bed gas. The present study has been undertaken to address the knowledge gap regarding the stable isotopic characteristics of coal bed gas and associated formation water of a productive Indian basin.

The Raniganj Basin is one of the most productive basins in India, which has been widely explored for coal bed gas (Mendhe et al., 2017; Singh et al., 2018). The gas-bearing coal beds of Raniganj Formation have a depth range varying from 26 to 1250 m and the gas from these coal beds is explored in three blocks: south block, north-central block and northeast block (Mendhe et al., 2017). GEECL is producing 0.25 million m^3 of gas from 40 wells whereas the production of gas by Essar is about 0.1 million m^3 from 25 wells (Mendhe et al., 2017). However, the stable isotopic signatures of gas and associated formation water of this Basin have received a little attention. The primary objective of this study is to document the source and characteristics of the explored coal bed gas and associated formation water.

This isotopic study also may help more broadly in enhanced recovery of microbial coal bed gas through determining the microbial pathway if any are active in the coal bed environment. If the coal bed gas generation could be enhanced by adding nutrients (such as phosphorous or sulfur), micro-nutrients (such as vitamins), carbon dioxide and acetate to stimulate the growth of microbial communities in the existing wells, it may help to recover more gas (Ritter et al., 2015). Laboratory experiments were carried out to enhance the production of methane using synthetic nutrients (Davis and Gerlach, 2018; Jones et al., 2010; Zhang and Liang, 2017), yeast extraction (Zhang et al., 2016), monosaccharides (Huang et al., 2017) etc. Some companies also had attempted commercially to enhance the gas production (Davis and Gerlach, 2018). Luca Technologies, INC used a mixture of nutrients including synthetic vitamins and minerals, yeast extract, glycerol, soy proteins and weak organic acids to enhance the recovery of methane in Uinta Basin, San Juan Basin and Black Warrior Basin (Davis and Gerlach, 2018). Additionally, Next Fuel, INC had applied non-carbonaceous nutrients, trace metals and vitamins at different sites in India, China, and Indonesia (Davis and Gerlach, 2018). If any microbial pathway has been found to be active in the coal beds of Raniganj Formation, more methane would be recovered commercially by the both Governmental and privately-owned companies through the proper application of these techniques. Then, a target of profitable commercial approach for enhancing the recovery of methane would be set throughout the CBM sites of India. Hence, the present study can be considered as the initial stage to reach that target.

2. Geological setting

The Raniganj Basin (23°22′ N and 23°52′ N; 86°36′ E and 87°30′ E) has an aerial extent of 1900 km^2 between the Damodar and Ajay rivers. It forms the easternmost intracratonic rift basin of the Damodar Valley. It has a semi-elliptical elongated shape and is characterized by the presence of both the Lower Gondwana (Permian) and Upper Gondwana (Triassic-Lower Cretaceous) Formations (Gee, 1932; Hazra et al., 2015). The Gondwana Supergroup is subdivided into six units that were deposited in a tectonic trough with faults on both the boundaries (i.e., northern and southern faulted boundaries) on either side of the Damodar river that flows on the faulted trough (Fig. 1a and b). The Raniganj Basin is also faulted down on the south and the west. The southern boundary is characterized by a series of faults and shows an en-echelon pattern with a general strike of E-W. The strata generally dip in the range between 5° and 10°. Across the southern boundary fault zone, a throw had been estimated to be more than 1000–1500 m (Ghosh, 2002). The central part of the Raniganj Basin is marked by the presence of the Salma dolerite dyke, which forms a basement high running across the basin (Ghosh, 2002; Hazra et al., 2015). This basement high separated the eastern and western sub-basins of the Raniganj Basin during the deposition of Damuda Group (Barakar; Barren

Measures and Raniganj Formations). The general stratigraphic succession of the Raniganj Basin is given in Table 1.

The Raniganj Basin was initiated as a sag basin, where Talchir and Barakar sediments had been deposited (Fox, 1931; Gee, 1932). Later, it developed a homoclinal geometry having a normal depositional contact with the unconformity on the underlying granite gneiss in the northern side and progressively became deeper towards the south. In the northern part of the Raniganj Basin, the organic matter was deposited by meandering river systems in swamp areas to form the coal beds and in the eastern part, different Sub-Basins had accumulated fanglomeratic cones with intermittent coal swamps (Ghosh, 2002). In the western part of the Raniganj Basin, organic matter was deposited along with the clastic sediments by westerly flowing river systems to form the coal beds (Ghosh, 2002).

Lamprophyre dykes and sills, as well as dolerite dykes, occur extensively in the Raniganj Coal Basin (Ghosh, 2002; Hazra et al., 2015). Gondwana shales and sandstones were intruded by the lamprophyre sills, and these intrusives are found within the coal seams of the Barakar and Raniganj Formations (Ghosh, 2002). The Salma dolerite dyke cut across the lamprophyres and the thermal effects of this mafic intrusive are confined to few meters adjacent to the contact aureole within the Barakar and Raniganj Formations (Ghosh, 2002). Lamprophyres had produced natural coke or "jhama" and they continue into the surrounding country rocks (Gee, 1932). Even these ultramafic intrusives continue across the major southern boundary fault to the Raniganj Basin (Ghosh, 2002).

3. Materials and methods

Six coal bed gas samples and five associated coal bed formation water samples were collected from the three wells (at the depth of 450 m, 500 m, and 600 m respectively) drilled within the coal beds of Raniganj Basin in the South Raniganj Block, West Bengal, India (Fig. 1b) for stable isotope analysis. Additionally, three gas samples were collected from a gas gathering station. The coal bed methane samples were collected using Isotubes® (supplied by Isotech Laboratories, Texas, USA). During collection of gas samples from the wellheads, there may be a concern of mixing and contamination from the air in the Isotubes®. To ensure that there was no air present in the Isotubes®, those were flushed with the gas at the wellheads for three times (2 min each time) and after that, the Isotubes® were filled with gas. The water samples were collected in 500 ml containers after rinsing them five times repeatedly with formation water (3 min each time).

The gas samples were analyzed using an Isoprime Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometer (GC-C-IRMS) at the Stable Isotope Geochemistry Laboratory (SIGL) in The University of Queensland, Australia. To determine the δ^{13}C of CH_4, the gas samples were analyzed in triplicate with 3×30 μl injections with 20:1 split. An Agilent gas chromatograph (GC) with 50 m $\times$ 320 μm $\times$ 5 μm CP-PoraBOND Q column was set to flow at a rate of 1.2 ml/min with an oven temperature of 40 °C. After that, the eluted sample from the GC was passed through ceramic furnace packed with nickel and platinum wire and set to 1020 °C. It oxidized the CH_4 to generate CO_2 for measurement in the IRMS. Any CO_2, if present in the samples, passed through unaffected. Calibration of data was via a three-point normalization using Oztech CO_2 standards (δ^{13}C -3.6‰; -40.75‰) and laboratory standard methane (δ^{13}C -35.6‰).

To document the δD of the CH_4, the gas samples were analyzed using the same GC settings used during determination of δ^{13}C of CH_4 but here, the eluted samples from the GC were pyrolyzed by passing them through ceramic furnace set at the temperature of 1400 °C. Calibration was via three-point normalization using two Oztech international hydrogen standards (δ^2H -125‰, -365‰) and laboratory standard methane (δ^2H -154‰). Precision is quoted at $\pm$ 0.3‰ for δ^{13}C and $\pm$ 3‰ for δD with all gas standards calibrated against international standards defining the "Vienna Pee Dee Belemnite" (VPDB) and "Vienna Standard Mean Ocean Water" (VSMOW) scales.